A STUDY OF THE CO-ORDINATION BEHAVIOUR OF THE CHALCOGENOCYANATE IONS

by

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PUBLICATIONS

Part of the work reported in this thesis has been published as the following papers:

(i) 'A convenient method for the analysis of organometallic and related compounds' by S.J. Anderson, D.S. Brown and A.H. Norbury, J. Organometal. Chem., 64, 301 (1974).

(ii) 'Linkage isomers of the cyanate group: O-cyanato- and N-cyanato-tris(triphenylphosphine)rhodium(I)' by S.J. Anderson, A.H. Norbury and J. Songstad, Chem. Comm., 37 (1974).

SUMMARY

The co-ordination behaviour of the pseudohalide ions (NCO^- NCS^- $NCSe^-$ $NCTe^-$) has been studied. A number of N- and S-bonded thiocyanate complexes of rhodium(I), of the type $Rh(PPh_3)_2(L)CNS$ (L = ligand), have been prepared. The mode of linkage of the thiocyanate group has been established by means of infrared spectral measurements. The preparation of $Rh(PPh_3)_2$(piperidine)NCS clearly demonstrates that a strongly π-accepting ligand such as CO is not a prerequisite for a N-thiocyanato complex of the type $Rh(PPh_3)_2(L)NCS$. In addition, the complexes $Rh(PPh_3)_2(C_6H_6)SCN$ and $Rh(PPh_3)_2SCN$, which are of special interest from the point of view of their bonding and co-ordinating number respectively, have been prepared. Some selenocyanato complexes of rhodium(I), of the type $Rh(PPh_3)_2(L)SeCN$, have also been synthesised similarly. Cyanato-tris(triphenyl phosphine)-rhodium(I) and its linkage isomer have been prepared in the solid state, and characterised by means of infrared spectral measurements. Attempts have been made to prepare tellurocyanate complexes of rhodium(I) and the results are discussed.

The co-ordination behaviour of organic thiocyanates and isothiocyanates to a class 'a' metal has been studied by means of proton magnetic resonance spectroscopy and the use of the lanthanide shift reagent $Eu(fod)_3$. A number of inorganic-thiocyanate complexes have also been examined, and it has been found that N- and S-bonded thiocyanate complexes containing organic ligands can be readily distinguished by virtue of differences observed in chemical shift by the nuclei of the organic ligands. The method has been extended in order to provide a means of determining the mode of co-ordination in cyanate complexes.

Thiocyanate complexes of rhodium(III) and iridium(III) have been prepared by the oxidative addition reactions of organic thiocyanates and isothiocyanates to rhodium(I) and iridium(I) complexes, and the mode of co-ordination of the thiocyanate group has been established by infrared measurements. Complexes have been prepared where the bonding of the thiocyanate group in organic isothiocyanates occurs through carbon and sulphur. The oxidative addition reactions of allyl thiocyanate or allyl isothiocyanate to rhodium(I) and iridium(I) complexes is followed by the reductive elimination of allyl chloride. Similar behaviour occurs when ethyl cyanate is used.

The X-ray crystal and molecular structures of $(\pi\text{-cp})_2\text{Ti(NCO)}_2$ have been determined. The cyanate groups are shown to be N-bonded in the solid state.

A convenient method of analysis by X-ray spectrometry has been developed, where small amounts of sample are presented as borax discs. The method is especially suitable for compounds which are not amenable to conventional combustion analysis.

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NOMENCLATURE

The formula for an N-bonded thiocyanate complex will be written M-NCS and an S-bonded or normal thiocyanate will be written M-SCN. The corresponding formalism will apply to the selenocyanate and cyanate ions. Where the mode of co-ordination is not known or is undecided, the complex will be written M-CNX, where X = O, S, or Se, and should not be confused with fulminates or thiofulminates etc.

The following abbreviations will be used:

bipy = 2,2-dipyridine.
bu = butyl.
cp = cyclopentadienyl, C_5H_5.
dien = diethylenediamine.
DH = dimethylglyoximato anion (univalent).
DMSO = dimethyl sulphoxide.
dpm = 2,2,6,6,-tetramethylheptane-3,5,-dione.
Et = ethyl, C_2H_5.
L = ligand.
Me = methyl.
pic = picoline.
Ph = phenyl.
phen = 1,10-phenanthroline.
py = pyridine.
R = alkyl or aryl.
trien = triethylenetetraamine.

CHAPTER 1

AN INTRODUCTION TO THE CO-ORDINATION BEHAVIOUR OF THE CHALCOGENOCYANATE IONS IN METAL COMPLEXES

AN INTRODUCTION TO THE CO-ORDINATION BEHAVIOUR OF THE CHALCOGENOCYANATE IONS IN METAL COMPLEXES

The chalcogenocyanates or pseudohalides have the general formula NCX^- (X = O, S, Se or Te). They are all potentially ambidentate, that is they can form a co-ordinate bond to a Lewis acid through N or X. Thus, for example, the thiocyanate ion may form N-or S-bonded complexes depending on the nature of the ligand, and this preference may be modified by the presence of other ligands, or by whether the complex is in the solid state or in solution. The chalcogenocyanates can also be present in a variety of bridging modes. There are many examples of complexes containing the thiocyanate group, and a variety of reasons have been proposed, sometimes conflicting, to explain the co-ordination behaviour. The remaining chalcogenocyanates have not been studied to the same extent, but they show similar co-ordination characteristics, and similar arguments have been applied.

1) Thiocyanate Complexes

The varying co-ordination behaviour of the thiocyanate ion towards different types of metals was first observed by Lindquist and Strandberg(1). This behaviour parallels the division of metals into class 'a' and class 'b' acceptors(2). The general pattern found is one where "soft acceptors" or class 'b' metals form S-thiocyanate complexes, whilst "hard acceptors" or class 'a' metals form N-thiocyanato complexes as observed in the mode of co-ordination of the thiocyanate group in known homogeneous anionic complexes(3).

However, the co-ordination behaviour of the thiocyanate group may be influenced by the nature of other ligands present, as exemplified by some examples presented in Table 1.1. This does not occur for every metal but if the metal belongs to class 'b', or shows characteristics between class 'a' and class 'b', then ligand effects may be important in determining the co-ordination behaviour, for which a variety of explanations have been proposed.

(a) Steric Effects

The thiocyanate group co-ordinated through sulphur makes greater steric demands than the N-thiocyanate group, because the M-SCN bond is usually bent (bond angles of 100^{o} are common) whereas the M-NCS bond is usually linear. It is, of course, impossible to separate steric arguments from electronic factors completely. Nevertheless, steric arguments have been applied to explain the co-ordination behaviour in a variety of complexes. The formation of $Pd(SbPh_3)_2(SCN)_2$, in contrast to $Pd(PPh_3)_2(NCS)_2$, has been attributed to the larger antimony atom reducing the steric effects of the phenyl groups, whereas with the smaller phosphorus atom overcrowding round the central atom is increased, which is reduced by the thiocyanate group adopting a linear Pd-NCS bond(5). A clearer example of such an effect is demonstrated by the cations $[Pd\ dien(SCN)]^+$ and $[PdEt_4dien(NCS)]^+$ where the introduction of four ethyl groups around the vacant co-ordination position cause the only example of a linear Pd-NCS group in an amine complex of Pd(II) (6).

The Effect of Ligand on Thiocyanate Co-ordination in Some Complexes*

$Pd(SCN)_4^{2-}$	$Co(NCS)_4^{2-}$
$Pd(NH_3)_2(SCN)_2$	$[Co(NH_3)_5NCS]^{2+}$
$Pd(PEt_3)_2(NCS)_2$	$[Co(NH_3)_4(NCS)]^{+}$
	$[Co(en)_2(L)NCS]^{2+}$
Pd biby $(NCS)_2$	L = Cl^- or NCS^-
Pd (4,4 Me_2bipy)(NCS)(SCN	[I] $Co(DH)_2(L)NCS$
$Pd(phen)(SCN)_2$	
$Pd(5,NO_2\text{-}phen)(NCS)_2$	$Co(DH)_2(L)SCN$
	$[Co(CN)_5(SCN)]^{3-}$
$Pd(PPh_3)_2(NCS)_2$	$Co(bipy)_2(SCN)$
[I] $Pd(AsPPh_3)_2(NCS)_2$	
$Pd(SbPh_3)_2(SCN)_2$	$[Rh(SCN)_6]^{3-}$
	$[Rh(NH_3)_5NCS]^{2+}$
$[Pd\,dien(SCN)]^+$	
$[Pd(Et_4dien)(NCS)]^+SCN^-$	$Mn(CO)_5NCS$
$[Pd(Et_4dien)(SCN)]^+PBh_4$	$Mn(CO)_3(PPh_3)_2SCN$
$Rh(PPh_3)_2(CO)NCS$	
$Ir(PPh_3)_2(CO)NCS$	

*from Norbury 3, 4 and references therein.

[I] Stable linkage isomer.

Table 1.1.

The importance of steric effects becomes apparent in the series of Pd(II) - diphosphine complexes ($Pd\ Ph_2P(CH_2)_nPPh_2(NCS)_2$),n = 1-3, reported by Meek, et al.(7), where the thiocyanate groups are each trans to two equivalent phosphorus atoms. The donor atom changes from sulphur to nitrogen as the carbon chain between the phosphorus atoms is lengthened, (see Table 1.2.); this leads to a large increase in the P-Pd-P angle whilst still maintaining essentially constant electronic character. The increase in the P-Pd-P angle results in an increasing steric interaction between the phenyl groups and the co-ordinated thiocyanates which is reduced by the formation of Pd-NCS bonds. Similarly, the existence of $Pd(Ph_2PCH = CHPPh_2)SCN_2$ as the S-bonded isomer may be attributed to the shorter length of the C=C bond (1.33^{o}A ,cf 1.54^{o}A for C-C bond) which in essence pulls the phenyl groups away from the thiocyancate group allowing both thiocyanates to be S-bonded(8).

(b) Electronic Effects

The co-operative effect of ligands was originally introduced by Turco and Pecile(9). They attributed the differing modes of co-ordination of the thiocyanate group in $Pd(NH_3)_2(SCN)_2$ and $Pd(PEt_3)_2(NCS)_2$ to the π-withdrawing ability of the other ligands present. They argued that although the sulphur atom is a weaker σ-donor than the nitrogen atom the metal sulphur covalent bond may be stabilised by back-bonding as in $Pd(NH_3)_2(SCN)_2$ since NH_3 as a σ donor ligand would increase the electron density on the central metal atom. On the other hand, the central metal atom in $Pd(PEt_3)(NCS)_2$ has reduced electron density and

The Effect of Steric Control on Thiocyanate Co-ordination in Pd(II) Complexes

$PhP_2(CH_2)_nPPh_2$	P-Pd-P	Mode of Co-ordination
n = 1	73.2°	$Pd(SCN)_2$
n = 2	85.1°	$Pd(NCS)(SCN)$
n = 3	89.1°	$Pd(NCS)_2$

Table 1.2.

assumes more ionic character, due to back-bonding between the filled metal and empty phosphorus d orbitals, and hence the more ionic Pd-NCS linkage is favoured.

However, steric effects could provide as valid an explanation for the Pd(II) complexes as does the π-bonding hypothesis. This is exemplified by cis-Pd($Ph_2PCH = CHPh_2$)$(SCN)_2$(8) which involves a phosphine with better π-acceptor properties than that in cis-Pd($Ph_2PCH_2CH_2PPh_2$)(NCS)(SCN)(7), but whose steric requirements are less.

Nevertheless, there are a number of amine complexes where the π-bonding hypothesis does provide an explanation for thiocyanate co-ordination behaviour. The presence of electron withdrawing substituents, like the nitro group in phenanthroline, increases the ability of the ligand to take part in π-backbonding and thus explains the co-ordination behaviour in Pd(phen)$(SCN)_2$ and Pd(5-NO_2phen)$(NCS)_2$(6). Conversely the presence of electron donating substituents would decrease the ability of a ligand to form a π-bond with a metal, as observed in Pdbipy$(NCS)_2$(10) and Pd(4,4 dimethylbipy)(NCS)(SCN)(6).

On the other hand, octahedral cobalt (III) complexes, exemplified by the stable isomers $[Co(NH_3)_5NCS]^{2+}$ and $[Co(CN)_5\ SCN]^{3-}$(12), also clearly illustrate a co-operative ligand effect. In contrast to the previous discussion on class 'b' metals, cobalt is a class 'a' metal and ligands of strong π-bonding ability favour S-thiocyanate co-ordination, whereas σ donors such as NH_3 favour thiocyanate bonding through nitrogen.

The co-ordination behaviour of metal carbonyl thiocyanates reported by Wojcicki and Farona(13), is in general agreement with that of Cobalt (III). Thus, of the two linkage isomers $Mn(CO)_5SCN$ and $Mn(CO)_5NCS$, the S-bonded isomer is the more stable, and substitution of two CO groups by weaker π-bonding ligands, such as amines and phosphines, generally yields N-bonded complexes, $Mn(CO)_3L_2NCS$(14). [In order to explain apparent exceptions i.e. cis-$Mn(CO)_3L_2SCN$ (L=$AsPh_3$ $SbPh_3$) it is suggested that steric factors play a major role in stabilising the angular M-SCN linkage in these compounds.] Similarly, the co-ordination of the thiocyanate group in the stable linkage isomers of $(\pi\text{-}C_5H_5)Fe(CO)_2(CNS)$ and $(\pi\text{-}C_5H_5)Mn(CO)_3(CNS)$(15) is through sulphur.

These examples for class 'a' metals are in disagreement with the π-bonding hypothesis of Turco and Pecile, but may be explained in terms of symbiosis, as proposed by Jorgenson(18), such that like ligands "flock" together. Therefore, in the ion $[(Co(NH_3)_5NCS]^{2+}$, the hard NH_3 and N-bonded thiocyanate co-ordinate to cobalt, whilst in $[Co(CN)_5SCN]^{3-}$ the soft cyanide and S-bonded thiocyanate are found. However, when the palladium (II) complexes are considered symbiosis predicts the wrong effect.

Pearson has extended his principle of hard and soft acids and bases (19, 20) and introduced the idea of antisymbiosis(21) by applying the original concept of Chatt and Heaton(22), "that groups of high trans effect, such as ethylene in $Pt(C_2H_4)Cl_3^-$ render the position in mutual trans position more susceptible to bonding by what are known as hard bases". Whether a trans activating group is a σ-donor or π-acceptor is of little consequence. In either case it is advantageous to have an ionic ligand trans to a strongly covalent ligand. Pearson states "two soft ligands in mutual trans position will have a destabilising effect on each other when attached to class 'b' metals". This concept, like symbiosis, has wider chemical application but when used to explain thiocyanate co-ordination behaviour it would thus predict that cis-palladium-phosphine complexes would contain N-thiocyanate groups while the corresponding trans compounds would be S-bonded. Burmeister and Melpolder(23) have prepared a series of thiocyanate gold complexes of the type LAu(SCN) containing ligands of varying trans influence, where the steric environment remains essentially constant. They concluded that the proportion of N-bonded isomer in the complexes increased as the trans influence of the complex increases, in accordance with Pearson's antisymbiolic principle.

Norbury, however, provides a semi-quantitative approach to explain thiocyanate co-ordination behaviour for both class 'a' and class 'b' metals(24), based on Klopman's polyelectron pertubation theory(25). Molecular orbital calculations show that the electron distribution in the two most energetically available orbitals of the thiocyanate ion is unequal, being concentrated more on the nitrogen atom in σ_4 and on the sulphur atom in σ_3(26). It is argued that both these orbitals would play an important part in thiocyanate co-ordination. Although these orbitals energies are constant for each orbital, regardless of which atom acts as a donor, the de-solvation energy, however, will be very much dependent upon whether the nitrogen or sulphur atom is being desolvated before co-ordination. Calculation of hardness and softness parameters of each donor atom in each available orbital, shows that there are four softness parameters, depending upon which atom is co-ordinated and on which orbital is considered. It also takes into account the variation of softness or hardness with dielectric constant of the solvent used, as the results illustrate in Fig. 1.3.

It is thus argued that since the hardest centre available is the nitrogen end of the σ_4 orbital, this is the most likely donor to the hardest Lewis acids, namely class 'a' metals, surrounded by hard ligands e.g. $[Co(NH_3)_5NCS]^{2+}$. The softest centre is also a nitrogen atom but now that of the σ_3 orbital, which will bond to the softest Lewis acid available, namely a class 'b' metal surrounded by soft ligands (e.g. Pd(II) - phosphine complexes). Intermediate situations involving a class 'a' metal with soft ligands or class 'b' with hard ligands would each prefer to co-ordinate with the sulphur atom e.g. $[Co(CN)_5SCN]^{3-}$.

The major disadvantage of all previous arguments is that they neglect any π-bonding between the thiocyanate group and the metal. Gutterman and Gray(27) have suggested that S-bonded thiocyanates act not as a π-acceptor as indicated for 2nd and 3rd row complexes but rather as a π-donor ligand due to the availability of two ~~2~~ π electrons on sulphur. Marzilli et al.(28) have used these conclusions to explain the influence of <u>trans</u> ligands of varying π-acceptor ability in $Co(DH)_2(L)SCN$ on the equilibrium between N-and S-bonded isomers. However, such behaviour may equally be explained in terms of the semi-quantitative approach discussed previously as applied by Norbury et al. to a more extended series of results on $Co(DH)_2(L)SCN$(29).

It is evident that no one explanation seems satisfactory. Although the co-operative ligand effect is electronic in nature, the factors governing such an effect are complex, and further understanding is required.

(c) Solvent effects

The advantage of the semi-quantitative approach by Norbury(24) is that not only does it allow a description for both class 'a' and class 'b' metals, but also the effect of solvents. Burmeister et al. (30, 31) observed that the co-ordination behaviour of $Pd(Ph_3As)_2(NCS)_2$ and similar Pd(II) complexes may be modified in solution by the solvent. They concluded that the S-bonded thiocyanate complex ~~was~~ is favoured by solvents of high dielectric constant, whilst in solvents of low dielectric constant, the N-bonded isomer predominates.

On the other hand, experimental evidence for $Co(DH)_2pySCN$ indicates the reverse and that solvents of high dielectric constant favours the thiocyanate group bonded through nitrogen and in solvents of low

Variation of Hardness or Softness of the NCS-Group with Dielectric Constant

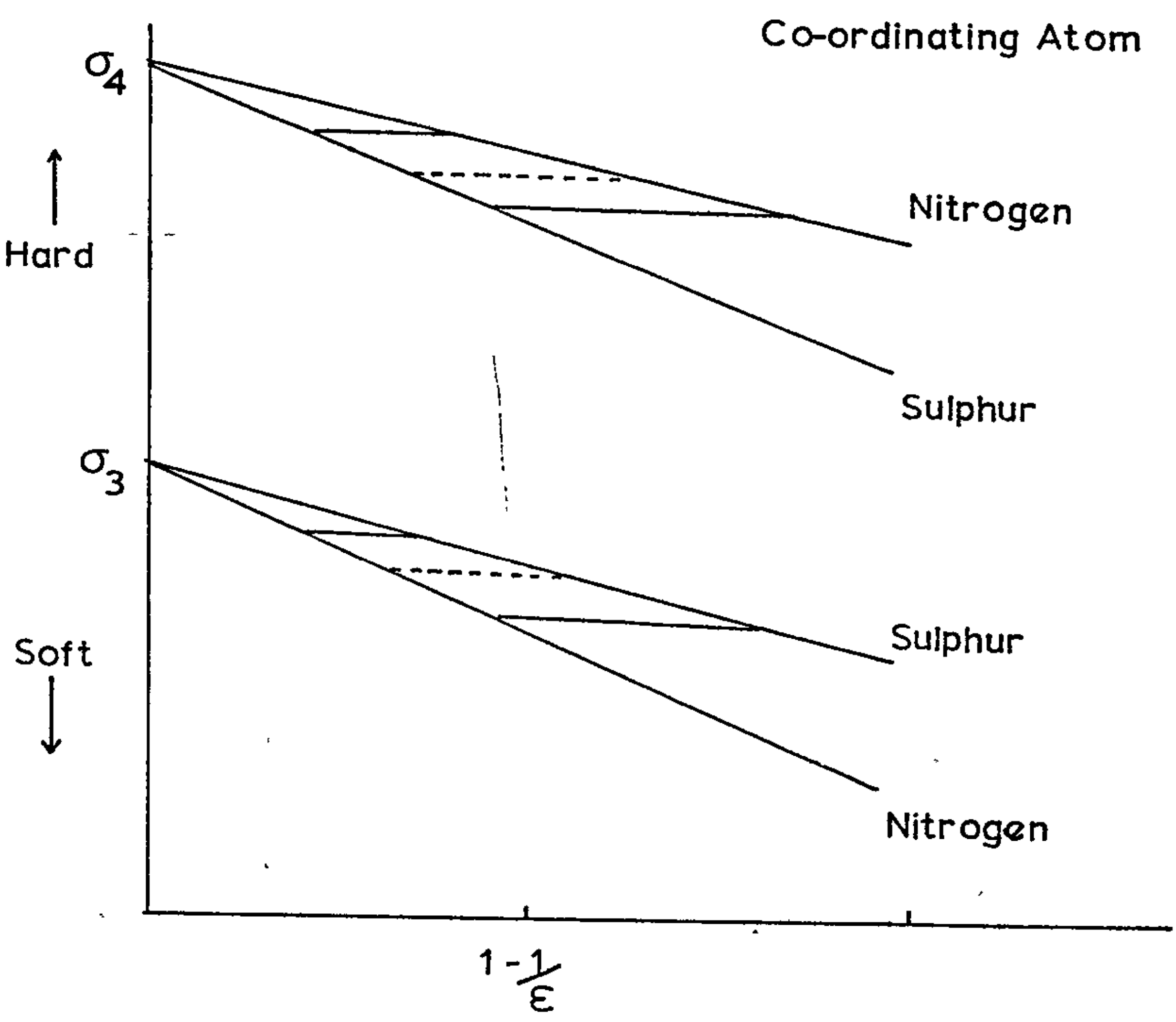


Fig. 1.3.

dielectric constant through sulphur(32). However, evidence for a solvent effect is limited, but it does appear that for linkage isomers in a high dielectric constant M-NCS bonding is favoured for class 'a' metals and M-SCN for class 'b' metals. The opposite effect is observed in solvents of low dielectric constant. By applying the semiquantitative approach of Norbury, Fig. 1.3. shows that, assuming the metal is unaffected by changes in the solvent, for a class 'a' metal, increasing the dielectric constant changes the preference from M-NCS to M-SCN (dotted line Fig. 1.3.). For class 'b' metals the opposite effect is observed, consistent with the experimental evidence obtained.

Since the factors governing the co-ordination behaviour of the thiocyanate group will be in approximate balance for linkage isomerism to occur, other small energy changes may be important, which are not taken into account by the above treatment. For instance, the fine balance of ligational effects may be perturbed by the solvent.

(d) Counter-Ion Effects

The mode of the co-ordination of the thiocyanate group may be affected by the nature of the counter ion in charged complexes. Solid $[Pd(Et_4dien)(SCN)]PF_6$ does not readily isomerise whereas isomerisation does occur in $[Pd(Et_4dien)(SCN)]$ NCS(33). Similar behaviour is exhibited by $[Pd(Et_4dien)(NCS)]$ BPh_4 to give $[Pd(Et_4dien)(SCN)]$ BPh_4 in the solid state where isomerisation is ascribed to the interaction of the sulphur with the phenyl groups in the crystal which over-rides its interaction with the co-ordinated amine(34). A similar type of effect has been observed with cations. $K_3Co(CN)_5SCN$ is the stable isomer in the solid state(12), although its linkage isomer is known(35). When the cation is replaced by $n\text{-}Bu_4N^+$, isolation of a pure S-bonded isomer was found impossible, and further isomerisation to give $(Bu_4N)_3Co(CN)_5NCS$ was rapid(37). It was suggested(36) that the stabilisation of the N-bonded isomer was due to an electronic effect in which the polarisable end of the thiocyanate group is better accommodated by the soft non-polar environment of the $n\text{-}Bu_4N$ cation while the hard K^+ undergoes a more favourable interaction with the hard nitrogen atom. This explanation would predict the wrong results if applied to the Pd complexes, and steric arguments do not apply to the latter. Unfortunately, there are too few examples to make generalisations.

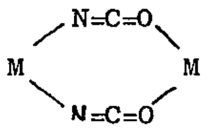
2) Selenocyanate Complexes

Although the selenocyanate group has not been so well studied, certain comparisons can be made with the thiocyanate group. The homogeneous anionic selenocyanate complexes show a similar behaviour to the thiocyanate complexes, in that the selenocyanate ion prefers co-ordination to class 'a' metals through nitrogen, whilst in class 'b' metals bonding through selenium is preferred(3). In mixed ligand complexes, although the selenocyanate group is less sensitive to ligand effects, it is subject to the same differences in co-ordination behaviour in class 'a' and class 'b' metals which prevail in thiocyanate co-ordination(3).

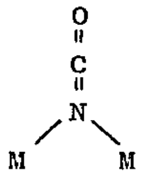
3) Cyanate Complexes

Of the homogeneous anionic cyanate complexes, only the compounds, namely $[Re(OCN)_6]^{2-}$, $[Re(OCN)_6]^{-}$ and $[Mo(OCN)_6]^{3-}$(37) and $[Hg(OCN)_4]^{2-}$(38) have been reported to contain the O-bonded cyanate group based on the fundamental cyanate vibrations. The others are regarded as isocyanate complexes metal-N bonding. Only for the latter compound has any confirmatory measurement been attempted, in which case ^{14}N nmr showed a relatively small upfield shift characteristic for an N-bonded compound(39).

The cyanate group seems insensitive to variations in the electronic environment of the metal in mixed ligand complexes. Norbury and Sinha have studied a variety of Pd(II) and Pt(II) complexes of the type $ML_2(NCO)_2$ containing a variety of σ-and π-bonding ligands, and without exception all were N-bonded(40, 41). The few reported mixed ligand O-cyanate complexes are $K[Cu(picoline)_2OCN]$(42) and the series of complexes $Cp_2M(OCN)_2$ [M=Ti,Zr,Hf](43, 44). However, there is conflicting evidence on the co-ordination behaviour of the cyanate group in the latter series which will be discussed further in chapter II. The existence of an oxygen-bonded complex has not been unambiguously demonstrated by an X-ray crystal structure determination. The preparation and crystal structure determination of $[Ni_2tren_2(NCO)_2]BPh_4$(45) is the only unequivical proof that the oxygen of the cyanate group is involved in bonding where the cyanate group is acting as an end-to-end bridge(I) Fig. 1.4.(I).



(I)



(II)

The other type of bridging normally found in cyanate complexes is of a single atom variety where the nitrogen atom is involved(II)(46). These facts suggest that the oxygen atom of the cyanate group is involved in co-ordination only with reluctance, and hence no comparison can be made with the other pseudohalide complexes.

4) Tellurocyanate Complexes

The existence of the TeCN ion has only recently been established (47, 48, 49). No tellurocyanate complexes have as yet been reported.

5) Physical Methods for Determining the Mode of Co-ordination of the Chalcogenocyanate Ions

The mode of co-ordination of the chalcogenocyanate ligands has been determined by a number of techniques. However, in certain cases, e.g. assignment of O-and N-bonded cyanates, anomalies and difficulties arise, and X-ray crystallography remains the only reliable method.

Infrared spectroscopy, U.V spectroscopy, ^{14}Nn.m.r., Mass Spectrometry, ^{1}H proton n.m.r. spectroscopy and dipole moments have been applied in order to determine the mode of co-ordination but, of these, the former has the widest application, and has been used extensively in this work. For these reasons it is convenient to survey only infrared spectrophotometric measurements for determining the mode of co-ordination of the chalcogenocyanate group.

Infrared spectroscopy

This technique is the most important for making structural assignments and has recently been reviewed by Bailey et al.(50). The normal vibrations of a linear triatomic molecule NCX are:-

$\vec{N}-\overset{\leftarrow}{C}-\overset{\leftarrow}{X}$ $_1$pseudo-assymmetric stretch (νCN)

$N-\overset{\uparrow}{C}-X$ $_2$ (δNCX)

$\vec{N}-\vec{C}-\overset{\leftarrow}{X}$ $_3$ pseudo-symmetric stretch (νCX).

These vibrations have been examined in order to correlate frequency shifts with the mode of bonding of the various pseudo-halides.

Thiocyanate complexes

The infrared spectra of thiocyanate complexes have been extensively studied, and a number of examples are presented in Table 1.5.

On co-ordination of the thiocyanate group through nitrogen or sulphur the CN stretching frequency is slightly changed from the free ion value (ν(CN)2053cm^{1}). Whilst N-bonding leads to little change and sometimes a decrease below the free ion value, shifts in the order of 50-70cm^{-1} are reported for co-ordination through sulphur. However, it has been observed that overlap between the frequency ranges of S- and N-bonded complexes may arise and sometimes be reversed, as demonstrated by the linkage isomers Co(DH)$_2$py(CNS)(32) (Table 1.5). It has been shown that other possible electronic and structural factors prevent

Infra red Spectra of Some Thiocyanate Complexes (cm^{-1})*

	$\nu(CN)$	$\nu(CS)$	$\delta(NCS)$	A^a
π-$C_5H_5Mo(CO)_3NCS$	2099^b_s	-	-	9.80
π-$C_5H_5Mo(CO)_3SCN$	2114^b_m	699w		2.19
$Mn(CO)_5SCN$	2160	676w		
$Mn(CO)_5NCS$ (in CH_3CN)	2113	813		
$Mn(CO)_3(AsPh_3)_2SCN$	2148^b_m	-		
$Mn(CO)_3(AsPh_3)_2NCS$	2103^b_m	814m		
π-$C_5H_5Fe(CO)_2NCS$	2123^b_s	830m		6.70
π-$C_5H_5Fe(CO)_2SCN$	2118^b_m	698w		1.64
trans-$Co(DH)_2pyNCS$	2128s,sp	837w		10.24
trans-$Co(DH)_2pySCN$	2118s,sp			1.2
$[Co(NH_3)_5NCS](ClO_4)_2$	2125b	806		
$[Co(NH_3)_5SCN](ClO_4)_2$	2100sp	710w	426	
$Pd(AsPh_3)_2(NCS)_2$	2089s,br	845m		
$Pd(AsPh_3)_2(SCN)_2$	2119s,sp			
$[PdEt_4dienNCS]^+$	2060	830		
$[PdEt_4dienSCN]^+$	2125	710		

The data were recorded as mull spectra unless otherwise indicated.

*From Norbury ref.3.

(a) $x10^{-4}M^{-1}cm^{-2}$

(b) In $CHCl_3$

(c) Includes $\nu(CN)$ for cyano-groups

Table 1.5.

this criterion from having a general application(51, 52, 53). The CN stretching mode for bridging thiocyanates normally occurs at higher frequencies than in terminal complexes(54, 55).

If the CS stretching frequency is considered, bands at 700 cm^{-1} are indicative of bonding through sulphur, whilst those between 800-830 cm^{-1} suggest N-bonding(56). As well as being subject to possible structural and electronic factors, this frequency also occurs in the same region of the spectrum as frequencies associated with other ligands or counter-ions, so that being only of medium or weak intensity it is difficult to assign. A further complication is that it can be sometimes confused with the first overtone of the bending frequency(57).

Finally, a single sharp band at ~480 cm^{-1} has been assigned to the bending mode in an N-bonded complex in contrast to the several low intensity bands near 420 cm^{-1} observed in S-thiocyanates(56, 58). These splittings in the latter case may be due to the removal of degeneracy attributable to the lower symmetry of the non-linear M-SCN bond. However, it has been shown that the double degeneracy of the bending mode is sometimes resolved in the case of the isothiocyanate complexes as well(59).

It is clear that change in the mass, size of charge on the metal can have profound consequences on the position of a given frequency, not withstanding the further effects due to the size or electronic nature of the ligand. Kharitonov et al.(60) have calculated theoretical changes in the vibrational frequencies with changes in the force constants of M-N and M-S bonds on the assumption that the internal force constants remained unchanged from the free ion values. Their conclusions have been summarised by Bailey et al.(50) and by Norbury(3) in their reviews.

Further clarification of the bonding mode of the thiocyanate group, can be made by measuring the integrated absorption intensity of the CN stretching frequency, (i.e. the area under the absorption peak) (61, 62). Ramsey's method of direct integration is often used(63). The equation is:

$$A = \frac{\pi}{2Cl} \log \frac{I_0}{I} \Delta\nu\tfrac{1}{2}.$$

where C = concentration in moles/litre l = cell thickness, $\frac{I}{I_0}$ = fraction of transmitted light, and $\Delta\nu\frac{1}{2}$ = width of the absorption band at half the height of its peak.

Values in the region 3-5 x 10^4 $M^{-1}cm^{-2}$ are found for the free thiocyanate ion, whilst integrated intensities below this are recorded for S-thiocyanate and values of greater than 9 x 10^4 $M^{-1}cm^{-2}$ are found for N-bonded complexes (See Table 1.5.) A theoretical justification (61, 64) for such results is that co-ordination through S would favour an increased contribution from N≡C-S of the three resonance forms of the ions (see Table 1.6.), such that the dipole moment of the ion would be decreased. Conversely, for the N-bonded case, there is an increase in contribution from the other two resonance forms resulting in an increase of the dipole moment of the ion. The argument is based on the assumption that a change in the magnitude of the dipole moment causes a corresponding change of the dipole during vibration, and hence a change in the intensity of the band.

Percentage Contribution of the Principal Resonance
Forms of the Chalcogenocyanate Ions*

	$N\equiv C-X^-$	$^-N=C=X$	$^{2-}N-C\equiv X^+$
X = O	75	1	24
S	76	5	19
Se	88	0	12
Te	90	4	6

*From Norbury ref.3.

Table 1.6.

Since measurements are made in solution, care must be taken in interpreting results as the integrated intensity may be influenced by a number of factors. As discussed previously, the mode of co-ordination may be influenced by the nature of the solvent. Also, line broadening may arise when using hydrogen bonding solvents.

Measurement of integrated intensities has been extended to insoluble compounds using KBr discs(64). Satisfactory results have been obtained for both S-and N-bonded complexes. The method has been refined by the use of internal standards, such as using the CO stretching frequency of salicylic acid(65). Integrated intensities in either case are cited per thiocyanate. Problems may arise in interpretation when a complex contains more than one thiocyanate group. In view of the difficulties, care should be taken in assigning the mode of bonding purely on infrared data alone, and supplementary measurements should also be made.

Selenocyanate Complexes

Kharitonov et al.(60) have applied a similar treatment as previously described to selenocyanate complexes, and their conclusions are the same in both cases. Examination of the infrared spectra of some selenocyanate complexes (Table 1.7.) indicates a similar situation to the thiocyanates.

On co-ordination of the selenocyanate group through either end, the stretching frequency is slightly increased from the free ion value. However, as in the case of the thiocyanate complexes, the change in CN stretching frequency alone does not provide a reliable criterion for the diagnosis of the bonding mode of the selenocyanate group. When the selenocyanate group acts as a bridging ligand, the CN stretching frequency is appreciably increased relative to the free ion value. The C-Se stretching mode of the selenocyanate ion is increased on N-co-ordination and decreased on Se-co-ordination. The SeCN bending frequencies show at least one component below 400 cm^{-1} while the N-bonded complexes, even when split, do not lie this low and generally occur

Infra red Spectra of Some Selenocyanate Complexes (cm^{-1})*

	ν_{CN}	ν_{CSe}	δ_{NCSe}	A^a
π-cpFe(CO)(PPh_3)NCSe	2120 m	663 mw		
	2107 m^b			5.3
π-cpFe(CO)(PPh_3)SeCN	2112 mw	532 w		
	2117 mw^b			1.7
cis-Co$(DH)_2(H_2O)$NCSe	2075	605		
trans-Co$(DH)_2(H_2O)$SeCN	2140			
Rh$(PPh_3)_2$CO(NCSe)	2094			7
Rh$(PPh_3)_2$MeCN(SeCN)	2135			2.3
$[Pd\ Et_4\ dien\ NCSe]^+$	2085 s,br	618		
	2089^c			6.6
$[Pd\ Et_4\ dien\ SeCN]^+$	2121 s,sp	533 w	404 w	
	2125^c			0.63

The data are recorded as mull spectra unless otherwise indicated.

*From Norbury ref.3.

(a) x 10^{-4} M^{-1} cm^{-2}.

(b) In $CHCl_3$.

(c) In acetone.

Table 1.7.

above 400 cm^{-1}.

The relative contributions of the resonance forms of $NCSe^-$ (Table 1.6.) are comparable to those of NCS^- so that integrated intensities can be used in a similar way.

Cyanate Complexes

The use of infrared measurements to determine the mode of co-ordination in cyanate complexes becomes even more difficult for two reasons: (i) there is more mixing between the cyanate frequencies than is observed for the other ions and this is also observed in complexes, (ii) there are very few reported O-bonded cyanates, none of which have been confirmed by X-ray crystallography. Only the complex $(\pi\text{-cp})_2Ti(OCN)_2$ has been studied by techniques other than infrared (66, 44, 67), but these measurements gave conflicting results.

The infrared spectra of a number of cyanate complexes are recorded in Table 1.8. including the spectra of a number of organic cyanates. Infrared spectral and other measurements indicate that most of the complexes are N-bonded; the CN stretching frequency increases and the NCO bending frequency slightly decreases, as might be expected from previous arguments. Similarly, the CO stretching frequency slightly increases in N-cyanate complexes.

The percentage contributions of the different resonance forms (Table 1.6.) are comparable with those of the other ions, and this

Infra red Spectra of Some Cyanate Complexes (cm^{-1})*

	ν_{CN}	ν_{CO}	δ_{NCO}	A[a]
CH_3OCN	2256 s,sp	1100 s,sp		
		1218 mb		
C_2H_5OCN	2245 s,sp	1102 s,sp		
		1127 w,sw		
		1173 m,sp		
$n\text{-}C_3H_7OCN$	2247 s,sp	1107 ss		
		1165 m		
$(\pi\text{-cp})_3CeNCO$	2145 s	1310		-
$(C_9H_7)_2Ce(NCO)_2$	2225 m	1320 m		
$(\pi\text{-cp})_2Ti(OCN)_2$[I]	2235[b]	1132 m	626 m	13
	2196[b]		593 m	18
$(\pi\text{-cp})_2TiNCO$	2216[c]	1302 ms	599 m	-
			590 m	
$(\pi\text{-cp})_2Zr(OCN)_2$[I]	2233[b]	1257 w	631 m	12
	2200[b]	1070 sh	607 m	16
$(\pi\text{-cp})_2Hf(OCN)_2$	2246[b]	1257 w	632 m	12
	2211[b]	1071 sh	606 m	18
$[Mo(OCN)_6]^{3-}$	2205 s	1296 m	595 m	
		1140 m		
$[Re(OCN)_6]^{2-}$	2224 s	1306 w	595 m	
		1138 w		
$[Re(OCN)_6]^{-}$	2220 s	-	-	

	ν_{CN}	ν_{CO}	δ_{NCO}	A^a
Pd py_2 $(NCO)_2$	2180-2210 s	1332 m,sp	586 m, sp	
.	2202^d			21.4
$Pt(Ph_3P)_2(NCO)_2$	2230 sh	1355 vw	590	
	2200 s,sp	1312 m,br		
	2258^e			13.0
K[Cu pic_2 (OCN)]	2143	1205	630	
			625	

The data are recorded as mull spectra unless otherwise indicated.

*From Norbury, ref. 3.

(a) x 10^{-4} M^{-1} cm^{-2}.

(b) In CH_2Cl_2.

(c) In acetone.

(d) In $CHCl_2$.

(e) In CH_3NO_2.

[I] One or other of these structures is incorrectly formulated.

Table 1.8.

would indicate that integrated intensity criteria could be used as before. The integrated intensities for a series of palladium and platinum complexes cited per cyanate group are in the range 13-23x10^4 $Moles^{-1}cm^{-2}$ and larger than the free ion value of 8.4, indicating N-bonding(40). However, the integrated intensities of $(\pi-C_5H_5)_2M(OCN)_2$ (N=Ti,Zr,Hf) are also larger than the free ion values, and it has been suggested that this criterion is inapplicable to cyanate complexes because of the small difference in mass between the nitrogen and oxygen(44).

For the O-bonded cyanates reported, ν(CN) increases and δ(NCX) also decreases in the same order as N-bonded cyanates. However, two bands are often observed for the bending vibration (~600 cm^{-1}) in the O-bonded cyanates which might be expected. The removal of the degeneracy of the corresponding NCS mode due to the lower symmetry of the non-linear M-SCN group has been used as a criterion for S-bonding in thiocyanate co-ordination(50). Similarly, the M-OCN unit might also be expected to be non-linear, in which case if the degeneracy of the deformation mode is removed then two bands would be predicted. However, splitting of this frequency is sometimes observed in N-bonded cyanates.

It is the CO stretching frequency which has been important in determining O-cyanate complexes. Fermi resonance occurs between ν(CO) and 2δNCO in the free ion(70), (e.g. KNCO, ν(CO) 1300 cm^{-1}, 1205 cm^{-1} -calculated value 1254 cm^{-1}(71)). On co-ordination through nitrogen ν(CO) generally increases in magnitude and δ decreases. The medium strong band at 1302cm^{-1} in cp_2TiNCO has been attributed to ν(CO) for an N-bonded species without Fermi resonance on this basis(44). (See also Table 1.8.) For these or for other reasons, Fermi resonance has not been observed in N-cyanate complexes. In O-bonded cyanates there is ample opportunity for the phenomenon of Fermi resonance to be maintained. Such Fermi resonance is exhibited in the infrared spectra of organic cyanates where two bands attributed to the CO stretching frequency are observed in the region 1200-1100cm^{-1}(68). Similarly, the bands at approximately 1300cm^{-1} and 1140cm^{-1} in $[Re(OCN)_6]^{2-}$ and $[Mo(OCN)_6]^{3-}$ have been assigned on this basis(37). Burmeister et al. have attributed the bands at ~1257cm^{-1} in $cp_2M(OCN)_2$ [M=Zr, Hf] to Fermi resonance(44). No such splitting is observed in $cp_2Ti(OCN)_2$ and it is argued that Fermi resonance does not occur. However, evidence does suggest that one or more of this series of complexes is incorrectly assigned which will be discussed in a later chapter.

Therefore, the determination of the co-ordination of the cyanate group by infrared measurements can only be treated with the utmost caution, finding further data, i.e. crystal structure determination of O-bonded cyanate complex.

CHAPTER 2

THIOCYANATE COMPLEXES OF RHODIUM(I)

THIOCYANATE COMPLEXES OF RHODIUM(I)

A series of complexes of the type $Rh(L)_2(CO)NCS$ (L = phosphine, arsine or stibine) and $Rh(L)_3NCS$ ($L = P(OC_6H_5)_3$) have been prepared and studied by Jennings and Wojcicki(72). The mode of co-ordination of the thiocyanate group in all the complexes was found to be exclusively through nitrogen. This is in contrast to the isoelectronic Pd(II) complexes where, depending on the other ligand, both Pd-NCS and Pd-SCN linkages have been obtained as have some examples of linkage isomers e.g. trans $Pd(AsPh_3)_2(CNS)_2$(5, 9, 10, 57).

It was observed that there was a great tendency on the part of aryl-arsine and triphenyl-phosphite rhodium(I) derivatives to form dinuclear thiocyanato-bridged species in solution (Fig. 2.1.) These complexes also showed an ability, in the presence of excess thiocyanate ion, to form bis thiocyanate rhodium(I) complexes, as shown in Fig.2.1., although no evidence was offered for the nature of the particular NCS-bridge.

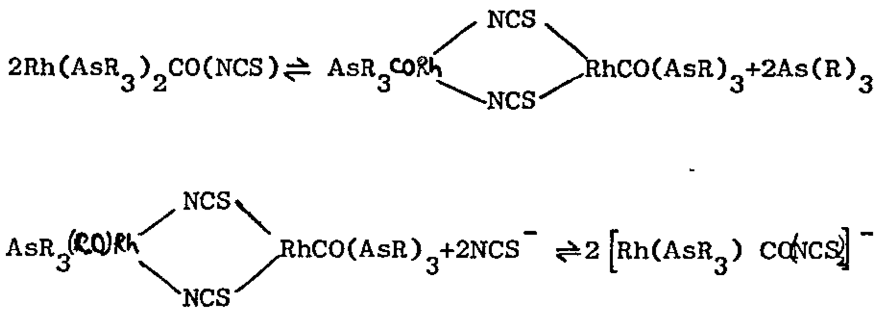


Fig. 2.1.

No attempts were made, however, to study the thiocyanate - tris(triphenyl phosphine)rhodium(I) system. This chapter describes the preparation and some of the reactions of this compound. Because of the complexity of the system the results-discussion section has been divided in the following manner:-

(i) An infrared spectral study of the reaction of the Me_4NSCN with $Rh(PPh_3)_3Cl$.

(ii) The preparation and reactions of $Rh(PPh_3)_3NCS$

(iii) The preparation of $Rh(PPh_3)_2(L)SCN$ $[L = C_6H_6, C_6H_5Cl]$

(iv) The preparation of $Rh(PPh_3)_2SCN$ - A three co-ordinate rhodium(I) complex.

(v) Oxygen adducts of rhodium(I)-thiocyanate complexes.

(vi) Catalytic properties of $Rh(PPh_3)_3NCS$.

Results and Discussion

(i) An Infrared Study of the Reaction of Me_4NSCN with $Rh(PPh_3)_3Cl$

When the reaction between Me_4NSCN and $Rh(PPh_3)_3Cl$ in MeCN was followed by infrared spectral measurements the solution spectrum showed that the thiocyanate group co-ordinated initially through nitrogen as indicated by the CN stretching frequency at 2095cm^{-1} (cf $Rh(PPh_3)_2(CO)NCS$ ν(CN) 2095cm^{-1} in $CHCl_3$): subsequently a very insoluble bright yellow compound was formed. The infrared spectrum of this solid exhibits a CN stretching frequency at 2135cm^{-1}, higher than that for $Rh(PPh_3)_2(CO)NCS$, (73) and an integrated intensity lower than the free ion value indicating co-ordination of the thiocyanate group through sulphur (See Fig. 2.8.). Further,no bands occur between 700-900cm^{-1} which may be attributable to the CS stretching frequency for an N-bonded complex; $Rh(PPh_3)_2(CO)NCS$ exhibits a CS stretching frequency at 838cm^{-1}. The CS stretching frequency range for the S-bonded case is obscured by triphenylphosphine bands. On the basis of analytical data and the foregoing infrared data,the complex is formulated as $Rh(PPh_3)_2(MeCN)SCN$. The CN stretching frequency for acetonitrile in the complex at 2257cm^{-1} is slightly shifted from that of the free solvent where ν(CN) occurs at 2253cm^{-1}. When the reaction was performed using less solvent (half quantities), a yellow compound was obtained whose analysis is consistent with the formulation $Rh(PPh_3)_2(CNS)MeCN$ (%Rh14.2, %P8.9, Found, %Rh14.2, %P8.7, Calculated), but whose infrared mull spectrum exhibits two ν(CN) bands at 2135cm^{-1} and 2095cm^{-1} attributed to both N- and S-bonded isomers.

Approximate Frequency Range for Thiocyanate Co-ordination*

	ν(CN)(cm^{-1})	ν(CS)(cm^{-1})	δ(NCS)(cm^{-1})	A(x10^{-4}M^{-1}cm^{-2})
NCS^-	2053	746	486,471	3-5
M-NCS	2100-2050 s,b	870-820 w	485-475	7-11
M-SCN	2130-2085 s,sp	760-700	470-430	1-3
M-NCS-M	2165-2065	800-750	470-440	

*From Norbury (3)

Fig. 2.2.

The complex $Rh(PPh_3)_2(Me_2CO)SCN$ was prepared similarly from the reaction of Me_4NSCN with $Rh(PPh_3)_3Cl$ in acetone. Its infrared spectrum indicates that the thiocyanate group is again co-ordinated through sulphur (Table 2.8.) and that an acetone molecule is co-ordinated (Table 2.9.), as indicated by the CO stretching frequency for acetone at $1710cm^{-1}$ compared with that for the free solvent at $1718cm^{-1}$. Co-ordinated acetone in $Ir(PPh_3)_2(CO)Me_2CO)(NCSe)$(73) exhibits a CO stretching frequency at $1712cm^{-1}$. It has been shown that the CN stretching frequency for MeCN does increase to higher wavenumbers on co-ordination, as in $Cu(MeCN)_4ClO_4$(74) where ν(CN) occurs at $2270cm^{-1}$. Although the shift of this frequency in $Rh(PPh_3)_2(MeCN)SCN$ is small, it does imply that acetonitrile is co-ordinated, as with acetone. Furthermore, the analyses for these complexes remain unchanged even after drying for several hours under vacuum, and the infrared spectra showed that the acetone or acetonitrile band had not decreased in intensity.

(ii) The Preparation and Reactions of $Rh(PPh_3)_3NCS$

The complex $Rh(PPh_3)_3NCS$ can be prepared from the reaction of Me_4NSCN with $Rh(PPh_3)_3Cl$ in acetonitrile containing excess triphenylphosphine. The infrared spectrum of this complex exhibits ν(CN) at $2095cm^{-1}$ and ν(CS) at $811cm^{-1}$, similar to $Rh(PPh_3)_2(CO)NCS$, and an integrated absorption intensity for the CN stretching mode which is larger than that of the free ion ($A=8.5x10^4M^{-1}cm^{-2}$ in KBr).

(a) The reaction of $Rh(PPh_3)_3NCS$ in solution.

When the complex $Rh(PPh_3)_3NCS$ is added to solvents such as acetonitrile, acetone, or diethyl ether under nitrogen the bright yellow compounds $Rh(PPh_3)_2(L)SCN$ $[L=MeCN, Me_2CO, Et_2O]$ are isolated (Table 2.8.). These will be discussed in greater detail in a later chapter. All these observations are consistent with the following reaction scheme:-

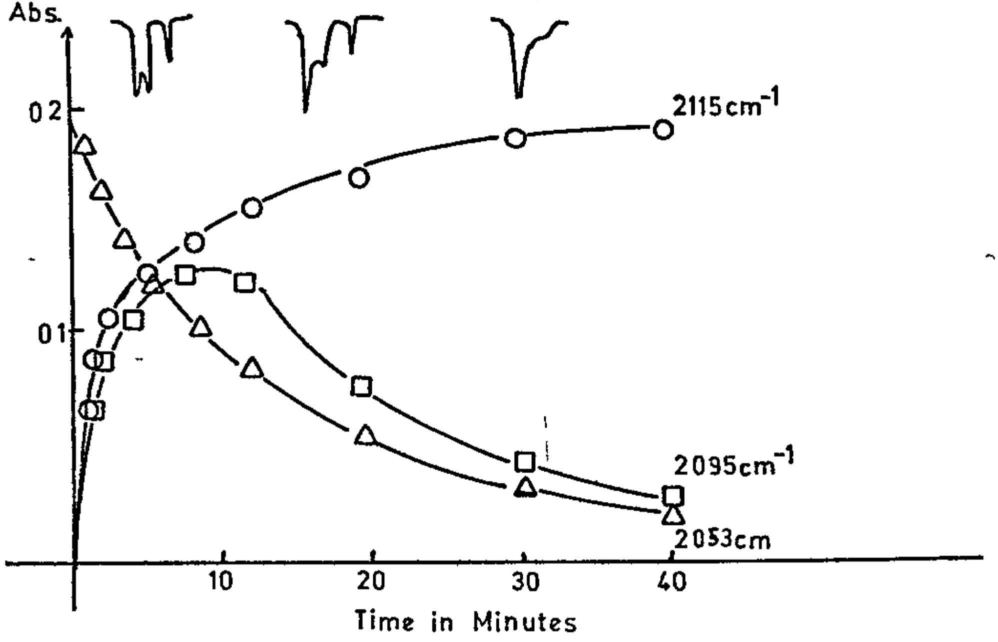
$$\begin{array}{l}
Rh(PPh_3)_3Cl + Me_4NSCN \rightarrow Rh(PPh_3)_3NCS \rightarrow Rh(PPh_3)_2(L)NCS \\
\hspace{8cm}\downarrow \\
\hspace{6.5cm} Rh(PPh_3)_2(L)SCN.
\end{array}$$

(b) The reaction of $Rh(PPh_3)NCS$ with excess Me_4NSCN.

When a solution of $Rh(PPh_3)_3NCS$ in $CHCl_3$/MeCN was treated gradually with tetramethylammonium thiocyanate, the intensity of the band at 2095cm^{-1} decreased and a new peak appeared at 2110-2115cm^{-1}. When $Rh(PPh_3)_3Cl$ was similarly treated with twice the mole amount of Me_4NSCN, the infrared solution spectrum showed initially a band at 2095cm^{-1} and then the appearance of a band at 2115cm^{-1} (Fig.2.3.). Both the infrared solution spectra showed eventually the complete disappearance of ionic thiocyanate (as demonstrated in Fig. 2.3.) simultaneously with the formation of the ν(CN) band at 2115cm^{-1} which gave an integrated intensity of $15.0\times10^4 M^{-1}cm^{-2}$ ($A=7.5\times10^4 M^{-1}cm^{-2}$ per thiocyanate) consistent with the formation of $[Rh(PPh_3)_2(NCS)_2]^-$ However, attempts to isolate this species were unsuccessful.

Infrared Solution Spectral Studies of the Reaction between $Rh(PPh_3)_3X$ and NCS^-

$Rh(PPh_3)_3Cl + NCS^-$



$Rh(PPh_3)_3NCS + NCS^-$

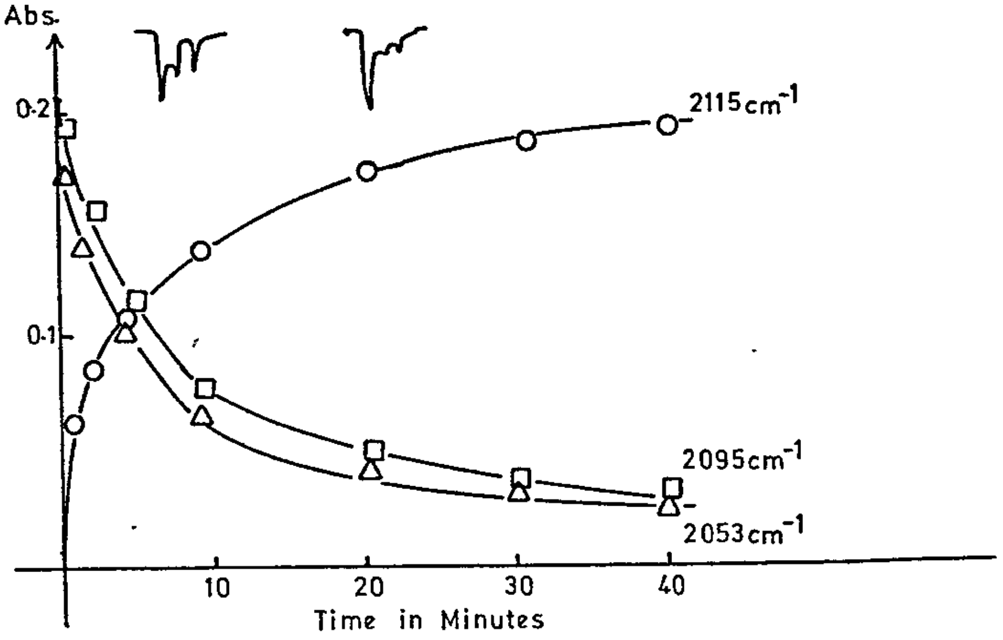


Fig. 2.3

(c) The Reaction of carbon monoxide with $Rh(PPh_3)_3NCS$ and related complexes.

It was found that bubbling carbon monoxide through a suspension of $Rh(PPh_3)_3NCS$ or $Rh(PPh_3)_2(L)SCN$ [L=MeCN,Me_2CO] in acetonitrile resulted in the formation of the N-bonded complex $Rh(PPh_3)_2(CO)NCS$ from infrared spectral and analytical data. Similar results were obtained by passing carbon monoxide over the S-bonded complexes in the solid state. In no case was it possible to detect any bands in the infrared spectrum which might correspond to $Rh(PPh_3)_2(CO)SCN$.

(d) The Reaction of $Rh(PPh_3)_3NCS$ in Benzene.

The infrared spectral solution of $Rh(PPh_3)_3NCS$ in benzene in the presence of air exhibits two $\nu(CN)$ bands at $2155cm^{-1}$ and $2095cm^{-1}$, the former being consistent with the formation of bridging thiocyante. The gradual addition of triphenylphosphine results in the diminution of the band at $2155cm^{-1}$ and eventually the complete disappearance of this absorption. This agrees with the results of Jennings and Wojcicki(72) and is consistent with the type of equilibrium in Fig. 2.1. Similarly, when the insoluble S-bonded complexes are refluxed in benzene for several minutes dissolution results, and their infrared spectra exhibits in solution bands at

2155cm^{-1} and at 2095cm^{-1} attributable to bridging and terminal thiocyanate species respectively. Addition of triphenylphosphine again results in the disappearance of the band at 2155cm^{-1}. When $Rh(PPh_3)_3NCS$ is added to benzene under nitrogen, the infrared solution spectrum exhibits only one band at 2095cm^{-1} due to an N-bonded thiocyanate species. A bright yellow solid eventually precipitates and is described in the next section.

(iii) The preparation of $Rh(PPh_3)_2(L)SCN$ where L = C_6H_6, C_6H_5Cl

The infrared spectrum of the complex isolated from the reaction of $Rh(PPh_3)_3NCS$ in benzene, illustrated in Fig. 2.4., exhibits a ν(CN) band at 2142cm^{-1} (A=2.9x10^{4}M^{-1}cm^{-2} in KBr). Analytical data indicate the formulation $Rh(PPh_3)_2(C_6H_6)SCN$. Because of triphenylphosphine ligand vibrations it is difficult to discern any definite bands attributable to benzene in the complex, although the band at 672cm^{-1} could be due to the benzene γ(CH) vibration. The complex $Rh(PPh_3)_2(C_6H_5Cl)SCN$ was prepared similarly. The infrared spectrum exhibits bands at 1583 and 472cm^{-1} which may be assigned to ν(CC) and X-sensitive vibrations of cholorobenzene respectively. These bands occur at 1588 and 470cm^{-1} in free chlorobenzene (Fig. 2.4.) The analyses of both these complexes after drying for several hours under a flow of nitrogen show no change, and the intensity of the bands in the infrared spectrum attributable to chlorobenzene in $Rh(PPh_3)_2(C_6H_5Cl)SCN$ does not decrease. In the

The Infrared Spectra of $Rh(PPh_3)_2SCN$ and $Rh(PPh_3)_2(L)SCN$

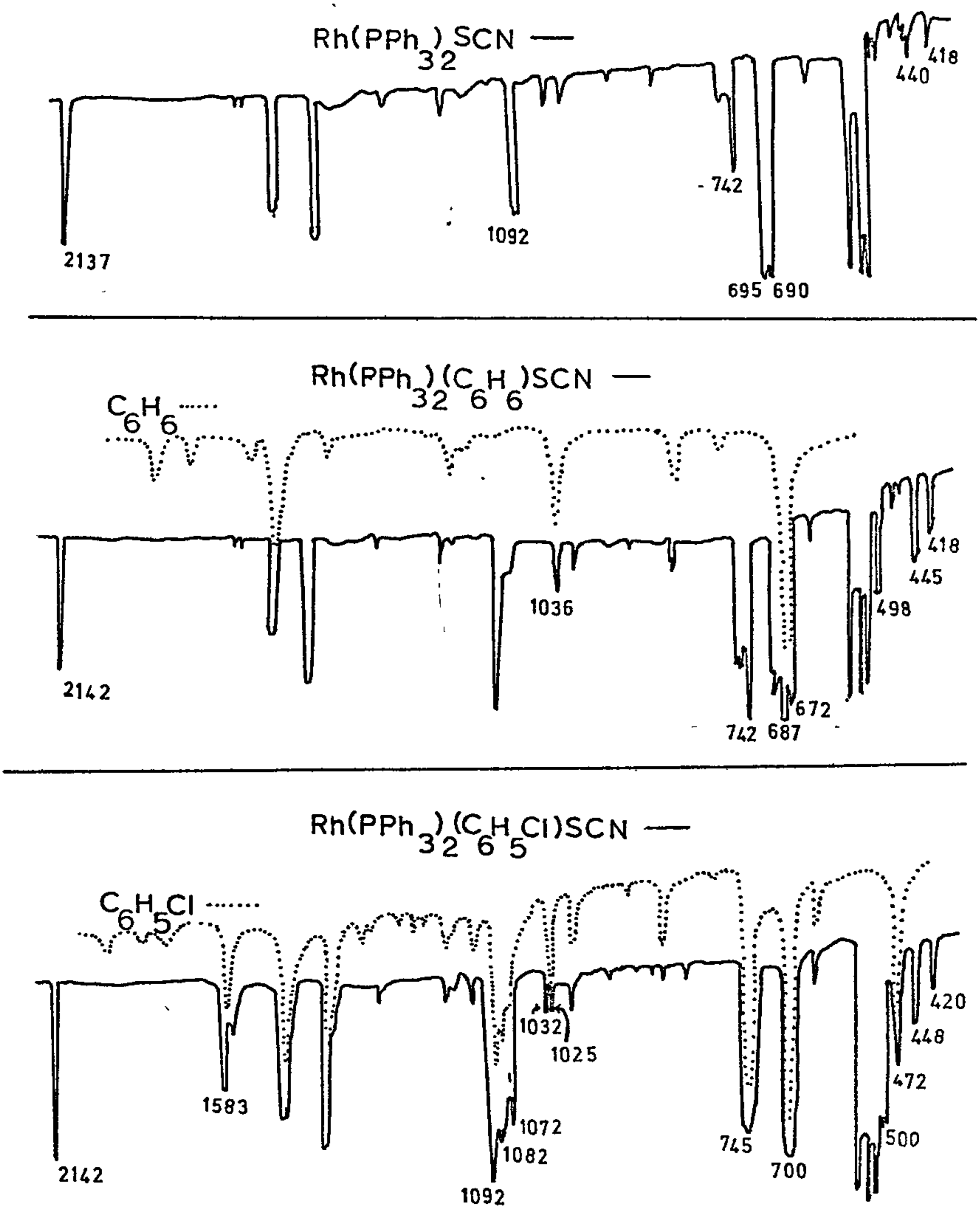


Fig. 2· 4

presence of air, the complexes readily lose these solvent molecules and the rapid uptake of oxygen occurs.

It has been argued that the complex $[RhCO(SbPh_3)_3Cl]\cdot C_6H_6$ is a pentaco-ordinate species stabilised by large stibines where benzene is present as a tightly held clathrated molecule(75). In the infrared spectra of the complexes $Rh(PPh_3)_2(L)SCN$ ($L = CH_3CN$, Me_2CO) shifts, albeit slight, are observed in the principle bands of acetonitrile and acetone compared with the free molecules. Shifts in the CN stretching frequency of the thiocyanate group compared with $Rh(PPh_3)_2SCN$, which will be discussed shortly, also occur. Similarly,the CN stretching frequency in the benzene and chlorobenzene complexes is different from that observed in $Rh(PPh_3)_2SCN$,as shown in Fig. 2.4.,and small shifts are also observed in the principle bands of the chlorobenzene in the complex. It may be concluded,therefore, that the solvent molecules are co-ordinated in the complexes $Rh(PPh_3)_2(L)SCN$, where $L = C_6H_6$ and C_6H_5Cl.

(iv) Preparation of $Rh(PPh_3)_2SCN$ - A Three Co-ordinate Rhodium(I) Complex

Whilst successive washing of the benzene analogue with dry hexane shows no change in its analytical composition, the chlorobenzene complex, on the other hand, seems less stable, and washing with hexane results in a weight loss equivalent to one molecule of chlorobenzene and this is confirmed by subsequent analyses. The infrared spectrum of this complex now shows no bands attributable to chlorobenzene and the CN stretching frequency of the thiocyanate group shifts from $2142cm^{-1}$ to $2137cm^{-1}$.

Similarly, gentle heating of the complex $Rh(PPh_3)_2(C_6H_6)SCN$ under a nitrogen atmosphere results in a weight loss equivalent to one molecule of benzene. Analytical data are consistent with the formulation $Rh(PPh_3)_2SCN$ and the infrared spectrum also shows a shift of the CN band from $2142cm^{-1}$ to $2137cm^{-1}$. The integrated absorption intensity of this vibration is $3.0x10^4m^{-1}cm^{-2}$ in KBr similar to the integrated absorption intensity of the ν(CN) stretching frequency observed in $Rh(PPh_3)_2(L)SCN$, indicating that the co-ordination of the thiocyanate group is unchanged i.e. terminal bonding of the thiocyanate group occurs through sulphur.

When the complex is treated with refluxing benzene, it slowly dissolves and the infrared solution spectra exhibit a band at $2155cm^{-1}$, characteristic of a bridged thiocyanate species. When treated with CO or with other solvents, $Rh(PPh_3)_2SCN$ readily takes up a further molecule to form $Rh(PPh_3)_2(CO)NCS$ or $Rh(PPh_3)_2(L)SCN$ where L = MeCN, C_6H_6 etc.

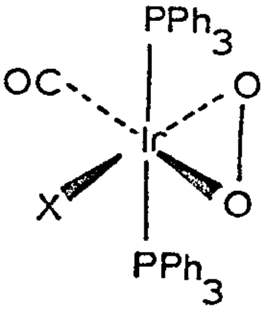
The evidence does suggest that $Rh(PPh_3)_2SCN$ is a three co-ordinate complex, probably stabilised by the bulky phosphine groups and co-ordination of the thiocyanate group through the large sulphur, and with favourable crystal packing in the solid state. The most likely structure for this complex would be one with trigonally disposed ligands.

(v) Oxygen Adducts of Rhodium(I) - Thiocyanate Complexes.

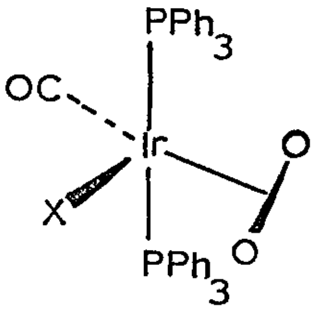
Oxygen complexes of iridium and rhodium complexes have attracted much interest as a model system for biological oxygen uptake. Since the initial preparation and studies of $Ir(PPh_3)_2(CO)Cl.O_2$ by Vaska(76), a number of related iridium complexes have been prepared and X-ray structure determinations performed (77, 78, 79). The complexes are shown to contain oxygen bonded sideways on to iridium. The complexes can be depicted by the two geometrically equivalent structures (Fig. 2.5.I & II,. which are valence bond representations of the limiting oxidation states iridium (III) and iridium (I) respectively).

The oxygen-oxygen bond length varies considerably with the ligands co-ordinated to iridium. For instance, the O-O bond lengths in the chloride and iodide complexes of $Ir(PPh_3)_2(CO)X.O_2$, [X=Cl, I] are 1.30^{o}A and 1.51^{o}A respectively(79). The oxygen adducts are characterised by an infrared band of medium intensity between 900-850cm^{-1} which is insensitive to O-O distance, suggesting that it is not a pure O-O stretching mode(79).

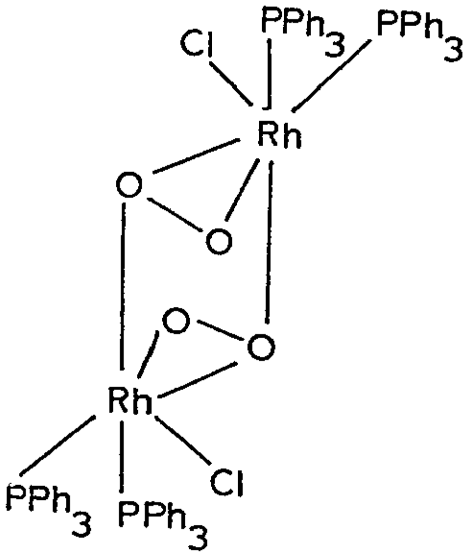
On bubbling oxygen through a solution of $Rh(PPh_3)_3Cl$ in CH_2Cl_2, brown crystals were obtained, whose infrared spectrum exhibited a band at 900cm^{-1} due to co-ordinated oxygen(80). The structure of this complex has also been determined by X-ray crystallography, and shown to contain dimeric units with an unusual O_2 bridge (Fig.2.5.III)(81).. Augustine and Van Peppen(82) showed that uptake of oxygen by $Rh(PPh_3)Cl$ in solution was solvent dependent. In methanol a complex, whose analysis indicated a formulation $Rh_2(PPh_3)_4Cl_2O_5$, was formed, Fig. 2.5.(V), whilst in ethanol extensive oxygen uptake occurred.



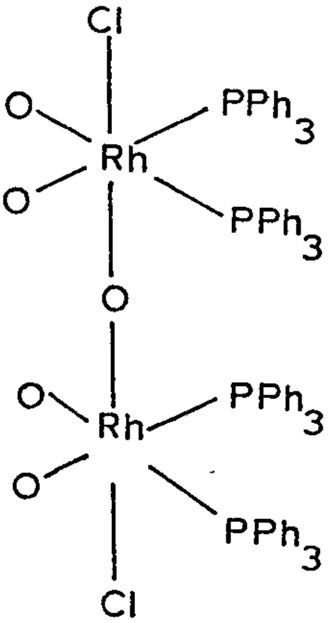
I



II



III



IV

Fig. 2.5

The reaction of $Rh(PPh_3)_3Cl$ with Me_4NSCN in acetonitrile containing an excess of triphenylphosphine in the presence of air gives a greenish brown complex $Rh(PPh_3)_3NCS.O_2$. The infrared spectrum of this complex shows a band at 885cm^{-1} due to co-ordinated oxygen but no bands attributable to PO stretching frequencies. The infrared spectrum, in contrast to the ν(CN) band at 2095cm^{-1} in $Rh(PPh_3)_3NCS$, exhibits a CN stretching frequency at 2110cm^{-1} and a ν(CS) band at 825cm^{-1}. The integrated absorption intensity of both complexes are similar and greater than the free ion value. This indicates that the N-bonded co-ordination of the thiocyanate group is retained in the oxygen complex.

Addition of $Rh(PPh_3)_3NCS$ to diethyl ether in the presence of air gives the greenish-yellow complex $Rh(PPh_3)_2(Et_2O)SCN.O_2$. The infrared spectrum exhibits a band at 905cm^{-1} due to co-ordinated oxygen. The thiocyanate group is co-ordinated through sulphur, as indicated by the ν(CN) band at 2146cm^{-1} ($A=3.1x10^4M^{-1}cm^{-2}$ in KBr). The addition of $Rh(PPh_3)_3NCS.O_2$ to diethyl ether or acetonitrile under N_2 showed no indication of giving an S-bonded product and extraction of the product from acetonitrile showed the presence of Ph_3PO bands in the infrared spectrum.

The complexes probably have a similar structure to the iridium analogues, as shown in Fig. 2.5., and they further demonstrate the ability of rhodium and iridium complexes to co-ordinate molecular oxygen.

(vi) Catalytic Properties of $Rh(PPh_3)_3NCS$.

In view of the ability of these complexes to take up oxygen, it was interesting to determine whether they exhibited catalytic properties similar to that of $Rh(PPh_3)_3Cl$(80, 83-88).

Oxygen was bubbled through a solution of xylene containing triphenylphosphine and a small quantity of $Rh(PPh_3)_3NCS$ in the mole ratio of 20:1 for one hour. The infrared spectrum of the residue, after removal of the rhodium(I)-complex, exhibited strong bands due to triphenylphosphine oxide ($1120cm^{-1}$, $720cm^{-1}$). Bubbling oxygen through a solution of triphenylphosphine containing no $Rh(PPh_3)_3NCS$ gave no indication of forming triphenylphosphine oxide.

The complex $Rh(PPh_3)_3Cl$ has also been shown to readily catalyse the hydrogenation of olefins(83). However, the complex $Rh(PPh_3)_3NCS$ gave no indication of co-ordinating ethylene or hydrogen. Bubbling ethylene through a solution of $Rh(PPh_3)_3NCS$ in benzene only resulted in the isolation of $Rh(PPh_3)_2(C_6H_6)SCN$. Similarly, passing hydrogen or ethylene over the complex $Rh(PPh_3)_2SCN$ as a solid or as a slurry caused no change in its infrared spectrum nor any increase in weight.

However, the complex $Rh(PPh_3)_3NCS$ was found to effectively catalyse the decarbonylation of benzaldehyde(83, 85). Reactions performed using both $Rh(PPh_3)_3Cl$ and $Rh(PPh_3)_3NCS$ as catalyst under identical reaction conditions, gave yields of benzene four times greater in the latter case.

Conclusions

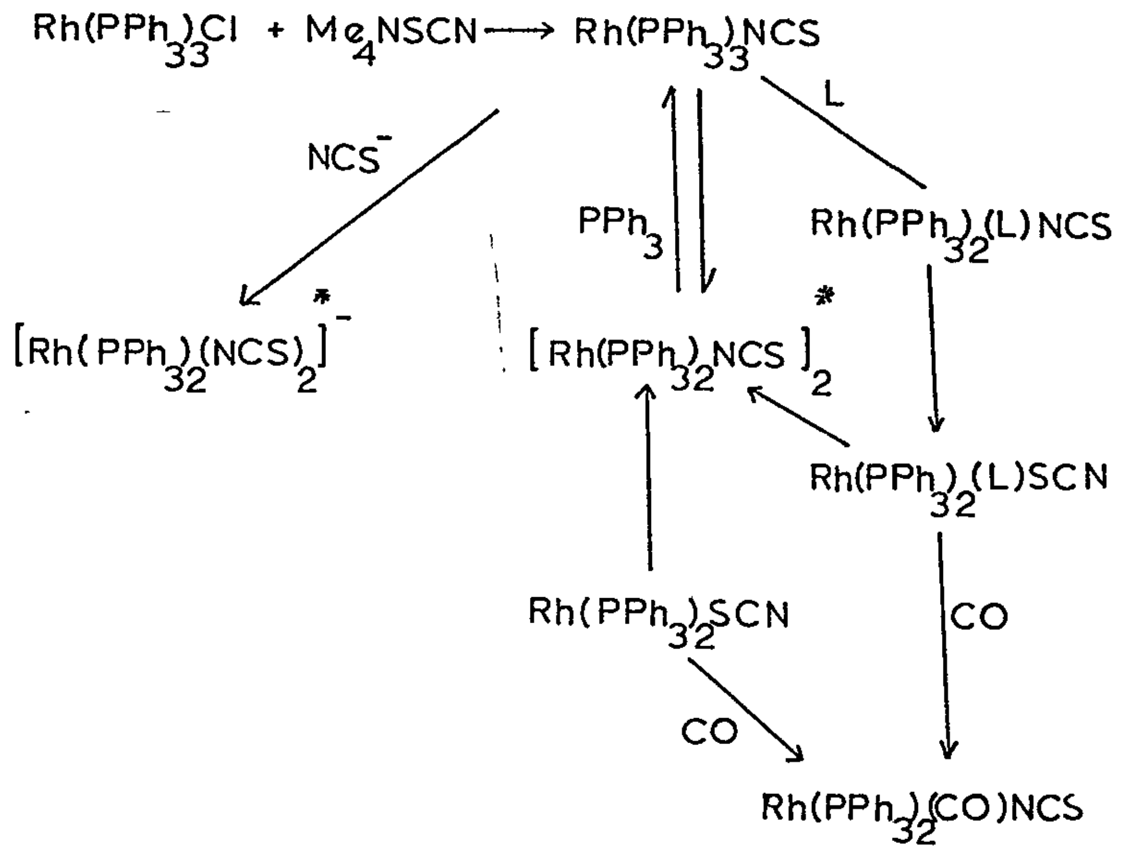
The results described in this study are summarized in the reaction scheme proposed in Fig. 2.6. and show that the reaction of N-thiocyanatobiotris(triphenylphosphine)rhodium(I) in solution can proceed in one of two ways:-

(1) The formation of dinuclear-bridged thiocyanate in accordance with the results of Jennings and Wojcicki,

or (2) The formation of four co-ordinate species in which one molecule of PPh_3 has been replaced by a solvent molecule.

Such behaviour can be compared with $Rh(PPh_3)_3Cl$. The latter complex dissolves in strong donor solvents (L), such as pyridine, dimethylsulphoxide and acetonitrile to yield complexes of the type $Rh(PPh_3)_2(L)Cl$. The dimer $[Rh(PPh_3)_2Cl]_2$ is obtained, however, from benzene solutions(83). The dissociation of $Rh(PPh_3)_3Cl$ has been extensively studied(82, 83, 89-91). Evidence now suggests that dissociation is not extensive in the absence of oxygen(89-91), but is promoted in its presence, and that it is this reactive dissociated species which is important in explaining its catalytic behaviour(82). It has not yet been established whether the dissociated three co-ordinate species $Rh(PPh_3)_2Cl$ or a complex containing a weakly donating solvent ligand occupying the vacant fourth site exists in solution.

The Reaction of Me_4NSCN with $Rh(PPh_3)_3Cl$



* Species identified in solution only.

Fig. 2.6

The complex $Rh(PPh_3)_3NCS$ behaves in a similar fashion. It readily dissociates in solution, and the products may dimerize to form $[Rh(PPh_3)_2NCS]_2$ or the fourth vacant site may be occupied by a solvent ligand(L) to form $Rh(PPh_3)_2(L)SCN$. The essential point is that whilst the dimer is formed in the presence of oxygen, the solvated complexes are formed in its absence. This suggests that although the dissociation of $Rh(PPh_3)_3NCS$ is extensive, the fourth position may be occupied by a solvent molecule, even a weakly co-ordinating donor molecule such as benzene. Further dissociation only arises in the presence of oxygen. For example, the complexes $Rh(PPh_3)_2(L)SCN$ in the solid state readily lose the solvent ligand(L) when left in the air i.e. in the presence of oxygen, but may be stored indefinitely under nitrogen.

In terms of the reaction scheme,described in Fig. 2.6.,there is evidence to show that $Rh(PPh_3)_2(L)NCS$ is a key intermediate in the formation of $Rh(PPh_3)_2(L)SCN$. Whether $Rh(PPh_3)_2NCS$ is also involved is not clear, but evidence has been obtained for the three co-ordinate complex $Rh(PPh_3)_2SCN$, which also tends to lend support to hypotheses for the existence of a dissociated species in $Rh(PPh_3)_3Cl$ systems(82, 83).

In addition, the complex $Rh(PPh_3)_2(C_6H_6)SCN$ is also of particular interest and prompts the question: Is benzene co-ordinated? On balance, when compared with $Rh(PPh_3)_2(L)SCN$ [where L=MeCN or Me_2CO] evidence does suggest that it could be co-ordinated, but it is not clear how this occurs. The available pπ orbitals on benzene are in such a position as to favour a six electron donation as in $(\pi\text{-}C_6H_6)Cr(CO)_3$(92), and this in terms of the E.A.N. rule for the rhodium(I) complex would mean 2 electrons more than the rare gas configuration. However, benzene has been shown to co-ordinate through only one localised pair of π-electrons as in $Ag(C_6H_6).ClO_4$(93), $C_6H_6.AgAlCl_4$(94) and $C_6H_6.CuAlCl_4$(95). Also if benzene is regarded as a type of 'wedge' the position of the available orbitals would only allow back donation of electrons from rhodium to benzene.

Finally, this study has established that it is possible to make a series of complexes of the type $Rh(PPh_3)_2(L)SCN$ containing a variety of ligands(L). These complexes will be discussed in the following chapter.

Experimental

All the solvents used were carefully dried according to the methods described by Weissberger(96). Tetramethylammonium thiocyanate was prepared according to Songstad and Strangeland(97). The complex $Rh(PPh_3)_3Cl$ was prepared according to the method of Wilkinson and co-workers(83). All reactions were performed under nitrogen except those for the preparation of the oxygen products.

The Preparation of the Rhodium(I)-Thiocyanate complexes.

N-thiocyanato tris(triphenylphosphine)rhodium(I).

Tetramethylammonium thiocyanate (0.26g, 2mmole) and triphenylphosphine (0.8g, 1.3mmole) were dissolved in degassed acetonitrile (80 ml.). Tris(triphenylphosphine)chlororhodium(I) (0.46g, 0.5mmole) was added and the reaction mixture stirred at room temperature. The product precipatated as a bright orange solid which was removed by filtration under nitrogen. Yield = 0.38g, (80%).

S-thiocyanatobis(triphenylphosphine)(acetonitrile)rhodium(I)

Tetramethylammonium thiocyanate (0.066g, 0.5mmole) was dissolved in degassed acetonitrile (60 ml.). Tris(triphenylphosphinechlororhodium(I) (0.23g, 0.25 mmole) was added and the reaction mixture stirred at room temperature. The product precipitated as a bright yellow complex which was removed by filtration and dried under nitrogen. Yield = 0.15g, (82.5%).

S-thiocyanatobis(triphenylphosphine)(acetone)rhodium(I)

The complex was prepared similarly using 200 mls. of acetone. Yield 0.16g, (88%).

S-thiocyanatobis(triphenylphosphine)(L)rhodium(I) [L=MeCN, Me_2CO, Et_2O, C_6H_6, C_6H_5Cl]

N-thiocyanato-tris(triphenylphosphine)rhodium(I) (0.5g) was added to the respective degassed solvent (50 ml.) and the mixture stirred at room temperature for one hour. The products precipitated as bright yellow solids which were removed by filtration under a nitrogen atmosphere. Yields 0.25-0.35g, % Yield 63-88%

N-thiocyanatotris(triphenylphosphine)(dioxygen)rhodium(I)

The complex was prepared similar to N-thiocyanatotris(triphenylphosphine)rhodium(I) in the presence of air. The reaction mixture was stirred over 18 hours. The product precipitated as a greenish brown solid which was removed by filtration. Yield 0.2g, (42%).

S-thiocyanatobis(triphenylphosphine)(diethylether)(dioxygen)rhodium(I)

N-thiocyanatotris(triphenylphosphine)rhodium(I) (0.5g) was added to diethylether (30 ml.) and stirred at room temperature in the presence of air for 30 minutes. The product precipitated as a greenish-yellow solid which was removed by filtration. Yield 0.3g, (80.0%).

Catalytic reactions of thiocyanate-rhodium(I) complexes

Oxygen was bubbled through a solution of triphenylphosphine (5g) in xylene (5g) in xylene (50 ml.) containing N-thiocyanato tris(triphenylphosphine)rhodium(I) (0.1g) and stirred for 2 hours.

Decarbonylation

A suspension of $Rh(PPh_3)_3X$ where X=Cl or NCS in benzaldehyde (40 mls) was gently refluxed for 10 hours. Fractionation of the solution between 58-70°C yielded small quantities of benzene.

General Properties

The complex $Rh(PPh_3)_3NCS$ is a bright orange solid which readily dissolves in benzene, acetone and chloroform. Addition of the complex under nitrogen conditions to solvents such as benzene, acetone and acetonitrile results in the formation of bright yellow complexes of the type $Rh(PPh_3)_2LSCN$ (L=solvent molecule). These complexes and $Rh(PPh_3)_2SCN$ are highly insoluble and will only dissolve in chloroform or benzene under reflux conditions. All the compounds slowly decompose in the presence of air with the uptake of oxygen. However, the compounds are stable when stored under nitrogen conditions, at room temperature, but decompose without melting on heating

Analysis

Attempts to characterise the S-bonded thiocyanate complex from C, H and N analyses, obtained by combustion* were found unsatisfactory. However, analysis of rhodium, sulphur and phosphorus by X-ray fluorescence spectrometry using a Philips PW1540 vacuum spectrograph (see chapter 12) gave satisfactory results and are recorded in Table 2.7. The brown complexes $Rh(PPh_3)_2(CO)NCS$ and $Rh(PPh_3)_3NCS.O_2$ have been characterised by both methods.

Infrared spectra

The positions of infrared absorption bands due to the thiocyanate group in these complexes were obtained by a comparison of their spectra with that of the complex $Rh(PPh_3)_3Cl$. Bands observed in the mull spectra, and as KBr discs using a Perkin-Elmer 457 spectrophotometer are recorded in Tables 2.8.; those for tetramethylammonium thiocyanate and the known complex $Rh(PPh_3)_2(CO)NCS$ are also included. The intergrated intensities of the CN stretching frequency were measured as KBr discs; those for $Rh(PPh_3)_3NCS$ and $Rh(PPh_3)_2CONCS$ were also recorded in chloroform. All bands were recorded to within an accuracy $\pm$ 1cm^{-1} against a polyethylene film as standard.

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*Analysed by the Micro-analytical Laboratory, Manchester University.

Analytical Data for Rhodium(I)-Thiocyanate Complexes

Complex	Found						Calculated					
	%Rh	%P	%S	%C	%H	%N	%Rh	%P	%S	%C	%H	%N
$Rh(PPh_3)_2CONCS$	14.5	8.9	4.6	63.9	4.2	2.6	14.5	8.8	4.5	63.7	4.2	1.9
$Rh(PPh_3)_3NCS$	10.8	9.6	3.4				10.9	9.6	3.6			
$Rh(PPh_3)_2SCN$	14.9	9.25	4.6				15.0	9.1	4.7			
$Rh(PPh_3)_2SCN(L)$												
L=MeCN	14.2	8.8	4.3				14.2	8.7	4.4			
Me_2CO	13.9	8.4	4.2				13.9	8.4	4.3			
Et_2O	13.6	8.2	4.3				13.6	8.2	4.2			
C_6H_6	13.4	8.2	4.1				13.5	8.2	4.2			
C_6H_5Cl	13.4	8.1	4.1				12.9	7.77	4.0			
Oxygen Complexes												
$Rh(PPh_3)_3NCS.O_2$	10.3	9.7		65.7	4.5	1.2	10.5	9.5		67.0	4.7	1.4
$Rh(PPh_3)_2\ (Et_2O)SCN.O_2$	13.3	8.0					13.5	8.1				

Table 2.7.

Infrared Frequencies of the Thiocyanate Group in Rhodium(I) Complexes

	(a) ν(CN)(cm^{-1})	(a) ν(CS)(cm^{-1})	A(10^{-4}M^{-1}cm^{-2})
Me_4NSCN	2055 s	746 w	
$Rh(PPh_3)_2CONCS$	2095$^{(b)}$s,b	838 w	12.0$^{(b)}$ (73)
$Rh(PPh_3)_3NCS$	2095$^{(b)}$s,b	811 w	8.5$^{(b)}$
	2095 s,b		8.3
$Rh(PPh_3)_2SCN$	2137 s,sp	-	2.5
$Rh(PPh_3)_2SCN(L)$			
L=MeCN	2135 s,sp	-	3.0
$=Me_2CO$	2134 s,sp	-	2.8
$=Et_2O$	2138 s,sp	-	3.1
$=C_6H_6$	2142 s,sp	-	2.9
$=C_6H_5Cl$	2142 s,sp	-	3.2

(a) Presented as KBr disc unless otherwise stated.

(b) Chloroform solution.

No bands have been assigned to δNCS due to the complexity of the spectra between 500-400cm^{-1}.

Table 2.8.

Infrared Spectral Data for the Principle Solvent Ligand(L) Vibrations(cm^{-1}) in the Complexes $Rh(PPh_3)_2(L)SCN$

$Rh(PPh_3)_2(L)SCN$		Free Solvent
$L=Me_2CO$	1710 s (ν(CO)), 1225 m	1718 s (ν(CO)), 1224 m
$=MeCN$	2257 w (ν(CN))	2253 m (ν(CN))
$=Et_2O$	(a)	
$=C_6H_6$	(a)	
$=C_6H_5Cl$	1583 s (ν(CC)), 472(X-sens) 1025, 903	1588 s (ν(CC)), 470(X-sens) 1025, 903

(a) No bands could be attributed with certainty because of triphenylphosphine ligand vibrations.

Table 2.9

Electrical Conductivity

The molar conductivity of Rh(PPh$_3$)$_3$NCS (10.0 ohms^{-1}cm^2) measured in acetonitrile using a Wayne-Kerr Conductivity bridge and platinised electrodes shows that it is a non-electrolyte. No other complex could be measured because of their high insolubility in all solvents.

CHAPTER 3

CO-OPERATIVE LIGAND EFFECTS IN RHODIUM(I) - THIOCYANATE COMPLEXES

CO-OPERATIVE LIGAND EFFECTS IN RHODIUM(I) - THIOCYANATE COMPLEXES

Since the π-bonding hypothesis put forward by Turco and Pecile to explain the co-operative effect of ligands in Pd(II) and Pt(II) complexes on thiocyanate co-ordination(9), other explanations for this phenomenon have been proposed including symbiosis(18), antisymbiosis(21), and the semiquantitative approach of Norbury(24). In the previous chapter it was shown that the lability of triphenylphosphine in $Rh(PPh_3)_3NCS$ could be exploited to give a number of rhodium(I) complexes of the type $Rh(PPh_3)_2(L)CNS$. Further complexes of this type have been synthesised using a range of ligands of varying σ-donor and π-acceptor ability, so that the effect of the ligand on the mode of thiocyanate linkage in these complexes may be evaluated.

Results

The complexes listed in Table 3.1. were prepared by either or both of the following methods:-

(1) Reaction of $Rh(PPh_3)_3NCS$ with the corresponding ligand as solvent, as previously described.

(2) Reaction of $Rh(PPh_3)_3NCS$ with the corresponding ligand in hexane.

General Properties

Whilst $Rh(PPh_3)_2(L)NCS$, [L= piperidine, quinoline] are only moderately soluble in chloroform and acetonitrile, the remaining S-bonded complexes

Analytical Data for Rhodium(I) - Thiocyanate Complexes

Complex	Method of Preparation (1 or 2)	% Found						% Calculated					
$Rh(PPh_3)_2(L)CNS$		Rh	P	S	C	H	N	Rh	P	S	C	H	N
L = piperidine	2	13.1	8.0	4.0	64.2	5.9	3.9	13.3	8.1	4.1	65.5	5.8	3.7
quinoline	2	12.4	7.5	4.1				12.6	7.6	3.9			
DMSO	1	13.6	8.1	8.3				13.5	8.2	8.4			
Me_2S	2	13.5	8.4	8.3				13.7	8.3	8.6			
EtCOOH	1	13.7						13.6	8.2	4.2			
EtOH	1	14.0						14.1	8.5	4.4			
MeCOOEt	1	12.8	8.4					13.0	7.9	4.1			
diacetone alcohol	1	12.6	7.9					12.8	7.7	4.0			

Table 3.1

$Rh(PPh_3)_2(L)SCN$ [MeCOOH, MeCOOEt, Me_2S, DMSO, EtOH, and diacetone alcohol] are insoluble in most solvents. The S-bonded complexes are moderately soluble in piperidine, aniline and pyridine but give N-bonded species in solution by the displacement of the ligand (L) by piperidine etc. All the complexes are air sensitive in the sense that the solvent ligands are lost and oxygen is taken up as indicated by the triphenylphosphine bands in their infrared spectra. However, the complexes remain unchanged over several weeks when stored under N_2. The ligand (L) in many of the complexes is displaced on heating and continual stirring in hexane results in the formation of $Rh(PPh_3)_2SCN$. All the compounds decompose without melting.

Electrical Conductivity

Electrical conductivities for the complexes $Rh(PPh_3)_2(L)SCN$ could not be measured because of their insolubility. The molar conductivities of $Rh(PPh_3)_2(L)NCS$ [L = quinoline, piperidine] measured in acetonitrile show that the complexes are non-electrolytes (Table 3.2.)

Compound	Solvent	Concentration 10^{-3} moles/litre	Molar Conductivity ohm^{-1} cm^2
$Rh(PPh_3)_2$(piperidine)NCS	MeCN	0.7	6.3
$Rh(PPh_3)_2$(quinoline)NCS	MeCN	0.5	7.2

Table 3.2.

Infrared spectra

The positions of the infrared absorption bands due to the thiocyanate group in these complexes were obtained by a comparison of their spectra with those of tris(triphenylphosphine)chloro rhodium(I) and N-thiocyanatobis(triphenylphosphine)carbonylrhodium(I) (see Chapter 2). Bands observed in the mull spectra or as KBr discs are recorded in Tables 3.3. and 3.4. The infrared spectra of all the complexes discussed in the previous chapter are also included. No bands have been attributed to the δ(NCS) bending mode in these complexes because of the complexity of triphenyphosphine ligand vibrations in the same region (500-400cm^{-1}).

The infrared spectra of the complexes $Rh(PPh_3)_2(L)NCS$ [L = piperidine and quinoline] have CN and CS stretching frequencies and integrated absorption intensities (Table 3.3.) all consistent with co-ordination of the thiocyanate group through the nitrogen atom, as is found in $Rh(PPh_3)_2(CO)NCS$ and $Rh(PPh_3)_3NCS$. Complexes containing aniline or pyridine could not be isolated,but addition of $Rh(PPh_3)_3NCS$ or $Rh(PPh_3)_2SCN$ to aniline or pyridine gave a ν(CN) band at 2100cm^{-1} and integrated absorption intensity of 8.9 and 10.1 $10^4M^{-1}cm^{-2}$ respectively, indicating the presence of N-bonded species in solution. On the other hand, the infrared spectra of the complexes $Rh(PPh_3)_2(L)SCN$ (L= Me_2S, EtOH, $EtCO_2H$, DMSO etc) exhibit similar CN stretching frequencies and integrated absorption intensities i.e. ~2135cm^{-1}, A = ~3.0 x 10^4 $M^{-1}cm^{-2}$, to those of the complexes $Rh(PPh_3)_2(L)SCN$ [L = Me_2CO, MeCN, C_6H_6 etc.], previously described, indicating that all these complexes are S-bonded

Infrared Spectral Data for Rhodium(I)-N-Thiocyanate Complexes

Complex	ν(CN)(cm^{-1})[a]	ν(CS)(cm^{-1})[a]	A(x10^{-4}M^{-1}cm^{-2})[b]
$Rh(PPh_3)_2(L)NCS$			
L = CO	2095 s,b[c]	838	12.0[c]
PPh_3	2095 s,b	811	8.5
piperidine, $(CH_2)_5NH$	2090 s,b	815	6.8 6.5[c]
quinoline, C_9H_7N	2090 s,b	d	6.5 7.4[e]
pyridine, C_5H_5N	2100 s,b[e]		10.1[f]
aniline, $C_6H_5NH_2$	2100 s,b[f]		8.9[g]

a KBr disc and nujol mull

b KBr disc

c $CHCl_3 \times 10^{-3}$ molar solution

d obscured by quinoline vibrations

e $Rh(PPh_3)_3NCS$ in quinoline, $\times10^{-3}$ molar solution

f $Rh(PPh_3)_3NCS$ in pyridine, $\times10^{-3}$ molar solution

g $Rh(PPh_3)_3NCS$ in aniline, $\times10^{-3}$ molar solution

Table 3.3.

Infrared Spectral Data for Rhodium(I)-S-Thiocyanate Complexes

Complex	$\nu(CN)(cm^{-1})$ [a]	$\nu(CS)(cm^{-1})$ [a]	$A(x10^{-4}M^{-1}cm^{-2})$ [b]
$Rh(PPh_3)_2(L)SCN$			
L = Me_2CO	2134 s,sp	-	2.8
MeCN	2135 s,sp	-	3.0
Et_2O	2138 s,sp	-	3.1
C_6H_6	2142 s,sp	-	2.9
C_6H_5Cl	2142 s,sp	-	3.2
EtOH	2142 s,sp	-	2.9
MeCOOH	2140 s,sp	-	2.8
MeCOOEt	2140 s,sp	-	2.8
diacetone alcohol $MeCOCH_2COH(Me)_2$	2140 s,sp	-	3.1
DMSO Me_2SO	2132 s,sp	-	2.3
Me_2S	2138 s,sp	-	3.5

a KBr disc and nujol mull

b KBr disc

Table 3.4.

Infrared Spectral Bands (cm^{-1}) of the Solvent-Ligand(L) in the Complexes $Rh(PPh_3)_2(L)CNS$

Complex	Ligand(L) vibrations in complex	Free ligand
$Rh(PPh_3)_2(L)CNS$		
L = piperidine $(CH_2)_5NH$	3260w, (νNH) 1040m, 1020m, 870m	3280 (νNH) 1048m, 1033m, 858m
quinoline C_9H_7N	1633m,w, 1620m, 1598m (νC=C)	1625m, 1595m, 1570m (νC=C)
	1502m, 1390m, 1382m, 872sm, 840m, 825m, 816sh, 810m, 790w, 640w, 610w	1502s, 1390, 1375, 806s, 786s, 760w, 738m
MeCOOH	1708s (νCO)	1712s (νCO)
MeCOOEt	1735s (νCO)	1740s (νCO)
diacetone alcohol	1710-1700s (νCO)	1700 (νCO)
EtOH	3400b (νOH)	3300 (νOH)
DMSO	1060-1030 sb (νSO)	1100-1050 (νSO)sb
Me_2S	1315 w, sh, 970w	1310m, 970s

Table 3.5.

(Table 3.4.).

The infrared spectra of the complexes suggest that the ligands(L) are co-ordinated (Table 3.5.). Small shifts, compared with the free ligands, are observed in the C=O stretching frequencies of acetic acid, ethyl acetate, and diacetone alcohol. The complex $Rh(PPh_3)_2(DMSO)SCN$ is of particular interest with respect to whether co-ordination of dimethyl sulphoxide occurs through oxygen or the sulphur atom. The SO stretching frequency for DMSO in the complex occurs at 1060-1030cm^{-1} lower than that for free dimethylsulphoxide which absorbs at 1100-1055cm^{-1}. A downward shift of this metal-sensitive SO stretching frequency has been shown to indicate co-ordination through oxygen (98): in contrast, the corresponding halogen complexes $Rh(PPh_3)_2(DMSO)X$ [Where X = Cl, Br, I] exhibit an upward shift of the SO stretching frequency in their infrared spectra indicating co-ordination through sulphur(99).

Whilst the addition $Rh(PPh_3)_3NCS$ to hexane and stirring for several hours causes little change in the complex, the addition of dimethylsulphide readily gives a complex which analyses as $Rh(PPh_3)_2(Me_2S)SCN$ and whose infrared spectrum exhibits bands at 1315 and970cm^{-1} due to Me_2S (these bands occur at 1310 and 970cm^{-1} in the free ligand). In the case of the N-thiocyanato complexes prepared in a similar manner to the dimethylsulphide adduct the band at 3260cm^{-1} in $Rh(PPh_3)_2$(piperidine)NCS is attributed to the ν(NH) stretching frequency of piperidine [ν(NH) in free piperidine occurs at 3280cm^{-1}], whilst the bands at 1625cm^{-1}, 1595cm^{-1} and 1570cm^{-1} due to C=C stretching frequencies in free quinoline are shifted to 1633, 1620 and 1598cm^{-1} in the complex(100). Significant shifts are also observed in the bands at 805 and 786cm^{-1} in free quinoline compared with the complex where bands are observed at 872, 840, 825, 816, 810, 790 and 782cm^{-1}: one of these bands may be attributable to the ν(CS) stretching frequency of the thiocyanate group. The relative intensities of the solvent-ligand bands in the complexes do not decrease after drying the complexes for several hours under nitrogen: indeed the complexes remain unchanged when stored under nitrogen for several months. However, it was found that the solvent ligands could be displaced from $Rh(PPh_3)_2SCN$ by stirring the complexes in hexane for several hours. Subsequent addition of the corresponding ligand to $Rh(PPh_3)_2SCN$ in hexane gave the four co-ordinate complexes again. Further, all the complexes slowly lose their solvent-ligands when exposed to air and their infrared spectra indicate bands attributable to triphenylphosphine oxide.

The Geometric Configuration of the Complexes $Rh(PPh_3)_2(L)CNS$

On consideration of trans-effects one would anticipate that one of the trans-phosphine groups in $Rh(PPh_3)_3NCS$ would be labile, and may be replaced by other ligands(83). For example, carbon monoxide may displace triphenylphosphine in $Rh(PPh_3)_3Cl$ to give $Rh(PPh_3)_2(CO)Cl$(83) which has been shown to have the *trans*-square-planar configuration, i.e. CO trans Cl, from dipole measurements(101), X-ray studies(102) and n.m.r. studies of related phosphine complexes(103). Similarly, an X-ray crystal structure determination of $Rh(PPh_3)_2(CS)Cl$ showed such a trans-square-planar configuration.

On this basis, the complex $Rh(PPh_3)_2(CO)NCS$ has been assumed by Burmeister(73) to have such a configuration, which is further indicated by dipole measurements performed on the complex $Rh[P(C_6H_{11})_3]_2(CO)NCS$(72). It was hoped to confirm the configuration of $Rh(PPh_3)_2(CO)NCS$ and the related complexes $Rh(PPh_3)_2(L)CNS$, from n.m.r. studies of the analogous complexes $Rh(PMePh_2)_2(L)CNS$. Unfortunately, attempts at the preparation of these latter complexes were unsuccessful in the time available. It has been found, however, that the ^{1}H n.m.r. spectra of the triphenylphosphine-rhodium(I) complexes can provide some information concerning their geometric configuration. The n.m.r. spectrum of triphenylphosphine exhibits a singlet at $\tau 2.78$ due to the phenyl protons. In contrast, the complexes trans-$Rh(PPh_3)_2(CO)Cl$ and $Rh(PPh_3)_2(CO)NCS$ both exhibit two distinct sets of peaks at $\tau 2.30$ and 2.62 for trans-$Rh(PPh_3)_2(CO)Cl$ and $\tau 2.40$ and 2.60 for $Rh(PPh_3)_2(CO)NCS$ which both integrate in the order of 2:3 respectively (Fig. 3.6). This splitting of the phenyl protons is typical of aromatic carbonyl compounds where the effect of a substituent, such as carbonyl, is to cause greater deshielding of the ortho protons rather than the meta and para protons. Hence the spectrum becomes a lower field two proton and a higher field three proton complex(105, 106), as found, for example, in benzaldehyde ($\tau \simeq 2.1$ and 2.4.). Deshielding of the phenylprotons by the carbonyl group is a magnetic anisotropy effect rather than induction i.e. it acts through space rather than through atoms. It is probably this effect which accounts for the similar behaviour in the rhodium complexes. Such splitting would only arise if the phenyl

The N.M.R. Spectra of $Rh(PPh_3)_3X$ and $Rh(PPh_3)_2(CO)X$

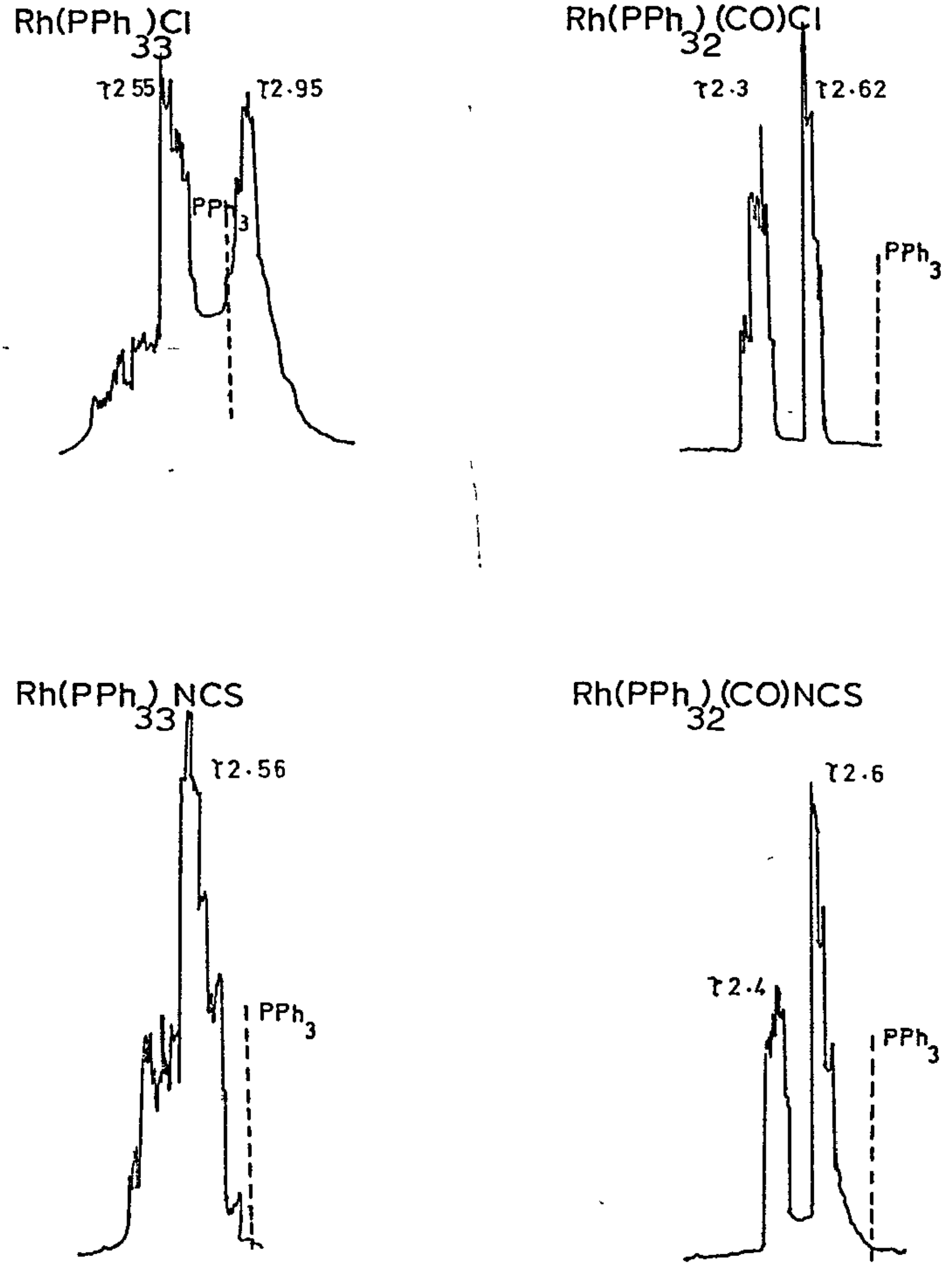
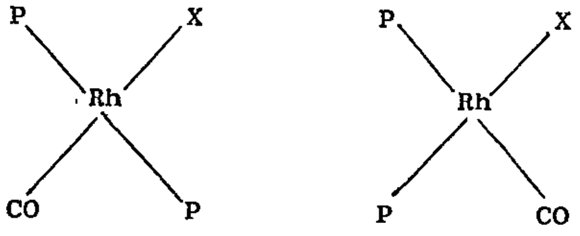


Fig 3:6

groups on each phosphine are in the same environment with respect to the carbonyl group i.e. the triphenylphosphine groups are trans to one another (Fig. 3.7.). If the phosphine ligands were cis to one another



(I) (II)

X = Cl or NCS$^-$

Fig. 3.7.

(II) the phenyl groups would be in different magnetic environments relative to the carbonyl group and such distinct splitting of the protons in the ratio of 2:3 would not be observed. Therefore, the n.m.r. spectra of the square-planar complexes Rh(PPh$_3$)$_2$(CO)Cl and Rh(PPh$_3$)$_2$(CO)NCS not only indicate that they have the same configuration but also that the phosphine groups are indeed trans to one another.

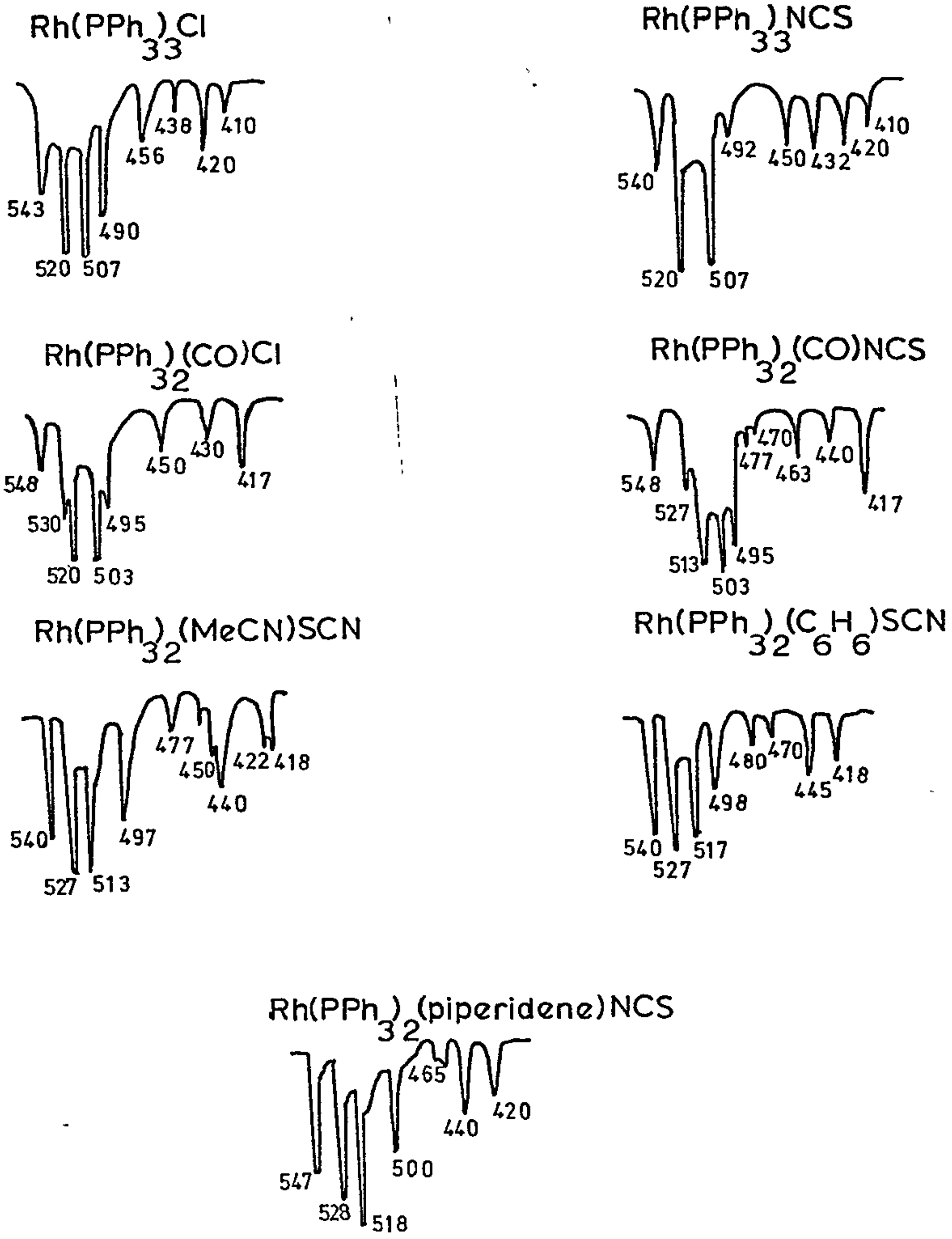
On the other hand, the n.m.r. spectrum of the complex Rh(PPh$_3$)$_3$NCS exhibits only one complex set of peaks centred at τ2.56 which could not be resolved (Fig. 3.6.). The n.m.r. spectrum of Rh(PPh$_3$)$_3$Cl is more complicated and exhibits two bands at τ2.55 and τ2.95 which integrate approximately in the order of 3:2 respectively (Fig. 3.6.). Thus, in neither Rh(PPh$_3$)$_3$Cl nor Rh(PPh$_3$)$_3$NCS is it possible to distinguish between the two geometrically different triphenylphosphine ligands. The nature of the splitting in $Rh(PPh_3)_3Cl$ is different from that observed in trans-$Rh(PPh_3)_2(CO)Cl$ and in aromatic carbonyl compounds. Such behaviour is probably due to an inductive effect stemming from the 'Rh-Cl' moeity, but it is more complicated than that observed normally in substituted aromatic compounds(105) where one might expect a deshielding of the ortho protons and an opposite shielding of the meta and para protons as observed in C_6H_5I, or alternatively a possible shielding of all the protons. No such simple explanation appears suitable for $Rh(PPh_3)_3Cl$.

Unfortunately, the conclusions reached for trans-$Rh(PPh_3)_2(CO)X$ where X = Cl or NCS cannot be applied to other rhodium(I)-thiocyanate complexes. The complex $Rh(PPh_3)_2$(piperidine)NCS only exhibits one complex set of unresolvable peaks centred at 2.6τ similar to $Rh(PPh_3)_3NCS$. This is expected since piperidine would not exhibit any magnetic anisotropy and any inductive effect would be small. The two complex sets of peaks due to the protons on piperidine centred at 6.9 and 8.3τ are shifted to lower field on co-ordination (τ7.3 and 8.5 in free piperidine). The n.m.r. spectra of $Rh(PPh_3)_3NCS$ recorded in solvents such as DMSO, acetone d^6 or CD_3COOH under normal conditions are similar to those recorded in $CDCl_3$ although the former spectra do give some indication of free triphenylphosphine showing that triphenylphosphine has been displaced. It has been demonstrated previously that these solvent molecules are labile in the rhodium(I) complexes in the presence of oxygen i.e. in air, (see Chapter 2). Preparation of the solutions under a nitrogen atmosphere resulted in the formation of the insoluble S-bonded complexes making measurements impossible.

An examination of the infrared spectra of the S-thiocyanato complexes provides possible evidence concerning their geometric configuration. Trans-or cis-isomers in Pd(II) and Pt(II), arsine, stibine and phosphine complexes can be distinguished using the X-sensitive y and u vibrations of the respective arsine, stibine or phosphine(107). These bands are degenerate and changes in their multiplicity are possible. In the case of trans-Pd(II) complexes e.g. trans-$Pd(AsPh_3)_2X_2$ [X = NCO, Cl] which have a D_{2h} symmetry, the X-sensitive y and u vibrations move upfield slightly. On the other hand, while the X-sensitive y and u vibrations of the corresponding Pt(II) complex move upfield as expected, increased multiplicity of these vibrations occurs because of a lower C_{2v} symmetry.

These criteria cannot be applied in the same way to $Rh(PPh_3)_2(L)CNS$ since the square-planar complexes would have a C_{2v} symmetry for a trans configuration and C_s for cis. There is, therefore, no difference in the number of allowed metal-ligand stretching frequencies in the infrared region. Only a general comparison can be made between the X-sensitive vibrations in the infrared spectra of these complexes which are recorded in Fig. 3.8. and Table 3.9. The infrared spectra of trans-$Rh(PPh_3)_2(CO)Cl$ and $Rh(PPh_3)_2(CO)NCS$ in the region of the X-sensitive vibrations are very similar, as might be expected where two complexes have the same trans-configuration. The majority of the complexes $Rh(PPh_3)_2(L)CNS$ all give identical shifts and multiplicity of the X-sensitive vibrations,

The Far Infrared Spectra(600-250cm^{-1}) of Rhodium(I)-Thiocyanate Complexes


Rh(PPh$_3$)$_3$Cl

Rh(PPh$_3$)$_3$NCS

Rh(PPh$_3$)$_2$(CO)Cl

Rh(PPh$_3$)$_2$(CO)NCS

Rh(PPh$_3$)$_2$(MeCN)SCN

Rh(PPh$_3$)$_2$(C$_6$H$_6$)SCN

Rh(PPh$_3$)$_2$(piperidene)NCS

Fig 3.8

The Far-Infrared Spectra (600-250cm^{-1}) of Rhodium(I) - Thiocyanate Complexes

Complex	x-sensitive y-vibrations of PPh_3	x-sensitive u-vibrations
$Rh(PPh_3)_3Cl$	542m, 520s, 507s, 490m	456m, 438w, 420m
$Rh(PPh_3)_3NCS$	540m, 520s, 507s, 492m	450m, 432m, 420m
$Rh(PPh_3)_2(CO)Cl$	548mw, 530m,sh, 520s, 503s, 495m	450m, 430w, 417m
$Rh(PPh_3)_2(CO)NCS$	548mw, 527m,sh, 513s, 503s, 495sm	463m, 440w, 417m
$Rh(PPh_3)_2(L)SCN$	540s, 525s, 513s, 497sm	456m,sh, 450m,sh, 440m, 422w, 417w
$Rh(PPh_3)_2(C_6H_6)SCN$ *	540s, 527s, 517s, 498m	445m, 418m
$Rh(PPh_3)_2(C_6H_5Cl)SCN$	540s, 528s, 517s, 505s, 500s	448m, 420m
$Rh(PPh_3)_2$(piperidine)NCS	547s, 528s, 518s, 500s	465w, 460w, 440m, 420m
$Rh(PPh_3)_2$(quinoline)NCS	540s, 525s, 518s, 500s	462m, 450w, 440m, 425m
PPh_3	512s, 497, 489s	433m, 423m

(a) L = MeCN, Me_2CO, ethyl acetate, EtOH, Me_2S, DMSO, Et_2O, MeCOOEt

*also diacetone alcohol.

Table 3.9.

but the infrared spectra of these complexes, although similar to, are not identical with those of the complexes trans-$Rh(PPh_3)_2(CO)X$ or $Rh(PPh_3)_3X$, where X = Cl or NCS (Fig. 3.8., and Table 3.9.). It is not possible, therefore, to claim that all these complexes have the same trans-configuration, nor that the S-thiocyanato series are cis-complexes. It does appear though, that the complexes $Rh(PPh_3)_2(L)CNS$ all have the same configuration.

Discussion

Since the previous evidence suggests that the complexes $Rh(PPh_3)_2(L)CNS$, excluding trans-$Rh(PPh_3)_2(CO)NCS$, all have the same configuration, there is no obvious reason why $Rh(PPh_3)_2(L)NCS$ [L = quinoline or piperidine] should have different steric requirements from $Rh(PPh_3)_2(L)SCN$ [L = C_6H_6, Me_2CO, DMSO etc.] whether the complexes have a cis or trans geometry. Indeed, it might be expected that the larger diacetone alcohol or ethyl acetate as ligands would exert a greater steric influence than piperidine, but they give S- rather than N-bonded products. In the case of $Rh(PPh_3)_3NCS$ the presence of the very bulky third phosphine may very well influence the co-ordination behaviour of the thiocyanate group, favouring the sterically less-demanding N-bonded thiocyanate. The rhodium complexes, excluding $Rh(PPh_3)_3NCS$, provide a clear example of a co-operative ligand effect which is electronic in nature, but which cannot be explained in terms of the π-bonding hypothesis. The mode of co-ordination of the thiocyanate group in both $Rh(PPh_3)_2(CO)NCS$ and $Rh(PPh_3)_2(piperidine)NCS$ is through the nitrogen atom and yet piperidine does not have any of the opportunities for backbonding which carbon monoxide has. Also, if backbonding is important, opportunities exist when L = Me_2CO, MeCN or DMSO etc. in $Rh(PPh_3)_2(L)SCN$ which are not present in $Rh(PPh_3)_2$(piperidine)NCS.

In terms of the semiquantitative approach of Norbury (Chapter 1)(24), it would be expected that the presence of the soft CO ligand in $Rh(PPh_3)(CO)NCS$ would promote bonding through nitrogen. Pearson's study of soft and hard acids and bases(201) classifies piperidine as a border line case between a soft and hard base, and it may be argued that piperidine in $Rh(PPh_3)_2$(piperidine)NCS is a sufficiently soft base when in a phosphine environment to promote bonding of the thiocyanate group through the nitrogen atom. Similar arguments may be applied to the corresponding quinoline complex. In contrast, the ligands Me_2CO, Et_2O and EtCOOH are classified as hard bases(20) such that their presence in $Rh(PPh_3)_2LSCN$ (L = Me_2CO, Et_2O EtCOOH) would decrease the softness of rhodium to such an extent as to promote thiocyanate bonding through sulphur. However, such arguments cannot be applied to $Rh(PPh_3)_2(L)SCN$ [L = C_6H_6, Me_2S,] where benzene and dimethyl sulphide are regarded as soft ligands.

If it is regarded that the complexes have a trans-configuration, arguments based on Pearson's concept of antisymbiosis may also be applied, such that the presence of a stronger trans-directing ligand, such as carbon monoxide or piperidine, will have a destabilising effect and the N-thiocyanate is preferred. It is difficult to account for the S-bonded thiocyanate complexes unless it is assumed that unlike their normal behaviour, the ligands such as MeCN, Me_2CO, DMSO, C_6H_6 etc.

are weaker trans-directors and cause no anti-symbiotic behaviour.

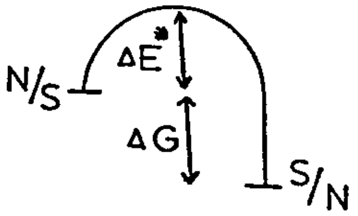
It is difficult to resolve the ligand effects in the rhodium(I)-thiocyanate complexes in terms of the explanations outlined in Chapter 1. This is perhaps explicable if the complexes are considered in terms of a simple thermodyanic approach as depicted in Fig. 3.10. The difference in free energy ΔG, between N- and -S co-ordination in the case of linkage isomers will undoubtedly be small (I). For example, the difference in free energy between the linkage isomers $Co(DH)_2py(NCS)$ and $Co(DH)_2py(SCN)$ was found to be 3.1 $kJmol^{-1}$(108). On the other hand, the activation energy ΔE^* may be large or small. In the situation where only one stable isomer is found, ΔG will be large (II), but changes in ligand e.g. MX_2YNCS to MX_2ZSCN may alter ΔG enough to allow a change in the mode of co-ordination (III).

It is possible that the isolation of the complexes $Rh(PPh_3)_2(L)SCN$ could result as a consequence of their much greater insolubility, thus obscuring the true values for ΔG and ΔE^*, but since the complexes remain unchanged for several months, this does suggest that they are the thermodynamically stable products. Similarly, the complex $Rh(PPh_3)_2SCN$ remains unchanged on heating at 120°C for several hours. Therefore, since it has been shown that $Rh(PPh_3)_2(L)NCS$ is formed prior to the S-bonded product, and that it has been possible to isolate a mixture of linkage isomers for $Rh(PPh_3)_2(MeCN)CNS$ (as discussed in Chapter 2), the difference in free energy between N- and S- co-ordination appears in these S-bonded complexes to be small. The isomerisation is also fairly

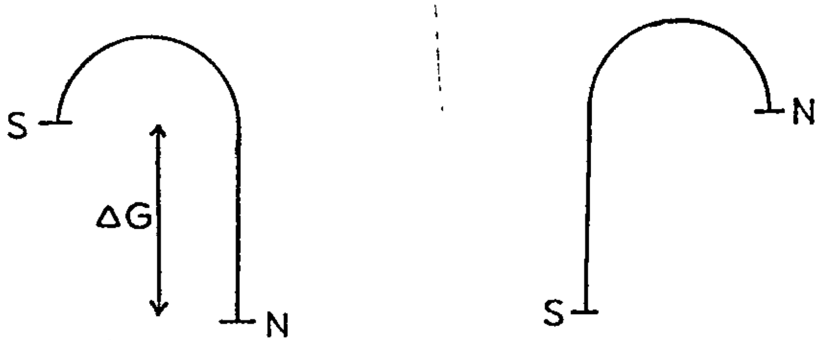
Possible Free Energy Changes in the Complexes

$Rh(PPh_3)_2(L)CNS$

Linkage Isomers (I)



Stable Thiocyanate Complex [e.g. $MX_2Y(NCS)$] (II)



(II) (III)

$$MX_2Y(NCS) + Z \longrightarrow MX_2Z(SCN) + Y$$

$Rh(PPh_3)_2(L)CNS$

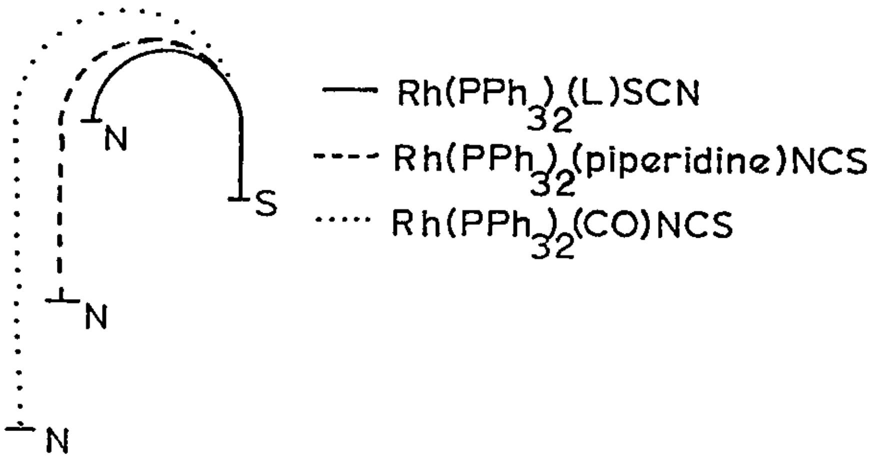


Fig 3.10

rapid and it seems that ΔE^* will also be small. The S-bonded three co-ordinate complex, on the other hand, is of greater stability; no N-bonded isomer has been identified. Therefore, excluding any possible changes in ΔE^* the difference in free energy between N- and S-co-ordination in the complex $Rh(PPh_3)_2(CO)NCS$ will be large favouring the thermodynamically stable N-bonded complex. On the other hand, in the complexes $Rh(PPh_3)_2(L)SCN$, compared with $Rh(PPh_3)_2SCN$, any change in ΔG still favours co-ordination through sulphur. Since ΔG is fairly small for $Rh(PPh_3)_2(L)SCN$ a ligand such as piperidine is sufficient to alter ΔG and to favour the N-bonded product. If ΔG was very large for this system piperidine would probably have little effect on the co-ordination behaviour.

The rhodium(I)-thiocyanate complexes thus resemble the situation for linkage isomers, where the energy difference between N- and S-co-ordination are very much in balance. For example, it has been shown that the equilibrium between N- and S-co-ordination in the linkage isomers $Co(DH)_2py(CNS)$ may be altered by small energy changes, as demonstrated by their solvent dependence discussed in Chapter 1(32). Therefore, although the accepted explanations including the π-bonding hypothesis may be adequate to explain thiocyanate co-ordination where energy differences are large, they must be treated with the utmost caution in the situation where any small energy change may result in a change in the co-ordination of the thiocyanate group as found in the rhodium(I)-thiocyanate complexes.

Finally, the compounds described represent the first examples of mixed ligand thiocyanate complexes in which a conventional solvent molecule is shown to have entered the co-ordination sphere of the metal. A number of studies on the effect of solvents on thiocyanate co-ordination to class 'a'(32) and class 'b'(30, 31) metals have been reported, in which isomerisation has been ascribed to some extra-molecular solvent effect as shown in the linkage isomers described above. The possibility of ligand replacement reactions in solution and isomerisation arising from a co-operative ligand effect can no longer be excluded.

Experimental

All solvents were dried according to the methods described by Weissberger(96). Tetramethylammonium thiocyanate was prepared according to the method described by Songstad and Strangeland(97). Tris(triphenylphosphine)chlororhodium(I)(83) was prepared by the method described by Wilkinson et al. All preparations were performed under nitrogen.

N-thiocyanatotris(triphenylphosphine)rhodium(I)

The complex was prepared as described in Chapter 2.

N-thiocyanatobis(triphenylphosphine)(piperidine)rhodium(I)

N-thiocyanatotris(triphenylphosphine)rhodium(I) (0.5g) was added to piperidine (3 ml.) in hexane (100ml.), and the reaction mixture stirred for two hours. The resultant bright yellow solid was filtered, washed with hexane, and dried under nitrogen. Yield = 0.36g (90%).

N-thiocyanatobis(triphenylphosphine)(quinoline)rhodium(I)

The complex was prepared in the same way as N-thiocyanatobis(triphenylphosphine)(piperidine)rhodium(I). Yield = 0.4g (90%).

N-thiocyanatobis(triphenylphosphine)(L)rhodium(I) (L = pyridine, aniline)

The attempted preparation of these complexes using the method described for N-thiocyanatobis(triphenylphosphine(piperidine)rhodium(I) resulted in the formation of oils and no compounds were isolated in the solid state.

S-thiocyanatobis(triphenylphosphine)(dimethylsulphide)rhodium(I)

The complex was prepared in the same way as N-thiocyanatobis(triphenylphosphine)(piperidine)rhodium(I). Yield = 0.35g (90%).

S-thiocyanatobis(triphenylphosphine)(acetic acid)rhodium(I)

N-thiocyanatotris(triphenylphosphine)rhodium(I) (0.5g) was added to acetic acid (50mls) and the reaction mixture stirred for one hour. The resultant bright yellow precipitate was filtered washed with hexane and dried under nitrogen. Yield = 0.25g (60%).

The complexes S-thiocyanatobis(triphenylphosphine)(L)rhodium(I) L = DMSO, MeCOOEt, EtOH, diacetone alcohol were all prepared in the same way as S-thiocyanatobis(triphenylphosphine)(acetic acid) rhodium(I). Yield 0.25-0.3g (60-80%).

The attempted preparation of tris(diphenylmethylphosphine)chlororhodium(I)

The preparation of this complex according to the method of Dewhirst, Keim and Reilly(109) resulted in the formation of a light brown solid and not bright yellow as quoted in the literature. It was found that the reaction of this complex with Me_4NSCN using the methods described previously was not possible.

Physical Measurements

The infrared spectra and electrical conductances were measured as described in Chapter 2. N.m.r. spectra were measured on a Perkin Elmer R32 n.m.r. spectrometer operating at 90MH_z.

Analyses

Rhodium, sulphur and phosphorus were analysed by X-ray fluorescence spectroscopy. Carbon, hydrogen and nitrogen for the complex $Rh(PPh_3)_2$(piperidine)NCS were analysed by the Microanalytical Laboratory, Manchester University.

CHAPTER 4

CO-OPERATIVE LIGAND EFFECTS IN RHODIUM(I)-SELENOCYANATE COMPLEXES

CO-OPERATIVE LIGAND EFFECTS IN RHODIUM(I)-SELENOCYANATE COMPLEXES

The selenocyanate group is less sensitive to ligand effects than the thiocyanate ion. It has a marked preference to co-ordinate in mixed ligand complexes of class 'b' metals through the selenium atom. Favourable circumstances to initiate M-NCSe co-ordination are found to exist in the presence of very bulky ligands where steric requirements are important e.g. $[Pd(Et_4dien)NCSe]BPh_4$(109). Co-operative electronic ligand control of the bonding mode of the selenocyanate group is not so apparent, although, in cobalt(III) complexes, the species $[Co(CN)_5SeCN]^{3-}$ (110, 111), $[Co(DH)_2(SeCN)_2]^-$(112) and $[Co(NH_3)_5NCSe]^{2+}$(110) parallel the behaviour of the corresponding thiocyanate complexes, except that linkage isomerism has not been observed in the first of the above compounds.

Co-operative ligand control of the bonding mode of the selenocyanate group in class 'b' metal seems less evident. In linear gold complexes of the type PPh_3AuXCN (X = S or Se)(23), where no steric requirements are in evidence, the selenocyanate complex showed no evidence of isomerisation, in contrast to the analagous thiocyanate complex. This "non-anti-symbiotic" behaviour was attributed to the softer character of the selenium atom. Trans-$Rh(PPh_3)_2(CO)NCSe$, which is the only rhodium(I)-selenocyanate complex reported in the literature, has been cited as demonstrating a co-operative electronic ligand effect by comparing it with trans - $Pd(PPh_3)_2(SeCN)_2$, where essentially the same steric factors are operative(73). However, the consequences of the change in metal were not discussed, and the N-bonding of the selenocyanate group observed in this system was ascribed to the strongly electron-withdrawing effect of the CO group trans to the ion in question.

Thus, it seemed of interest to prepare a series of rhodium(I)-selenocyanate complexes of the type $Rh(PPh_3)_2(L)SeCN$, analogous to the rhodium(I)-thiocyanate complexes, in order to evaluate any co-operative electronic ligand effect. Unfortunately, the complex $Rh(PPh_3)_3NCSe$ could not be prepared due to extensive deselenation of the selenocyanate group in the presence of excess triphenylphosphine (see preparation and properties of $Rh(PPh_3)_3NCS$, Chapter 2). However, it has been possible to isolate and characterise the complexes $Rh(PPh_3)_2(L)SeCN$ $[L = MeCN, Me_2CO]$.

Results

The reaction of Me_4NSeCN with $Rh(PPh_3)_3Cl$ in acetone or acetonitrile gave, in each case, a very insoluble yellow compound similar to the thiocyanate complexes. Analyses of the products indicated the similar formulation $Rh(PPh_3)_2(L)SeCN$ as shown in Table 4.1.

Analytical Data for Rhodium(I)-Selenocyanate Complexes

Complex	% Found			% Calculated		
	Rh	P	Se	Rh	P	Se
$Rh(PPh_3)_2(MeCN)SeCN$	13.2	8.0	10.1	13.3	8.0	10.2
$Rh(PPh_3)_2(Me_2CO)SeCN$	13.1	7.9	10.3	13.0	7.8	10.2

Table 4.1.

Infrared Spectra

The positions of the infrared absorption bands due to the selenocyanate group in these complexes were obtained by a comparison of their spectra with those of tris(triphenylphosphine)chlororhodium(I), tetramethylammonium selenocyanate and N-selenocyanatebis(triphenylphosphine)-carbonylrhodium(I) which are also included in Table 4.3. The approximate ranges of the principle selenocyanate vibrations for N-or Se-co-ordination, as presented by Norbury (3), are included in Table 4.2.

Approximate Frequency Ranges for Different Types of Selenocyanate Co-ordination

	ν(CN)(cu^{-1})	ν(CSe)(cu^{-1})	δ(NCSe)(cu^{-1})	A(x10^{-4}m^{-1}cu^{-2})
$NCSe^-$	2070	558	424, 416	2-3
M-NCSe	2090-205 s,b	650-600	460-410	5-12
M-SeCN	2130-2070 s,sp	550-520	410-370	0.5-1.5
M-NCSe-M	2150-2100	640-550	410-390	

Table 4.2.

The Infrared Spectra of Rhodium(I)-Selenocyanate Complexes

Complex	^{a} ν(CN)(cu^{-1})	^{a} ν(CSe)(cu^{-1})	^{a} A(x10^{-4}M^{-1}cu^{2})
Me_4NSeCN	2067	555	
$Rh(PPh_3)_2CONCSe$	2096 s,b^b	566 w	9^b
$Rh(PPh_3)_2(MeCN)SeCN$	2135 s,sp	-	2.3
$Rh(PPh_3)_2(Me_2CO)SeCN$	2135 s,sp	-	2.1

a KBr disc

b As quoted by Burmeister and DeStefano

Table 4.3.

Burmeister and DeStefano(73), who have prepared and characterised the complex $Rh(PPh_3)_2(CO)NCSe$, found that the selenocyanate group was co-ordinated through the nitrogen atom from infrared spectral studies. In contrast, the selenocyanate group in the complexes $Rh(PPh_3)_2(L)SeCN$ is co-ordinated through the selenium atom from the infrared spectral data. With respect to the free ion values, the ν(CN) frequency of the complexes are shifted to considerably higher frequencies (2135cm^{-1}), and the integrated absorption intensity of this band is smaller. The ν(CSe) frequency regions for Se co-ordination is obscured by triphenylphosphine vibrations. However, no bands were observed between 650-600cm^{-1} which could be attributable to the ν(CSe) for the N-bonded case. The infrared spectra of these complexes also indicate that acetonitrile and acetone are co-ordinated. Slight shifts of the C≡N and C=O stretching frequencies of MeCN and Me_2CO respectively, are observed in the complexes compared with the free ligands (see Table 4.4.) similar to the thiocyanate complexes. Furthermore, drying the complexes for several hours under a nitrogen atmosphere, caused no change in the intensity of these vibrations nor in the analytical results.

Principal Vibrations (cm^{-1}) of the Solvent-Ligand(L)
in the Complexes $Rh(PPh_3)_2(L)SeCN$

Complex	Ligand(L) vibrations in the complex	Free Ligand
$Rh(PPh_3)_2(MeCN)SeCN$	2258w (ν(CN))	2253n (ν(CN))
$Rh(PPh_3)_2(Me_2CO)SeCN$	1708s (ν(CO))	1718s (ν(CO))

Table 4.4.

Infrared solution spectral studies of the reaction between $Rh(PPh_3)_3Cl$ and Me_4MSeCN suggest that initial co-ordination of the selenocyanate ion was through nitrogen, as indicated by the CN stretching frequency at 2100cm^{-1} which diminished on formation of the insoluble Se-bonded product. This parallels the behaviour of the analagous thiocyanate reaction.

However, attempts at the preparation of $Rh(PPh_3)_3NCSe$ in the presence of excess triphenylphosphine similar to $Rh(PPh_3)_3NCS$, resulted in deselenation of the selenocyanate group. The infrared spectra of the products obtained gave a weak CN stretching frequency at 2120cm^{-1} attributed to a co-ordinated cyanide group. Although analytical data showed the absence of selenium, further satisfactory analyses were not obtained. Deselenation also resulted when $Rh(PPh_3)_2(CO)NCSe$ was added to acetonitrile containing excess triphenylphosphine. Such behaviour was noted by Jennings and Wojcicki when the N-bonded complex $C_5H_5Fe(CO)(PPh_3)NCSe$ was found to readily deselenate in the presence of excess triphenylphosphine and was shown to be due to the formation of Ph_3PSe(112). Although $Rh(PPh_3)_2(MeCN)$ SeCN slowly dissolved in piperidine an infrared spectrum of the resultant solution only exhibits a very weak ν(CN) band at 2115cm^{-1} similar to the CN stretching frequency observed in the infrared spectra of the deselenated products. It has not been possible, therefore, to extend the series of selenocyanate complexes in the same manner as the corresponding thiocyanate complexes. Tentatively, this is due to nucleophilic attack by the ligand species being used on the terminal selenium atom.

As for the complex $Rh(PPh_3)_2(CO)NCS$, it was assumed that $Rh(PPh_3)_2(CO)NCSe$ had a trans-square planar configuration. It appears that this is the case since the infrared spectra of the complexes $Rh(PPh_3)_2(CO)X$ [X = Cl, NCS, NCSe] (Table 4.5) are all very similar in the region of their X-sensitive triphenylphosphine vibrations (see Chapter 3). The infrared spectra of complexes $Rh(PPh_3)_2(L)SeCN$, [MeCN or Me_2CO] in this region, although similar, are not identical to that of $Rh(PPh_3)_2(CO)NCSe$. Thus, it is not possible to infer that the complexes have the same or different configuration.

Far Infrared Spectra (600-250cm^{-1}) of Rhodium(I)-Selenocyanate Complexes

Complex	X - sens y vibrations of PPh_3	X - sens u vibrations
$Rh(PPh_3)_2(CO)NCS$	548m, 580m,sh, 520s, 503s, 495m	463m, 440w, 417m
$Rh(PPh_3)_2(CO)NCSe$	545m, 530m,sh, 520s, 510s, 500m	456w, 448m, 420m
$Rh(PPh_3)_2(MeCN)SCN$	540s, 525s, 513s, 497sm	496m,sh, 450sh, 440, 422w, 417w
$Rh(PPh_3)_2(L)SeCN$	540s, 527s, 513s, 498sm	459m, 452m, 442w, 438m, 425w, 415w

Table 4.5.

Discussion

The results show that the co-ordination of the selenocyanate group in rhodium(I)-phosphine complexes is sensitive to a ligand effect. Whether this is steric or electronic in nature is not certain, since it cannot be established if the complexes trans-$Rh(PPh_3)_2(CO)NCSe$ and $Rh(PPh_3)_2(L)SeCN$ (where L = MeCN and Me_2CO) have the same configuration. (Steric arguments could be used to explain the co-ordination behaviour of the selenocyanate group in $Rh(PPh_3)_2(L)SeCN$ if the complexes have a cis-configuration). Nevertheless, co-operative ligand control in selenocyanate complexes may be important in determining the mode of co-ordination. In the Pd(II)-thiocyanate complexes $Pd(bipy)(NCS)_2$(5, 10) and trans-$Pd(PPh_3)_2(NCS)_2$(5, 57, 62) co-ordination of the thiocyanate ion occurs through the nitrogen atom, but in the corresponding selenocyanate complexes co-ordination is through the larger selenium atom which would be sterically less favourable than S-thiocyanate co-ordination. This is possibly due to a more favourable interaction between a class 'b' metal and selenium than between class 'b' and sulphur in the selenocyanate and thiocyanate ions respectively. Therefore, an electronic co-operative ligand control by the carbonyl group in trans-$Rh(PPh_3)_2(CO)NCSe$ could be important in determining N-co-ordination, as argued by Burmeister and DeStefano(73), and would certainly be established if it was confirmed that the complexes $Rh(PPh_3)_2(L)SeCN$ had the same trans-configuration.

Experimental

Acetone and acetonitrile were dried as previously described.

Tetramethylammonium selenocyanate was prepared according to the method described by Songstad and Strangeland(97). Tris(triphenylphosphine)chlororhodium(I) was prepared according to the method of Wilkinson co-workers (83). The reactions were performed under a nitrogen atomosphere.

Se-selenocyanato(acetronitrile)bis(triphenylphosphine)rhodium(I)

Tris(triphenylphosphine)chlororhodium(I) (0.46g 0.5m mole) was added to tetramethylammoniumselenocyanate (0.18, 1.0m mole) in acetonitrile (80 ml.) and the reaction mixture stirred for one hour. The resultant bright yellow precipitate was filtered and dried thoroughly under a nitrogen atmosphere. Yield o.25g (65%).

Se-Selenocyanato(acetone)bis(triphenylphosphine)rhodium(I)

The complex was prepared similarly using 250ml. of acetone. Yield 0.3g (76%).

Physical Measurements

Infrared spectra were recorded in the same manner as the thiocyanate complexes, described in Chapter 2.

Analyses

The complexes, like the corresponding S-thiocyanato complexes, were not amenable to conventional combustion analysis and were thus analysed for rhodium, phosphorus and selenium by X-ray fluorescence spectrscopy.

CHAPTER 5

LINKAGE ISOMERS OF THE CYANATE GROUP: O-CYANATO - AND N-CYANATO-TRIS(TRIPHENYLPHOSPHINE)RHODIUM(I)

LINKAGE ISOMERS OF THE CYANATE GROUP: O-CYANATO - AND N-CYANATO-TRIS(TRIPHENYLPHOSPHINE)RHODIUM(I)

O-bonded cyanates in inorganic systems are rare and are characterised only with difficulty. The hexa-O-cyanates of Mo(III), Re(IV) and Re(V) were assigned on the basis of their lowered (relative to the free ion) CO stretching frequencies(37) (See also Chapter 1). The same arguments were used for $(cp)_2M(OCN)_2$ [M = Zr, Hf,] (43,44) and, although the peak in question was not identified in $(cp)_2Ti(OCN)_2$, other spectral measurements indicated its similarity to the corresponding zirocene and hafnocene compounds and it was assigned a similar structure. However, there is conflicting evidence, and it is possible that one or more of the metallocene complexes may have been assigned incorrectly. This will be discussed in greater detail in a later chapter.

The first solid linkage isomers to be isolated which involve the cyanate group are reported here with the preparation of $Rh(PPh_3)_3NCO$ and $Rh(PPh_3)_3OCN$.

Results

Treatment of $Rh(PPh_3)_3Cl$ and Ph_4AsOCN in MeCN/EtOH yields an orange solid, whereas if MeCN alone is used a yellow solid is isolated. The two compounds give identical analyses for $Rh(PPh_3)_3CNO$.* The former complex is very stable and remains unchanged over several months in

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* 'CNO' is used to indicate that the mode of co-ordination of the cyanate group is unspecified.

the presence of air, whereas the yellow compound rapidly takes up oxygen and changes to a greenish yellow. Both the complexes are soluble in benzene, chloroform and dichloromethane. The yellow product is insoluble in MeCN but the orange product dissolves to give a non-conducting solution. The reflectance spectra of the orange products exhibits a band at ~410nm, whilst the yellow product exhibits a band at ~425nm. Both bands appear as shoulders on a strong absorption below 350nm.

Infrared Spectra

The positions of the infrared absorption bands due to the cyanate group in these complexes were obtained by a comparison of their spectra with those of the corresponding chloro-complexes. Bands observed as KBr discs are recorded in Table 5.1. The infrared spectra for tetraphenylarsonium cyanate dihydrate, ethyl cyanate and phenyl isocyanate are also included.

Approximate frequencies of the fundamental vibrations for different type of cyanate co-ordination are:-

	ν(CN)(cm^{-1})	ν(CO)(cm^{-1})	δ(NCO)(cm^{-1})	A(x10^{-4}M^{-1}cm^{-2})
NCO^-	2165	1254	637-628	8
M-NCO	2240-2170	1350-1320	640-590	12-20
M-OCN	2240-2200	1310-1070	630-590	-

From Norbury reference 3.

The Infrared Spectra of Rhodium(I) - Cyanate Complexes and Organic Cyanates

	ν(CN)(cm^{-1})	ν(CO)(cm^{-1})	δ(NCO)(cm^{-1})	A($x10^{-4}M^{-1}cm^{-2}$)
$Ph_4AsOCN \cdot 2H_2O$	2158s	1320vw, 1340vw	645wb 600vw	8.4
EtOCN	2245 s,sp$^{(c)}$	1102 s,sp 1127$^{(c)}$w,sh 1173 m,sp		2.0$^{(a)}$
PhNCO	2247s, 2220$^{(c)}$sh			17.0$^{(a)}$
$Rh(PPh_3)_3OCN$ orange	2215 s,	1318w	607w 590mw	9.0$^{(b)}$
$Rh(PPh_3)_3NCO$ yellow	2230 s,b	1330	592	12.6$^{(b)}$

(a) Chloroform solution

(b) KBr disc

(c) Neat liquid

Table 5.1.

In addition to the above results, the orange product exhibits a CN stretching frequency at $2220cm^{-1}$ ($A=8.1x10^4M^{-1}cm^{-2}$) when measured in acetonitrile. Infrared spectral results for EtOCN and PhNCO show that integrated intensity measurements can be used as a criterion for distinguishing between N- and O-bonded cyanates as for N- and S-bonded thiocyanates(61, 62) since the integrated intensity for the former is below that for the free ion, while considerably greater than the free ion value in the case of PhNCO. Therefore, the orange product may be formulated as $Rh(PPh_3)_3OCN$ since the integrated intensity of the CN stretching frequency is reduced to or below that of the free ion, whereas the yellow isomer has an integrated intensity significantly greater than that of the free ion, typical of an N-cyanato compound(40).

Further support for these formulations comes from the NCO deformation modes which occur at 592cm^{-1} for the yellow isomer but at 607cm^{-1} and 590cm^{-1} for the orange product. The removal of the degeneracy of the corresponding NCS mode due to the lower symmetry of the non-linear M-SCN group has been used as a criterion for S-bonding in thiocyanate co-ordination(50, 56, 58). The Rh-OCN unit might also be expected to be non-linear, in which case if the degeneracy of the deformation mode is removed then two bands would be predicted for the orange $Rh(PPh_3)_3OCN$ and only one for the yellow $Rh(PPh_3)_3NCO$, as is indeed observed.

The region in which the CO stretching frequency occurs is obscured to a great extent by triphenylphosphine vibrations. The yellow complex also readily takes up oxygen as indicated by vibrations due to triphenylphosphine oxide which also vibrates in this region. Considerable precautions have to be taken, therefore, to prevent contact with oxygen. However, a band is observed at 1330cm^{-1} in $Rh(PPh_3)_3NCO$ which is a typical value for the CO stretching frequency in N-bonded cyanate complexes [e.g. $Rh(PPh_3)_2(CO)NCO$ ν(CO) 1330cm^{-1}(73)]. The only band which possibly could be due to the CO stretching frequency in $Rh(PPh_3)_3OCN$ is that at 1318cm^{-1}. This frequency is towards the lower end of the range observed for N-cyanato compounds(50, 3), and above the free ion value and the values assigned previously for O-cyanates. However, the low intensity of the CO stretching frequency in general, and the complications arising from Fermi resonance between ν(CO) and the overtone of the deformation mode [bands at ~1300 and 1150cm^{-1} have been assigned to ν(CO) in hexa-O-cyanates of Mo(III) and Re(IV) on this basis(37)] make this an unrealistic criterion in these complexes. Thus, the difficulties of identifying the fundamental band or bands in question and making a definite assignment in this region of the spectrum preclude any firm conclusions on this point, although an increase in ν(CO) on co-ordination through oxygen was predicted theoretically(113).

Further, a medium weak band is observed at 332cm^{-1} in $Rh(PPh_3)_3OCN$ which is assigned to the Rh-O stretching frequency, whereas very weak bands are observed at 340cm^{-1} and at 300cm^{-1} in $Rh(PPh_3)_3NCO$ and $Rh(PPh_3)_3NCS$ respectively, which are assigned to the Rh-N ligand vibration.

Differences are also observed between the infrared spectra of the complexes other than the fundamental cyanate vibrations. Whilst the X-sensitive u and y vibrations of the triphenylphosphine ligand in $Rh(PPh_3)_3NCO$ show some increase in multiplicity, which might be expected for a complex with C_2V symmetry, there is considerable increase in the number of these vibrations in $Rh(PPh_3)_3OCN$ as shown in Fig. 5.2. This increased multiplicity might be due to a lowering of symmetry due to the non-linear M-OCN linkage.

The Far Infrared Spectra (600-250cm^{-1}) of $Rh(PPh_3)_3OCN$ and $Rh(PPh_3)_3NCO$

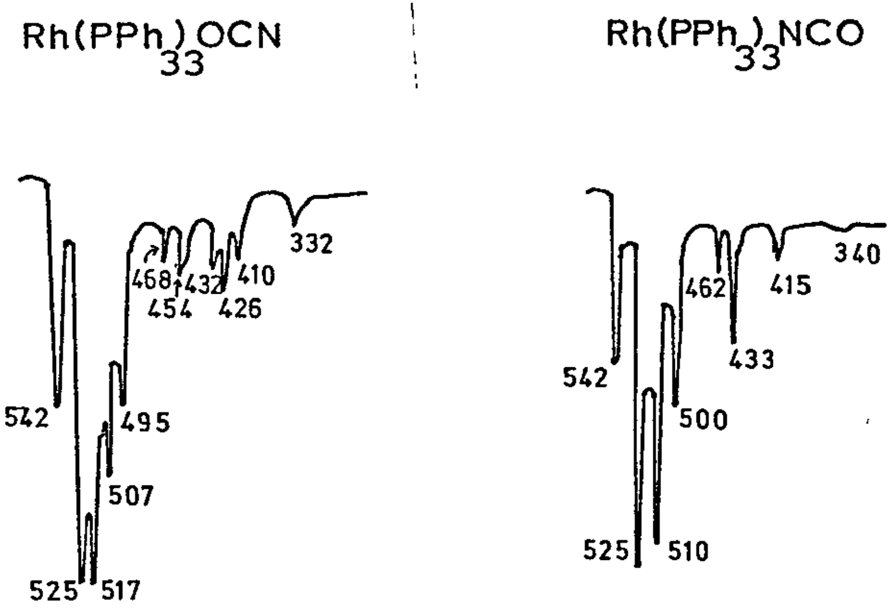


Fig. 5-2

The Nature of the Cyanate Species in Solution

The infrared solution and U.V. spectra of the two products have been measured in benzene, chloroform and acetonitrile, and the results are presented in Table 5.3.

Solvent	Infrared νCN(cm^{-1}) and A($x10^{-4} M^{-1} cm^{-2}$)	Ultra Violet nm$^{(c)}$
Benzene	2227s (A = 19)$^{(a)}$	(d)
Chloroform	2235s (A = 17)$^{(a)}$	(d)
MeCN	2220s (A = 8.1)$^{(b)}$	315w $^{(b)(e)}$

(a) Both compounds are identical in solution

(b) $Rh(PPh_3)OCN$ only: the N-bonded product is insoluble in MeCN

(c) As compared with the U.V. spectra of $Rh(PPh_3)_3Cl$

(d) There are no new bands in the U.V. spectra of both compounds compared with $Rh(PPh_3)_3Cl$

(e) Appears on a very strong absorption below 300nm.

Table 5.3.

The infrared solution and U.V. spectra show that the two products are identical in C_6H_6 or $CHCl_3$ but that the species observed in these solvents is different from that found in acetonitrile. Integrated intensity measurements indicate that the cyanate group is N-bonded in C_6H_6 or $CHCl_3$ whilst O-bonded in MeCN. In addition, when the reaction between Ph_4AsOCN and $Rh(PPh_3)_3Cl$ in MeCN was followed by infrared spectral measurements, the solution spectrum showed a band at 2220cm^{-1} similar to that for $Rh(PPh_3)_3OCN$. Whereas addition of EtOH gives the orange O-bonded isomer, continual stirring in MeCN eventually gives the insoluble yellow product. The infrared spectrum of the compound, while still moist, not only shows bands attributable to acetonitrile at 2260 and 382cm^{-1} [ν(CN) and δ(CH_3CN) occur at 2253 and 378cm^{-1} in free MeCN], but also shows differences in the principle cyanate vibrations [bands are observed at 2125cm^{-1}(νCN), 318cm^{-1}(νCO), 600, 590cm^{-1} (δNCO)] from the dried N-bond product, which are very similar to the O-bonded cyanate.

^{14}N Nuclear Magnetic Resonance Spectroscopy

An attempt has been made to provide further evidence for the mode of co-ordination of the cyanate group in these rhodium(I)-phosphine complexes by the use of ^{14}N n.m.r. spectroscopy. The application of ^{14}N n.m.r. spectroscopy to the problem of determining the mode of co-ordination of the chalcogenocyanate ions was first demonstrated by Howarth, Richards and Venanzi, in the case of the thiocyanate ion(114). It was shown that there was only a small downfield nitrogen shift, relative to the free ion if co-ordination occurred through sulphur, whereas nitrogen co-ordination produced a significant high field shift. In the case of cyanate co-ordination, it was shown similarly that a high-field shift occurred for N-cyanato complexes whereas a downfield shift was observed for EtOCN(115).

The ^{14}N n.m.r. spectra of $Rh(PPh_3)_3OCN$ and propyl cyanate have been measured. Unfortunately, in the case of $Rh(PPh_3)_3OCN$, the complex was not sufficiently soluble to achieve a signal. (Concentrations greater than one molar are required). On the other hand, the ^{14}N n.m.r. spectrum of n-propyl cyanate, measured as pure liquid or in acetonitrile, exhibits a resonance at +224p.p.m., similar to that observed for EtOCN (+222p.p.m.)(115).

Discussion

Although the CO stretching frequency cannot be used as a reliable criterion in these complexes to determine the mode of co-ordination of the cyanate, there is other strong infrared spectral evidence to show that the orange and yellow compounds may be formulated as $Rh(PPh_3)_3OCN$ and $Rh(PPh_3)_3NCO$ respectively. Differences between these two analytically identical products are further shown in their general physical properties and reflectance spectra.

The co-ordination of the cyanate group in these complexes appears to be particularly solvent dependent. Both O- and N-bonded compounds dissolved in $CHCl_3$ or C_6H_6 give identical solutions in which the cyanate group is found to be N-bonded, whereas $Rh(PPh_3)_3OCN$ dissolved in MeCN retains O-co-ordination. Such behaviour parallels the solvent dependence of thiocyanate co-ordination in class 'b' metals(30, 31, 116), e.g. $Pd(AsPh_3)_2(CNS)_2$, where solvents of high dielectric constant (e.g. MeCN) give the S-bonded product, and solvents of low dielectric constant (e.g. C_6H_6 and $CHCl_3$) the N-bonded isomer(30, 31). Whether the effect of solvent in these rhodium(I)-cyanate complexes is purely an extramolecular effect is not certain. The initial yellow complex, while still wet with acetonitrile, appears to be O-bonded from the infrared spectrum, whereas the dried solid is N-bonded: the possibility that acetonitrile can co-ordinate i.e. $Rh(PPh_3)_3(MeCN)OCN$ cannot be ignored. Furthermore, the O-bonded isomer can be recrystallised from saturated chloroform solutions even through the solution spectrum indicates co-ordination through nitrogen.

An attempt was made to confirm the mode of co-ordination of the cyanate group in $Rh(PPh_3)_3OCN$ unambiguously by X-ray crystallography. However, the bright orange crystals isolated from saturated chloroform solutions were always found to be twinned and in no case was a single crystal found, suitable for X-ray work.

Experimental

Acetonitrile and ethanol were dried according to the methods of Weissberger(96). Tris(triphenylphosphine)chlororhodium(I) was prepared as previously described in Chapter 2. Tetraphenylarsonium cyanate dihydrate was prepared according to the method described by Norbury and Sinha(40), and purified by dissolving in MeCN and removing the solvent under vacuum. This procedure was repeated three times before finally allowing the compound to dry under vacuum for several hours. The complex was then added to MeCN again, and allowed to stand for one hour. Any excess solid was filtered and the filtrate taken to dryness to give the anhydrous product. All reactions were performed under nitrogen.

O-cyanatotris(triphenylphosphine)rhodium(I)

Tris(triphenylphosphine)chlororhodium(I) (0.5g, 5.2 mmole) was added to acetonitrile (10 ml.) - ethanol (50 ml.) containing tetraphenylarsonium cyanate (0.25g, 6.0 mmole), and the reaction mixture stirred for two hours. The complex precipitated as a bright orange solid, which was filtered and dried thoroughly under vacuum. Yield 0.4g = (80%). $Rh(PPh_3)_3OCN$ requires 11.0% Rh, 10.8%P, 70.6%C, 4.8%H, 1.5%N. Found 11.0%Rh 10.0%P, 70.6%C, 4.8%H, 1.7%N.

N-cyanatotris(triphenylphosphine)rhodium(I)

Tris(triphenylphosphine)chlororhodium(I) (0.5g, 6.2 mmole) was added to tetraphenylarsonium cyanate (0.25g, 6.0 mmole) in acetonitrile (50 ml.) and the reaction mixture stirred for two hours. The complex precipitated as a bright yellow solid which was filtered and dried thoroughly under nitrogen. Yield 0.3g (60%). $Rh(PPh_3)_3NCO$ requires: 11.0%Rh, 10.0%P. Found 10.9%Rh, 10.0%P.

Electrical Conductivity

The molar conductance of $Rh(PPh_3)OCN$ measured in acetonitrile showed it to be a non-electrolyte (7.8 x 10^3 ohms^{-1} cm^2).

Physical Measurements

Electrical conductivity and infrared spectral measurements were made as described in Chapter 2. U.V. spectra were recorded on a

Unicam S.P.8000 using 1cm silica cells. Reflectance spectra were recorded on a Beckman DK-2A spectrophotometer. ^{14}N n.m.r. were recorded by the kind permission of Dr. N. Logan, at Nottingham University on a Varian HA-100 Spectrometer.

Analyses

The compounds were analysed for rhodium and phosphorus by X-ray fluorimetric spectroscopy. Carbon, hydrogen and nitrogen analysis were performed by the Microanalytical laboratory, Manchester University.

CHAPTER 6

THE PREPARATION OF TELLUROCYANATE COMPLEXES

THE PREPARATION OF TELLUROCYANATE COMPLEXES

The co-ordination behaviour of the chalcogenocyanate ions [NCO^-, NCS^- and $NCSe^-$] in rhodium(I) complexes have been extensively studied and described in the previous chapters. The existence of the tellurocyanate ion ($NCTe^-$), the remaining member of the chalcogenocyanate series, has only recently been established(47-49), and no complexes containing this group have as yet been reported. Therefore, it was of particular interest to attempt to prepare tellurocyanate complexes of rhodium(I) and to investigate the co-ordination behaviour of the tellurocyanate group. However, it will become apparent from the following results that it has not been possible to isolate a compound which can be clearly identified as a tellurocyanate complex.

Results and Discussion

Compared to the other chalcogenocyanates, the tellurocyanate ion is very unstable. It can only be isolated in the presence of large counter-ions, e.g. as $Ph_4AsTeCN$ or Ph_4PTeCN. In solvents such as alcohols, tellurium is readily displaced as the free element and the cyanide ion formed, but $TeCN^-$ is fairly stable in very dry acetonitrile or acetone. Therefore, it is possible to carry out reactions with the rhodium complexes $Rh(PPh_3)_3Cl$ and trans-$Rh(PPh_3)_2(CO)Cl$ in a similar manner to that described in previous chapters.

Unlike the reactions performed with the thiocyanate and selenocyanate ions, where it was possible to isolate very insoluble complexes of the type $Rh(PPh_3)_2(MeCN)XCN$ [where X = S or Se] from acetonitrile, the reaction of the tellurocyanate ion with the rhodium complexes resulted in the formation of dark brown solutions. Brown solids were obtained by precipitation in diethyl ether. When either $Rh(PPh_3)_2(CO)Cl$ or $Rh(PPh_3)_3Cl$ were added to a solution of the tellurocyanate ion, infrared solution spectra showed the rapid disappearance of the ν(CN) band of the free ion at 2083cm^{-1}, and the appearance of a new weak band at 2115cm^{-1}, indicating that the reaction is very fast. Furthermore, it was found that a two mole excess of tellurocyanate ion was needed to react completely with the rhodium starting material. The reactions were performed under varying conditions of time and in the presence of varying amounts of triphenylphosphine. Analytical, infrared and conductivity data for the products obtained are presented in Table 6.1.

When the reactions were performed for short periods, analytical data show that the ratio of Te:Rh is 2:1 in the products. The infrared spectra of the products show the presence of tetraphenylarsonium or phosphonium ions, and conductivity measurements, although low compared to tetraphenylphosphonium tellurocyanate, indicate that the compounds are ionic: the low condictivities may be due to the large size of the ions involved, and a consequent reduction in their ionic mobilities. In addition, analytical data for these compounds indicate that when $Rh(PPh_3)_3Cl$ is reacted with the tellurocyanate ion, the third phosphine has been displaced, and similarly the infrared spectra of the compound isolated from the reaction of trans-$Rh(PPh_3)_2(CO)Cl$ with $NCTe^-$ indicate the displacement of carbon monoxide. Although phosphorus analyses

Analytical, Infrared and Conductivity Data for the Reaction of the Tellurocyanate Ion with Rhodium(I) Complexes

Reaction Conditions	Reaction Time	Analysis						Atomic Ratio Found						Infrared	Conductivity
		%Rh	%Te	%P	%C	%H	%N	%Rh	%Te	%P	%C	%H	%N	cm^{-1}	ohms^{-1} cm^{2}
Rh$(PPh_3)_2$COCl+Ph_4AsTeCN	48 hrs.	12.5	38.4					1.0	2.5						
	48 hrs.	12.8	36.8					1.0	2.4						
	30 mins.	8.45	20.8		52.2	3.7	1.8	1.0	2.0		54.0	46.0	2.0	ν(CN)2115	90
+Ph_4PTeCN	24 hrs.	10.2	29.5	9.2				1.0	2.3	3.0					
	2 hrs.	9.2													
Rh$(PPh_3)_3$Cl+Ph_4AsTeCN	48 hrs.	10.3													
	48 hrs.	11.2	37.0		43.9	3.0	3.2	1.0	2.6		33.0	27.0	2.0		
+Ph_4PTeCN	48 hrs.	9.8	32.4	9.4				1.0	2.5	3.0					
	*1 hr.	10.3	25.8	9.5				1.0	2.1	3.0				ν(CN)2115	
	1 hr.	9.7	30.0	9.6				1.0	2.5	3.5					
	30 mins.	8.9	20.4	8.3				1.0	2.0	3.0					81.5
	*30 mins.	9.5	21.5	8.4				1.0	1.9	2.9					
Ph_4PTeCN														ν(CN)2083	182

*+excess PPh_3

Table 6.1.

indicate that two phosphine ligands are present, carbon analyses for these products are too low to account for these ligands, and may be because these compounds are not amenable to conventional combustion analysis in the same way as the rhodium(I) S-bonded thiocyanate and Se-bonded selenocyanate complexes previously described.

When the reactions were allowed to stand for long periods of time, analytical data for the isolated compounds show the presence of more than two tellurium atoms per rhodium and that further displacement of triphenylphosphine has occurred. The data are not consistent though, and one or more simultaneous reactions may be taking place. The resultant compounds are, therefore, possibly mixtures of products.

The infrared spectra of all the compounds exhibit a weak band at $2115cm^{-1}$. Such a band was found in the infrared spectrum of the product of deselenated trans-$Rh(PPh_3)_2(CO)NCSe$ and assigned to the CN stretching frequency of the cyano group. Similarly, the reaction of Ph_4AsCN with $Rh(PPh_3)_3Cl$ in the mole ratio of 2:1 respectively, gave a product whose infrared spectrum also exhibits a band at $2115cm^{-1}$. It has been found that the tellurocyanate ion does indeed readily react with triphenylphosphine to give $(PPh_3)_2Te$ and free cyanide (117). If such a reaction has occurred here and the rhodium compound does contain one or more cyanide groups, the problem of how the tellurium is bonded in these compounds still remains.

Experimental

All solvents were dried according to the methods previously described. Tris(triphenylphosphine)chlororhodium(I) was prepared as previously described (chapter 2). Bis(triphenylphosphine)carbonylchlororhodium(I) was prepared according to the literature methods(118). Tetraphenylarsonium and tetraphenylphosphonium tellurocyanate were kindly donated by Dr. J. Songstad, Chemical Institute, University of Bergen, Norway. The salts may be prepared according to the methods of Songstad and co-workers(48). All reactions were performed under nitrogen.

The reaction of Tetraphenylarsonium tellurocyanate with rhodium(I) complexes.

Tetraphenylarsonium cyanate (0.5 mmole) was dissolved in dry acetonitrile (50 ml.). Tris(triphenylphosphine)chlororhodium(I) or bis(triphenylphosphine)carbonylchlororhodium(I) (0.25 mmole) was added and the reaction mixture stirred. The resultant dark brown solution was filtered, and the product precipitated in diethyl ether. The compound was washed thoroughly with water, dissolved in chloroform and refiltered. The product was then reprecipitated in diethylether, filtered, and dried under vacuum for 24 hours.

The reaction time varied between 30 minutes to 48 hours and sometimes in the presence of triphenylphosphine. The reactions were also performed using tetraphenylphosphonium tellurocyanate.

Physical measurements

Infrared spectra and conductivity measurements were made as previously described in Chapter 2.

Analyses

The compounds were analysed for rhodium, tellurium and phosphorus, by X-ray fluorescence spectroscopy, and for carbon hydrogen, and nitrogen, by conventional combustion analysis as described in previous chapters.

CHAPTER 7

A STUDY OF THE CO-ORDINATION BEHAVIOUR OF ORGANIC THIOCYANATES AND ISOTHIOCYANATES BY MEANS OF N.M.R. SPECTROSCOPY AND LANTHANIDE SHIFT REAGENTS

A STUDY OF THE CO-ORDINATION BEHAVIOUR OR ORGANIC THIOCYANATES AND ISOTHIOCYANATES BY MEANS OF N.M.R. SPECTROSCOPY AND LANTHANIDE SHIFT REAGENTS

Little work has been reported on the co-ordination of organic thiocyanates and isothiocyanates to metal complexes in comparison to the co-ordination of the thiocyanate ion. Jain and Rivest have reported the 1:1 adducts of ethyl thiocyanate with $TiCl_4$, $TiBr_4$ and $SnBr_4$ and have proposed that ethyl thiocyanate co-ordinates through the sulphur atom (118). They argue that the small increased shift observed in the CN stretching frequency of EtSCN on co-ordination to $TiBr_4$ compared with that observed in the infrared spectrum of $EtSCN:TiCl_4$ is because of steric reasons, and is evidence for Ti-S bonding. They presume that because of the larger bromine atom, the Ti-S bond is weaker and thereby ν(CN) is increased to a smaller degree in the $TiBr_4$-thiocyanate adduct compared with $TiCl_4$:EtSCN. Goodall(119), on the other hand, assigned N-co-ordination in $\left[(C_2H_4)_2(SCN)_2.CoCl_2\right]_x$ on the basis of the large shift to higher wavenumbers of the CN stretching frequency of $C_2H_4(SCN)_2$ on co-ordination, but S-co-ordination in $\left[RhCl_3.C_2H_4(SCN)_2\right]_2$ and $\left[IrCl_3.C_2H_4(SCN)_2\right]_2$ because the CN stretching is altered very little. Others have similarly used the CN stretching frequency as being diagnostic for N- or S-bonding (120,121). Recently Wilkins has proposed that MeSCN co-ordinates to $NbCl_5$ and $TaCl_5$ through the sulphur atom, and, on the basis of two CN stretching frequencies observed in the infrared spectra of $MeMCl_4$.MeSCN and Me_2MCl_3.MeSCN $\left[M=Nb,Ta\right]$, concluded that mixtures of isomers were obtained in these compounds where MeSCN can co-ordinate through N or S(122). However, assignment of the mode of co-ordination of the organic thiocyanate or isothiocyanate based on a shift observed in the CN stretching frequency should be treated with the utmost caution. As discussed previously in Chapter 1, such a criterion is not diagnostic and can be misleading in assigning N- or S-co-ordination of the thiocyanate ion.

The use of lanthanide shift reagents in conjunction with proton magnetic resonance spectroscopy provides an alternative means of studying the co-ordination behaviour of organic thiocyanates and isothiocyanates to a class 'a' metal. The use of lanthanide shift reagents as a means of simplifying complex organic n.m.r. spectra was first initiated by Hinckley(123). Since then numerous papers have been reported on their use, and have recently been reviewed by Mayo(124) and by Cockerill et al.(125). Lanthanide shift reagents cause shifts to occur to a greater or lesser degree in protons largely by a pseudocontact mechanism (126). The substrate co-ordinates to the lanthanide shift reagent, referred to as the LSR, by virtue of the requirement that it contains heteroatoms which exhibit some degree of Lewis basicity, and greater shifts are caused by functional groups which are most basic(127). The basicity factor appears a most important criterion on which to judge the effectiveness with which a group will give a lanthanide induced shift (LIS)(124). Several workers have compared the co-ordinating ability of different functional groups to cause a LIS: for example, amines>hydroxyls>ketones>aldehydes>ethers>esters>nitriles.

The chemical shifts induced in a number of organic thiocyanates and isothiocyanates, by the lanthanide shift reagent $Eu(fod)_3$ [fod = 1,1,1,2,2,3,3, heptafluoro - 7,7, - dimethyl - 4,6, - octane - dionato] have therefore, been examined in order to evaluate how the thiocyanate or isothiocyanate co-ordinates to the europium.

Results and Discussion

(i) The Calculation of the Shift Parameters ΔB and K

Addition of a LSR to a solution of the substrate in a normal n.m.r. solvent leads to the formation of an equilibrium mixture as shown in equations (1) and (2):

$$[L] + [S] \xrightarrow{K_1} [LS] \qquad (1)$$

$$[LS] + [S] \xrightarrow{K_2} [LS_2] \qquad (2)$$

Where $[L]$ and $[S]$ are the concentrations of the LSR and substrate respectively, and $[LS]$ the concentration of the complex formed in solution; the ratios of these species depends on K_1 and K_2, the binding constants. The latter binding constant K_2 is usually assumed negligible i.e. a 1:1 complex is thought to be formed in most cases. Owing to the magnetic interactions with the metal ion in the complexed substrate, the n.m.r. positions of associated nuclei in the substrate differ from those in the uncomplexed state. The equilibrium in solution between these species is rapid on the n.m.r. timescale(129) so that only a single average signal is recorded for each nucleus in the different environments.

This does not mean that the whole spectrum is merely displaced since factors such as the distances of the nuclei from the metal ion cause a differential expansion of the spectrum. An expression has been derived for the lanthanide induced shift(LIS), denoted by $\delta\Delta$, of the nuclei of the substrate before and after addition of the L.S.R.(130):

$$\delta\Delta = \frac{K[LS]\Delta B}{1 + K[LS]}$$

where ΔB is the LIS of the complexed substrate $[LS]$, i.e. the bound chemical shift, and K the equilibrium constant of expression(1).

The shift parameters derived from experimental methods of adding LSR to substrate have found to be dependent upon the initial substrate concentration. The method of Armitage and co-workers has been adopted in these studies which enables the precise calculation of bound chemical shift ΔB and K, the binding constant(131,132). They use the expression:

$$[S_o] = \frac{[Lo]\cdot\Delta B}{\delta\Delta} - \left(\frac{1}{K} + [Lo]\right)$$

where $[So] >> [Lc]$; $[Lo]$ and $[So]$ are the respective initial concentrations of lanthanide and substrate, since only under these conditions, they argue, are the relative magnitudes for the various nuclei independent of substrate concentration. Shift parameters are calculated by measuring the chemical shift induced by a constant concentration (approx. 0.005M of $Eu(fod)_3$ together with varying concentrations (approx 0.03 - 0.2M) of substrate, and plotting $[So]$ versus $^1/\delta\Delta$ where the slope equals

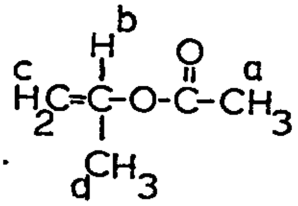
[Lo]. ΔB and the intercept $^1/K$ + [Lo]. Shift parameters for isopropenyl acetate have been calculated by this method [Fig. 7.1. and Table 7.2.] and the value obtained for K, the equilibrium constant, within experimental error, is in very good agreement with the value reported by Kelsey(133). The shift parameters for MeOH and EtOH have also been calculated and are included in Table 7.2.

(ii) Shift Parameters, ΔB and K, Calculated for Organic Thiocyanates and Organic Isothiocyanates.

The shift parameters for a number of organic thiocyanates and isothiocyantes have been calculated by the above method and the results are presented in Table 7.3., and also include values determined for some nitriles and dimethyl sulphide which provide similar donor atoms to those available for organic thiocyanates and isothiocyanates.

It can readily be seen that chemical shifts are induced in organic thiocyanates, although these are small compared to the stronger co-ordinating alcohols or ethers (as indicated by the differences in ΔB and K; see Table 7.2. and 7.3.), while no LIS are observed in the protons of any of the organic isothiocyanates when measured in CCl_4. Since a LIS is also observed in organic nitriles, but not in dimethyl sulphide, the indication is that co-ordination to europium occurs through nitrogen in organic thiocyanates, whilst in organic isothiocyanates, where the sulphur atom is the most available atom, little or no co-ordination occurs. This is consistent with europium being a class 'a' metal where there is a preference for the thiocyanate group to co-ordinate through

The Calculation of Shift Parameters, ΔB & K, for Isopropenyl Acetate



$\overset{c}{H_2C}=\underset{{}_{d}CH_3}{\overset{H^{b}}{C}}-O-\overset{O}{\overset{\|}{C}}-\overset{a}{CH_3}$

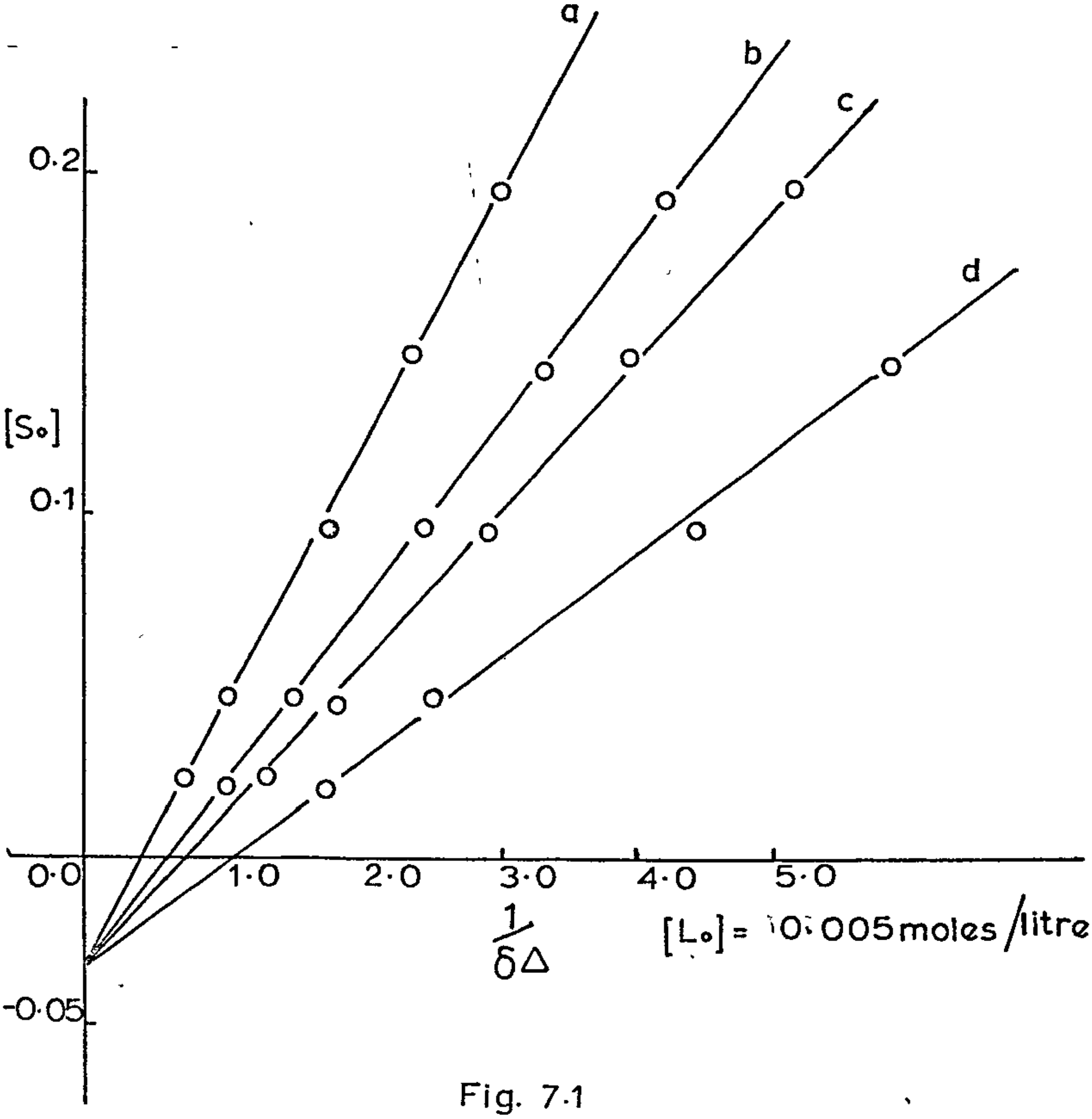
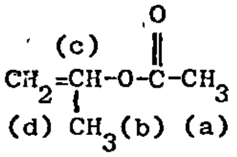


Fig. 7.1

Shift parameters Calculated for Isopropenyl Acetate, Methanol and Diethyl Ether

Substrate	K litre mole^{-1}	ΔB. p.p.m.
isopropenyl acetate  $CH_2=\underset{CH_3}{CH}-O-\overset{O}{\overset{\|}{C}}-CH_3$	28.6 (27.0 ± 3.0)(a)	18.0(a) 10.0(b) 11.6(c) 6.4(d)
CH_3OH	23.2	45.0(a)
(a)(b) $CH_3CH_2OCH_2CH_3$	36.0	22.0(a) 9.3(b)

Measurements were performed in CCl_4

(a) Value quoted by Kelsey(133).

Table 7.2.

Shift Parameters Calculated for Organic Thiocyanate and Isothiocyanates

R	R-SCN		R-NCS
	ΔBppm	K litre Mole^{-1}	
Me	8.3	11.8	No shift
$PhCH_2$	7.6	11.2	No shift
C_3H_5	-	-	No shift

	ΔBppm	K litre Mole^{-1}
Me_2S	No shift	
$PhCH_2CN$	19.00(CH_2)	9.3
MeCN	14.6	27.0

Table 7.3.

the nitrogen atom as found in $Eu(NCS)_6^{3-}$(134). Some co-ordination may occur between Eu and the sulphur atom since a very small induced shift is observed when measurements are performed in CS_2 which is a less donor competing solvent than CCl_4. It has been shown that there is a lowering of LIS going from $CS_2 < CCl_4 < C_6D_6 < CDCl_3 < CH_3CN$(128), as demonstrated by the induced chemical shifts observed in MeSCN measured in these solvents, (Table 7.4.). It appears, therefore, that the nitrogen atom in organic isothiocyanates is not available for co-ordination in the same way as in organic thiocyanates, and if co-ordination does occur through sulphur in organic isothiocyanates to europium, the ligands are very weakly bound.

The results obtained for the chemical shifts induced in organic thiocyanates and isothiocyanates by $Eu(fod)_3$ are extremely interesting in another sense. Such differences observed in induced chemical shift may be an important means of distinguishing between N- or S- co-ordination in inorganic thiocyanate complexes containing organic ligands. The chemical shifts induced in a number of inorganic complexes have, therefore, been examined.

(iii) Chemical Shifts Induced in Inorganic-Thiocyanate Complexes

It has not been possible to determine shift parameters from the n.m.r. spectra of metal-thiocyanate complexes containing organic ligands, except for $Co(DH)_2pySCN$, because the compounds are much less soluble so that accurate measurements over a range of concentrations are

Chemical Shifts Induced in MeSCN and MeNCS in Various Solvents

R	Chemical Shift Observed $\Delta\tau$		
	CCl_4	CS_2	$CDCl_3$
MeSCN	0.4	1.0	0.25
MeNCS	No shift	0.05	No shift

Mole Ratio $Eu(fod)_3$/substrate = 0.15

Table 7.4.

precluded. However, the chemical shifts induced in metal-thiocyanate complexes of known concentration on addition of known quantities of Eu(fod)$_3$ have been recorded and are presented in Table 7.5., and show that a similar behaviour is observed to that found for the organic thiocyanates, as is clearly illustrated by the linkage isomers (π-cp)Fe(CO)$_2$CNS (Table 7.5.). Furthermore, the equilibrium constant K calculated for Co(DH)$_2$pySCN is similar to that determined for the organic thiocyanates.

In the case of the linkage isomers Pd(AsPh$_3$)$_2$(CNS)$_2$, the mode of co-ordination of the thiocyanate group is dependent on the nature of the solvent(31), and therefore, shift measurements for the S-bonded isomer were performed in acetonitrile and for the N-bonded case in CS$_2$. Although a small shift is induced in the phenyl protons of Pd(AsPh$_3$)$_2$(NCS)$_2$ (cf MeNCS in CS$_2$) a much larger shift is observed for the S-bonded isomer, even though measurements are performed in acetonitrile, which is a much stronger donor competing solvent.

The results, therefore, clearly show that the use of Eu(fod)$_3$ and n.m.r. spectroscopy provides a reliable means of distinguishing between N- or S- thiocyanate co-ordination.

(iv) A Means of Distinguishing between N- and S- Thiocyanate Co-ordination using the t-Butyl Resonance of Eu(fod)$_3$

The t-butyl protons of Eu(fod)$_3$ resonate at τ8.15 in CCl$_4$ and τ8.25 in CDCl$_3$. It has been shown that this resonance moves upfield on

Induced Chemical Shifts in Thiocyanate Complexes

S-Thiocyanato	δΔ	N-Thiocyanato	δΔ
(π-cp) $Fe(CO)_2SCN$	0.6	(π-cp) $Fe(CO)_2NCS$	0.02
$Pd(AsPh_3)_2(SCN)_2$	0.3(a)	$Pd(AsPh_3)_2(NCS)_2$	0.05(b)
$Co(DH)_2py(SCN)$	0.8(c) K = 11.1		
		$Rh(PPh_3)_2(CO)X$ X = Cl or NCS	0.00 (0.05)(b)
		$Rh(PPh_3)_3NCS$	0.00
		$(\pi\text{-cp})_2Ti(NCS)_2$	0.00

All spectra were recorded in $CDCl_3$ unless otherwise stated. Concentration of substrate = 0.01 molar; Mole ratio $Eu(fod)_3$: substrate = 0.5 (except for $(\pi\text{-cp})_2Ti(NCS)_2$ which was 0.005 molar. Mole ratio = 1.0).

(a) recorded in MeCN

(b) recorded in CS_2

(c) K = litre $mole^{-1}$

Table 7.5.

co-ordination(135). Schwendiman and Zink have attributed this behaviour in $Eu(dpm)_3$ to changes in geometry of the lanthanide shift reagent on complexation, and have shown that the observed shift increases with increasing substrate basicity and concentration. A similar concentration dependence is demonstrated by $Eu(fod)_3$ as is clearly shown in Fig. 7.6. However, it is difficult to correlate the observed shift for the t-butyl resonance of $Eu(fod)_3$ with substrate basicity, because smaller shifts of the t -butyl resonance are observed in the presence of diethyl ether or Et_3N than are found for in the presence of RSCN or isopropenyl acetate, where the latter co-ordinates to a lesser extent.

Nevertheless, there is a marked difference between the shift induced in the t-butyl resonance by RSCN than by RNCS where a significant shift is observed in the t-butyl resonance on organic thiocyanate co-ordination, whereas only a small shift is induced in the presence of organic isothiocyanates, as might be predicted for a weakly co-ordinating substrate. Similar behaviour is observed for the metal-thiocyanate complexes, as shown in Table 7.7. Therefore, an observation of the shift induced in the t-butyl resonance of $Eu(fod)_3$ can provide a secondary way of confirming N- or S- co-ordination in thiocyanate complexes.

(v) Chemical Shifts Induced in Cyanate Complexes

Since it is possible to distinguish between N- and S-thiocyanate co-ordination, the use of lanthanide shift reagents might also provide a method of distinguishing between N- and O-bonded cyanate complexes; this is particularly important since infrared spectral studies cannot

Variation in Chemical Shift of the t-Butyl Resonance of $Eu(fod)_3$ with Concentration of Substrate

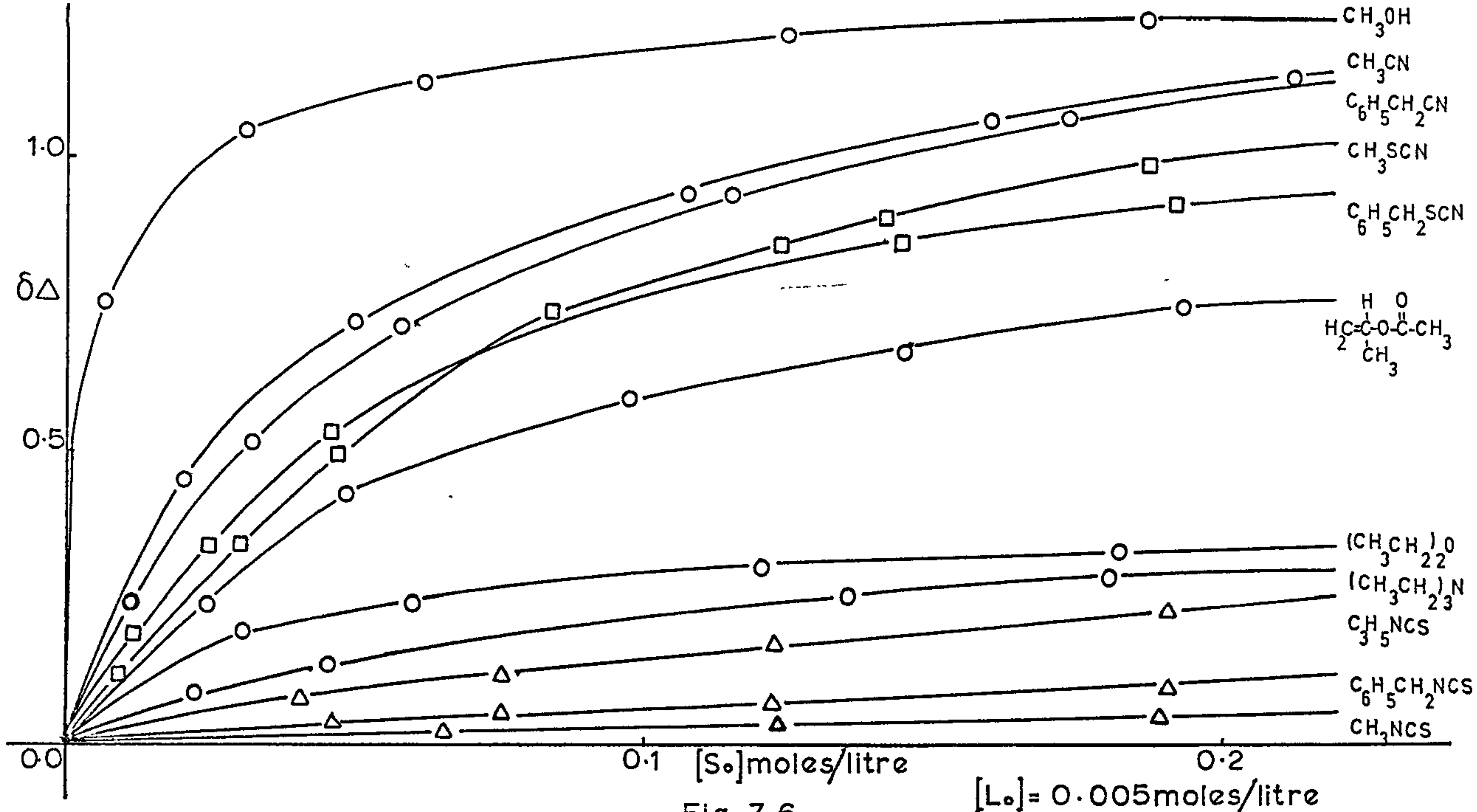


Fig. 7·6

The Chemical Shift Induced in the t-Butyl Resonance of $Eu(fod)_3$ by Thiocyanate Complexes

S-Thiocyanato	δΔ	N-Thiocyanato	δΔ
$(\pi\text{-cp})_2Fe(CO)_2SCN$	0.9	$(\pi\text{-cp})_2Fe(CO)_2NCS$	0.07
$Pd(AsPh_3)_2(SCN)_2$ (measured in MeCN)	(a)	$Pd(AsPh_3)_2(NCS)_2$ (measured in CS_2)	0.2
$Co(DH)_2py(SCN)$	0.65		
		$Rh(PPh_3)_2(CO)NCS$	0.15
		$Rh(PPh_3)_3NCS$	0.1
		$(\pi\text{-cp})_2Ti(NCS)_2$	0.3

Concentration of substrate = 0.01 molar Mole ratio $Eu(fod)_3$: substrate = 0.5 (except for $(\pi\text{-cp})_2Ti(NCS)_2$ = 0.005 molar; Mole ratio 1.0).

(a) Shift not recorded due to donor effect of MeCN.

Table 7.7.

be used with total reliability especially in assigning O-co-ordination (see Chapter 1).

Shift parameters for EtOCN and PhNCO have been measured in a similar manner to that described previously for organic thiocyanates and isothiocyanates (Table 7.3.). It has been found that considerable chemical shifts are induced in EtOCN, larger than those for organic thiocyanates, whereas no shifts are induced in PhNCO (Table 7.8.). This suggests that a similar behaviour is observed to that found for the organic thiocyanates and isothiocyanates.

As previously described, there is conflicting evidence as to whether cyanate co-ordination is through O or N, in the complexes $(\pi\text{-cp})_2Ti(CNO)_2$ and $(\pi\text{-cp})_2Zr(CNO)_2$. Recently Burmeister et al., on the basis of dipole measurements, have suggested that cyanate co-ordination is through nitrogen in the titanium complex, and O-bonded in $(\pi\text{-cp})_2Zr(OCN)_2$(67). The X-ray crystal structure determination of the former, described later in this thesis, shows that cyanate co-ordination is indeed through nitrogen. Therefore, an examination of shifts induced in these metallocenes may provide further information concerning the nature of co-ordination of the cyanate group in the zirconium adduct.

Although it was found that small shifts are induced in $(\pi\text{-cp})_2Ti(NCO)_2$ on addition of $Eu(fod)_3$,much larger shifts were observed in the zirconium compound (Table 7.8.), suggesting O-bonding in the latter compound. Similarly, addition of $Eu(fod)_3$ to a solution of $Rh(PPh_3)_3OCN$ in $CDCl_3$ (the cyanate group is co-ordinated through nitrogen in solution; see Chapter 5) also shows a small induced shift, whereas addition of $Eu(fod)_3$ to a solution of $Rh(PPh_3)_3OCN$ in MeCN, where the cyanate group retains O-co-ordination, a larger induced shift is observed.

Although, as the evidence shows, co-ordination to europium does not occur to any great extent through the sulphur atom in N-thiocyanato complexes, in the case of N-cyanato complexes it is possible that co-ordination can occur through the oxygen atom (cf shift parameters for Me_2S and Et_2O). The results indicate the order of co-ordination is:

$M\text{-}NCS < M\text{-}NCO < M\text{-}SCN < M\text{-}OCN$ where M = organic or metal,

and this is in general accord with that expected for co-ordination to a class 'a' metal.

Conclusions

Not only does the use of $Eu(fod)_3$ and n.m.r. spectroscopy provide information concerning the nature of co-ordination of RNCS and RSCN to a class 'a' metal but also provides a reliable method other than infra-red spectroscopy in determining the mode of co-ordination of the thiocyanate and possibly the cyanate group in inorganic complexes. Although the method is restricted to the examination of complexes which are soluble in very weakly co-ordinating solvents, such as $CDCl_3$, CCl_4, C_6D_6

Chemical Shifts Induced in O-Cyanato and N- Cyanato Species

O-Cyanato		N-Cyanato	
EtOCN	$K^{(a)} = \sim 100, \Delta B^{(b)}_{CH_2}$ 8.0 $\Delta B^{(b)}_{CH_3}$ 6.0	PhNCO	No Shift
$(\pi\text{-cp})_2Zr(OCN)_2$	$\Delta\tau$ 0.9$^{(c),(d)}$	$(\pi\text{-cp})_2Ti(NCO)_2$$^{(c),(e)}$	$\Delta\tau$0.2
		$(\pi\text{-cp})_2Ti(NCS)_2$	No shift
$Rh(PPh_3)_3OCN$	$\Delta\tau$ 0.5$^{(a)}$	$Rh(PPh_3)_3NCO$	$\sim\Delta\tau$0.3
(in MeCN)		(in $CDCl_3$)	

(a) K = litre mole^{-1}

(b) ΔB = p.p.m.

(c) recorded in $CDCl_3$

(d) Concentration of substrate = 0.01 molar; Mole ratio $Eu(fod)_3$: substrate = 0.5

(e) Concentration of substrate = 0.005 molar; Mole ratio $Eu(fod)_3$: substrate = 1.0

Table 7.8.

and CS_2, it has the distinct advantage over ^{14}N n.m.r. spectroscopy in that much lower concentrations of substrate can be used.

Experimental

$Eu(fod)_3.H_2O$ was purchased from Lancaster Synthesis Ltd. the presence of water inhibits the LIS owing to competitive co-ordination, and was therefore removed by drying the shift reagent over P_2O_5 under vacuum for 48 hours. The organic thiocyanates, isothiocyanates and phenylisocyanate were purchased from Fluka Chemicals. EtOCN was prepared as described by Jensen, Due and Holm(136). Trans-$Rh(PPh_3)_2(CO)NCS$ was prepared according to Burmeister et al.(73). $Rh(PPh_3)_3NCS$ and $Rh(PPh_3)_3CNO$ were prepared as previously described. The complexes $(\pi\text{-cp})_2M(CNO)_2$ [where M = Ti and Zr] and $(\pi\text{-cp})_2Ti(NCS)_2$ were prepared according to Burmeister, Deardoff et al.(43, 44) and the linkage isomers $Pd(AsPh_3)_2(CNS)_2$ according to Burmeister, Hassel and Phelan(31). The linkage isomer $(\pi\text{-cp})Fe(CO)_2(CNS)$ were prepared according to Sloan and Wojcicki(15), and the complex $Co(DH)_2py(SCN)$ from the method described by Norbury and Sinha(137). All solvents used were purified and dried in the manner described by Weissberger(96). The n.m.r. spectra were recorded on a Perkin Elmer R32(90MHz) Spectrometer using TMS as internal standard.

The procedure for determining values of ΔB and K in organic substrates

Stock solutions of organic substrate (0.25 molar) and $Eu(fod)_3$ (0.025 molar) were made up as required in CCl_4. The n.m.r. spectra of pure substrate solution was recorded. A number of solutions of substrate and $Eu(fod)_3$ were made up in n.m.r. tubes by maintaining a constant quantity of $Eu(fod)_3$(100μl of stock solution) and varying the quantity of substrate (400-50μl) of stock solution. The total volume of solution (0.5 ml) was kept constant by the further addition of CCl_4. The n.m.r. spectra of solutions were recorded and values of δ_Δ calculated from δ(substrate + $Eu(fod)_3$) - δ(substrate).

The n.m.r. spectra of inorganic substrates of known concentration (0.5 ml. of 0.01 molar solutions) were recorded before and after the addition of small quantities of $Eu(fod)_3$ (10-20mg.).

CHAPTER 8

THE REACTIONS OF ORGANIC ISOTHIOCYANATES AND THIOCYANATES WITH $Rh(PPh_3)_3Cl$ and TRANS-$Ir(PPh_3)_2(CO)Cl$

THE REACTIONS OF ORGANIC ISOTHIOCYANATES AND THIOCYANATES WITH $Rh(PPh_3)_3Cl$ AND TRANS-$Ir(PPh_3)_2(CO)Cl$

Oxidative addition of covalent molecules to unsaturated d^8 complexes of the type $Rh(PPh_3)_3Cl$ and trans-$Rh(PPh_3)_2(CO)Cl$ have been extensively studied and reviewed(138-140). On the other hand, oxidative addition reactions which involve the thiocyanate group have only been studied to a small extent. Burmeister and Weleski have investigated the reactions of thiocyanogen with trans-$Rh(PPh_3)_2(CO)X$ (where X = Cl^-, NCO^-, NCS^-) and related complexes and found that co-ordination of the thiocyanate group was exclusively through sulphur in the products(141). Baird and Wilkinson have isolated the complex $Rh(PPh_3)_2(PhNCS)_2Cl$, and suggest a structure in which phenyl isothiocyanate is co-ordinated to rhodium as a three-membered ring with rhodium-carbon and rhodium-sulphur bonds, the metal being in the +III oxidation state(142), as shown in Fig. 8.1.

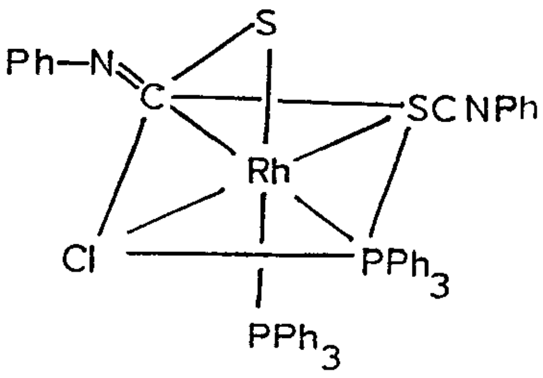


Fig. 8.1.

These studies have been extended, and the reactions of both organic isothiocyanates and thiocyanates with $Rh(PPh_3)_3Cl$ and trans-$Ir(PPh_3)_2(CO)Cl$ have been examined in order to evaluate the effect of change in oxidation state on the mode of co-ordination of the thiocyanate group and to investigate the possibilities of forming pairs of linkage isomers.by the two routes:

$$R\text{-}SCN + M \longrightarrow R\text{-}M\text{-}SCN$$

$$R\text{-}NCS + M \longrightarrow R\text{-}M\text{-}NCS$$

The results will be discussed as follows:

(i) The reaction of organic isothiocyanates with rhodium(I) and iridium(I) complexes.

(ii) The reaction of organic thiocyanates with rhodium(I) and iridium(I) complexes.

Results

(i) The Reaction of Organic Isothiocyanates with Rhodium(I) and Iridium(I) Complexes

Baird and Wilkinson(140) have attributed the CN stretching frequency around 1540cm^{-1} in the infrared spectrum of the complex $Rh(PPh_3)_2(PhNCS)_2Cl$ to the "π-bonded" phenylisothiocyanate group as shown in Fig. 8.1., whilst the bands at 2155cm^{-1} and 925cm^{-1} are attributed to the ν asym(NCS) and ν sym(NCS) of the donor S-bonded phenyl isothiocyanate. This complex has been reprepared in the manner described by Baird and Wilkinson, by heating a mixture of $Rh(PPh_3)_3Cl$ and PhNCS, and it has been found that

Infrared Spectral Data for Products obtained from the Reaction of RNCS with $Rh(PPh_3)_3Cl$ or trans-$Ir(PPh_3)_2(CO)Cl$

	donor RNCS			
$Rh(PPh_3)_2(RNCS)_2Cl$	ν(CN)	ν(CS)	ν(CN)	Rh-Cl
(a)R = Ph	2155s	925w	1540m,b	
	2170s	925w	1550m,b	310w
Me	2230s		1570m,b	300w
$PhCH_2$	2220s		1565m,b	310w
$Ir(PPh_3)_2(RNCS)_2Cl$				
Ph	2180m		1540m,b	
$PhCH_2$	2205m		1550m,b	
$Ir(PPh_3)_2(MeNCS)_2NCS$	2240s		2120s,b, 1550m	
			ν(CS) 830w	

The spectra were recorded as nujol mulls.

(a) Values taken from the results of Baird and Wilkinson.

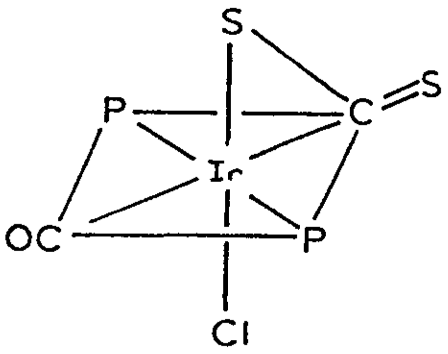
Table 8.2.

the infrared spectrum of the complex exhibited ν(CN), νasym(NCS) and νasym(NCS) and sym(NCS) at 1550cm^{-1}, 2170cm^{-1} and 925cm^{-1} respectively. Although these differences are reported the complex is clearly formulated as described.

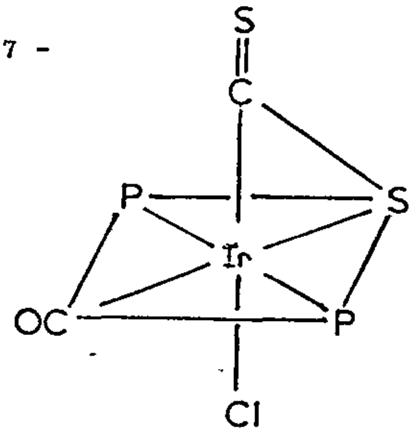
Heating a mixture of either methyl or benzyl isothiocyanate with either $Rh(PPh_3)_3Cl$ or trans-$Rh(PPh_3)_2(CO)Cl$, on the other hand, afforded a mixture of products which have not been identified. However, it has been possible to isolate complexes from the reaction of MeNCS or $PhCH_2NCS$ with $Rh(PPh_3)_3Cl$ in acetone which analyse as $Rh(PPh_3)_2(RNCS)_2Cl$ [where R = Me or $PhCH_2$]. Their infrared spectra (Table 8.2.) suggest a structure similar to that for $Rh(PPh_3)_2(PhNCS)_2Cl$ where RNCS co-ordinates to rhodium as shown in Fig. 8.1. and also acts as an unidentate ligand. Similarly, heating mixtures of trans-$Ir(PPh_3)_2(CO)Cl$ and phenyl or benzyl isothiocyanate afforded complexes which are formulated as $Ir(PPh_3)_2(RNCS)_2Cl$ [R = Ph or $PhCH_2$] and are isostructural to the analagous rhodium complexes. (Table 8.2.). Although all these complexes show that RNCS acts as a conventional ligand, no assignments have been made as to whether these ligands co-ordinate through S or N. As pointed out in the previous chapter, assignments based purely on shifts observed in the CN stretching frequency must be treated with the utmost caution.

On the other hand, the reaction of MeNCS with trans-$Ir(PPh_3)_2(CO)Cl$ gave a complex which analyses as $Ir(PPh_3)_2(MeNCS)_2$ NCS. In addition to the ν(CN) bands ascribed to the "π-bonded" methyl isothiocyanate and a methyl thiocyanate unidentate ligand (Table 8.2.), the infrared spectrum also exhibits a ν(CN) band at 2120cm^{-1} attributed to a terminal thiocyanate group probably co-ordinated to iridium through nitrogen: a weak band is also observed at 830cm^{-1} attributed to the CS stretching frequency for N-co-ordination. This thus suggests that the reaction not only involves oxidative addition but also that the chloride may have been replaced by a reductive elimination reaction as methyl chloride.

The infrared spectra of the rhodium complexes all exhibit bands at ~300cm^{-1} which can be assigned to the Rh-Cl stretching mode. Jenkins and Shaw (143,144) showed in a number of iridium(III) octahedral complexes that the Ir-Cl frequency depends primarily on the ligand trans to chlorine and is insensitive to the cis ligand. Brookes and Shaw(145) demonstrated a similar behaviour in a number of rhodium(III) complexes of the type $RhCl_3(L)_3$ [where L = PMe_2Ph, $PEt_3PPr^n_3$, $AsMe_2Ph$ etc.] and showed that the Rh-Cl stretching frequency occurred in the ranges 345-293cm^{-1} for mutually trans chlorine and 278-264cm^{-1} for chlorine. trans to phosphine in these complexes. On the basis of these studies, the band herein at ~300cm^{-1} suggests either chlorine trans to donor RNCS or chlorine trans to the 'π-bonded' organic isothiocyanate. In the case of the complexes $Ir(PPh_3)_2(RNCS)_2Cl$, their infrared spectra do not exhibit any band in the region 300-250cm^{-1}, thus indicating a different configuration to the rhodium complexes. Deeming and Shaw(146) have assigned either configuration (I) or (II) to the complex $Ir(PMe_2Ph)(CO)(CS_2)Cl$ on the basis of n.m.r. spectral data and of the Ir-Cl stretching frequency which occurs at 252cm^{-1}.



(I)



(II)

P = PMe_2Ph

It is possible, therefore, that in the case of the iridium complexes that chlorine is trans to the "π-bonded" organic isothiocyanate, while in the rhodium complexes chlorine is trans to donor RNCS.

(ii) The Reaction of Organic Thiocyanates with Rhodium(I) and Iridium(I) Complexes

(a) The Reaction of Organic Thiocyanates with Rhodium(I) Complexes

The interaction of $Rh(PPh_3)_3Cl$ with methyl or benzyl thiocyanate in cyclohexane and acetone respectively, give pink complexes which analyse as $Rh(PPh_3)_2(RSCN)(R)(SCN)Cl$ [where R = Me, $PhCH_2$]. Their infrared spectra exhibit CN stretching frequencies at 2130cm^{-1} for the MeSCN adduct and at 2125cm^{-1} for the $PhCH_2SCN$ adducts with integrated absorption intensities of 0.9 and 0.8 x $10^4 M^{-1} cm^{-2}$ respectively, and is consistent in both cases with a terminal thiocyanate group co-ordinated to rhodium through the sulphur atom (Table 8.3.). The CN stretching frequencies at 2205 and 2250cm^{-1} are attributed to co-ordinated MeSCN and $PhCH_2SCN$ respectively.

The nuclear magnetic resonance spectrum of $Rh(PPh_3)_2(MeSCN)(Me)(SCN)Cl$ measured in $CDCl_3$ shows phenyl group resonances (relative area 10) at τ2.6 with other peaks (each of relative area 1) at τ7.4 and 9.37. The

Infrared Spectral Data (cm^{-1}) for the Products Obtained from the reaction of RSCN with $Rh(PPh_3)_3Cl$ or trans-$Ir(PPh_3)_2(CO)Cl$

Complex	donor RSCN ν(CN)	ν(CN)	Rh-Cl
$Rh(PPh_3)_2(RSCN)(R)(SCN)Cl$			
R = Me(a)(b)	2205s	2130s,sp (A=0.9)(b)(c)	332w
= $PhCH_2$(a)(b)	2240s	2125s,sp (A=0.8)(b)(c)	290m,287m
$Rh(PPh_3)_2(MeSCN)(Me)(SCN)_2$(a)	2205s	2135s,sp, 2125s, sp	
$Rh(PPh_3)_2(MeSCN)(Me)(SCN)(NCS)$(b)	2205s	2130s,sp, 2100s,b, (A=1.7) (A=7.1) ν(CS)825	

(a) Nujol mull

(b) KBr disc A = X10^{4}M^{-1}cm^{-2}

(c) Also in $CHCl_3$ solution x10^{-3} molar solution

Table 8.3.

peak at τ9.37 is a broad singlet and is a typical tau value for a methyl group directly bound to rhodium(147, 148). Splitting of this peak might have been expected due to phosphorus and rhodium interaction [values of J_{PH} and J_{RhH} of the order 5 and 2Hz respectively, have been determined (147)] but the band in question is not resolved in this instance. The lower field peak at τ7.4 is attributed to the methyl protons of the co-ordinated methyl thiocyanate, shifted slightly upfield from free methyl thiocyanate. On addition of $Eu(fod)_3$, the methyl protons at τ9.37 are shifted downfield by τ0.5, and provide further confirmation that co-ordination of the terminal thiocyanate group is through sulphur (see Chapter 7). The methyl resonances at τ7.4 are shifted, but only by a small extent (0.05τ), as might be expected since chemical shifts induced by $Eu(fod)_3$ are distance dependent, and here the ligand methyl group is further away from the influence of the shift reagent than that directly attached to rhodium. This shift also provides further confirmation that the methyl thiocyanate group is co-ordinated since it has been found that considerable induced shifts are observed in free MeSCN (see Chapter 7).

Similarly, MeSCN will react with $Rh(PPh_3)_3NCS$ in cyclohexane to give a complex which analyses as $Rh(PPh_3)_2(MeSCN)(Me)(SCN)_2$. The infrared spectrum (Table 8.3.) presented as a nujol mull suggests a structure similar to that for $Rh(PPh_3)_2(MeSCN)(SCN)Cl$ but in this instance two terminal thiocyanate groups are co-ordinated through sulphur, as indicated by very sharp CN stretching frequencies at 2135cm^{-1} and 2125cm^{-1}. There are no bands in the region 900-700cm^{-1} which could have been attributed to the CS stretching frequency for the N-bonded case. The n.m.r. spectrum of this complex, measured in $CDCl_3$ under nitrogen, exhibits only two peaks at τ2.6 (relative area 10) and at τ7.43 (relative area 2). Addition of $Eu(fod)_3$, however, splits the peak at τ7.43 into two resonances at τ7.3 and τ7.4 (relative area 1:1 respectively) which can be attributed to the protons of the methyl group directly co-ordinated to rhodium and of the donor methyl thiocyanate ligand respectively. It is interesting to note that the resonance for the methyl group co-ordinated to rhodium, i.e. Rh-Me, is substantially downfield compared with the methyl resonance found in $Rh(PPh_3)_2(MeSCN)(Me)(SCN)Cl$. A similar tau value was found for the methyl resonance in $Rh(PPh_3)_2(MeI)(Me)(Cl)I$. ($\tau$Rh-Me = 7.16)(149).

The infrared spectra of the complexes $Rh(PPh_3)_2(RSCN)(R)(SCN)Cl$ (where R = Me or $PhCH_2$) presented as KBr discs show no differences to their spectra as nujol mulls. On the other hand, the infrared spectrum of $Rh(PPh_3)_2(MeSCN)(Me)(SCN)_2$ presented as a KBr disc shows marked differences in position and intensity of the CN vibrations, compared with the spectrum as a nujol mull; bands are exhibited at 2130 ($A = 1.7x10^4 M^{-1} cm^{-2}$) and $2100cm^{-1}$ ($7.1x10^4 M^{-1} cm^{-2}$) indicating that co-ordination of one of the thiocyanate groups is now through nitrogen. This is further substantiated by the appearance of a new band at $825cm^{-1}$, absent in the spectrum as a nujol mull, and is attributed to the CS stretching frequency for N-co-ordination. The isomerisation is a pressure effect rather than some effect due to KBr, since after applying a pressure of 70 tons/sq.in. to the pure complex, its mull spectrum showed identical changes in the CN stretching frequencies to those found in the KBr disc. No changes are observed in other ligand vibrations. The isomerisation appears to be irreversible since the infrared spectrum of this complex remains unchanged over several weeks.

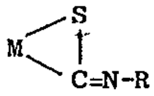
With regard to the general geometric configuration of the complexes $Rh(PPh_3)_2(MeSCN)(Me)(SCN)Cl$ and $Rh(PPh_3)_2(MeSCN)(Me)(SCN)_2$, the former exhibits a Rh-Cl stretching frequency at 330cm^{-1}. On the basis of Shaw's studies(143,144,145), the absorption at 330cm^{-1} suggests that the chlorine is trans to the thiocyanate group, thus implying the thiocyanate is cis to the methyl group. This is further supported by the n.m.r. spectrum on addition of $Eu(fod)_3$. Interaction between the europium complex and the nitrogen end of the thiocyanate group causes changes in the chemical shift as a result of primarily a pseudocontact magnetic anisotropy effect i.e. a through space effect. Therefore, a methyl group cis to the thiocyanate group would be much more susceptible to induced chemical shifts than one in the trans position. Small shifts for co-ordinated MeSCN may be attributed to increased distance from the europium complex whether in a cis or trans position. On the other hand, the n.m.r. spectrum of $Rh(PPh_3)_2(MeSCN)(Me)(SCN)_2$ only shows a small shift of the methyl protons on addition of $Eu(fod)_3$. In addition, it was found that the phenyl protons were split into two clear sets of peaks at τ2.7 & 1.9(relative areas 3.2 respectively) and parallels the magnetic anisotropy effect observed in the n.m.r. spectrum of trans-$Rh(PPh_3)_2(CO)NCS$ and suggest that the phosphine groups must be symmetrical with respect to each other. No such splitting of the phenyl protons was observed in the n.m.r. spectrum of the former. The infrared spectrum of $Rh(PPh_3)_2(PhCH_2SCN)(PhCH_2)(SCN)Cl$ exhibits two Rh-Cl stretching frequencies at 290 and 287cm^{-1}, these frequencies are significantly lower than those observed in the corresponding methyl thiocyanate and indicate that the chloro group is not trans to thiocyanate. The presence of two Rh-Cl vibrations may result because of different structural configurations, although solid state splitting cannot be ignored. Therefore, because of the differences observed between the infrared and n.m.r. spectra of the complexes, it is not possible to make definite structural assignments, and it can only be inferred that there are different geometric configurations involved.

(b) The Reaction of Organic Thiocyanates with trans-$Ir(PPh_3)_2(CO)Cl$

Heating mixtures of methyl or benzyl thiocyanate with trans-$Ir(PPh_3)_2(CO)Cl$ results in complexes which analyse for $Ir(PPh_3)_2(Me)(NCS)_2.\frac{1}{2}MeCl$ and $Ir(PPh_3)(PhCH_2)(NCS)_2.\frac{1}{2}PhCH_2Cl$ respectively. Their infrared spectra both exhibit strong CN stretching frequencies at 2100cm^{-1} attributed to terminal thiocyanate groups co-ordinated through nitrogen: CS stretching frequencies are also exhibited at 835 and 840cm^{-1} for the methyl and benzyl adduct respectively. There are no bands in the region 2200-2100cm^{-1} which may be associated with the CN stretching frequency for bridging thiocyanate. Heating the complexes at 100°C. causes a weight loss equivalent to $\frac{1}{2}$RCl. It, therefore, appears that not only has oxidative addition occurred but that it has been followed by the reductive elimination of RCl, and a subsequent oxidative addition of RSCN. The products have infrared spectra which show no evidence of carbon monoxide or a donor co-ordinated RSCN ligand being present and are thus tentatively formulated as described. These reactions resemble that of excess MeI with $Rh(PPh_3)_3Cl$ to give $Rh(PPh_3)_2(Me)I_2$ which has been clearly identified as a five co-ordinate complex from a crystal structure determination (150). Such a species may be present for $Ir(PPh_3)_2(Me)(NCS)_2$ but it seems unlikely that a four co-ordinate iridium(III) compounds exists as indicated by $Ir(PPh_3)(PhCH_2)(NCS)_2$.

Discussion

It is clear from the results that oxidative addition of organic isothiocyanate to rhodium(I) or iridium(I) does not take place in the same way as the oxidative addition of organic thiocyanates. In the former, RNCS co-ordinates to M as a three membered ring with metal-carbon and metal-sulphur bonds(I), whereas in the latter oxidative addition occurs by cleavage of the carbon-sulphur bond(II).



(I)


$R{-}M{-}SCN$

(II)

In both cases there is a preference for co-ordination of the thiocyanate group to co-ordinate through the sulphur atom, except in the cases of the reaction of RSCN with trans-$Ir(PPh_3)_2(CO)Cl$ where the thiocyanate group appears to be through nitrogen, but as shown these reactions are not just one simple oxidative addition.

The preference for S-bonding could be attributed to either the displacement of triphenylphosphine (in the case of organic isothiocyanate-iridium(III) complexes, carbon monoxide) or the change of oxidation state from (I) to (III). Burmeister has isolated the complexes $M(PPh_3)_2(CO)(SCN)_3$ [where M = Rh,Ir] from the reaction of thiocyanogen with $M(PPh_3)_2(CO)NCS$ [M = Rh,Ir]. They argue on the basis of the π-bonding hypothesis of Turco and Pecile(9) such that as the oxidation state of the metal is increased, the energy level of its dπ orbitals would decrease, making it possible for the S-bonded thiocyanate to function as both a σ- and a π-donor ligand. This was first proposed by Gutterman and Gray(27) (see Chapter 1) for the S-bonded thiocyanate group in the complex $[Co(CN)_5SCN]^{3-}$. Correspondingly, the interaction of the metal dπ orbitals with the π* orbitals of the CO group would also be expected to diminish as the oxidation state of the metal is decreased. Conversely, if the metal is in a lower oxidation state, the energy level of its dπ orbitals would be higher and, according to Turco and Pecile, they would normally preferentially interact with the vacant dπ (or π*) orbitals of the S-bonded thiocyanate as in $[Pd(SCN)_4]^{2-}$ and $[Pt(SCN)_4]^{2-}$. However, this interaction is destroyed by the presence of a stronger π- acceptor such as CO, and a σ-N-bonded mode results.

However, it could be equally argued that rhodium in a +III oxidation state is a class 'a' metal rather than a class 'b' metal. The N-bonded complex $[Rh(NH_3)_5NCS]^{2+}$ is the thermodynamically stable isomer(151,152), and can be compared with $[Co(NH_3)_5NCS]^{2+}$ where the co-ordination of the thiocyanate group was attributed to the 'hardening' effect of the amine ligands on a class 'a' metal (see Chapter 1). Therefore, in the case of the complexes discussed by Burmeister, it would be predicted that rhodium, being a class 'a' metal and surrounded by soft ligands (e.g. CO PPh_3), the thiocyanate group would prefer to co-ordinate through the sulphur atom(24).

Both arguments could similarly be applied to the organic thiocyanate and isothiocyante complexes described in this study. However, it is difficult to rationalise the isomerisation of $Rh(PPh_3)_2(MeSCN)Me(SCN)_2$ on the basis of such arguments. Isomerisation of the thiocyanate group as a result of a pressure effect has been reported only once previously. Drickamer et al.(153) have made the interesting observation from Mössbauer measurements that iron(III) compounds are reversibly reduced to iron(II) at high pressures. They record that the asymmetric spectrum of a compound they formulate as $K_3Fe(SCN)_6$ shows an increasing proportion of Fe(II) and, on pressure release, a symmetric spectrum which is regenerated on repeating the experiment. The authors ascribe these changes to reversible reduction associated with linkage isomerism. However, it has been pointed out that the original formulation of $K_3Fe(NCS)_6$ as the S-thiocyanato complex was incorrect (3), so that this interpretation must be treated with caution.

On the other hand, there is clear evidence to show that a pressure effect causes the isomerisation of $Rh(PPh_3)_2(MeSCN)(Me)(SCN)_2$ to give $Rh(PPh_3)_2(MeSCN)(Me)(SCN)(NCS)$. It is likely that the energy differences between N- and S- co-ordination are small. Indeed the pressures involved are not particularly large and would be equivalent to a small energy change, assuming that any volume change is small. Both steric (e.g. possible changes in geometric configuration) and electronic factors may play an important part in the isomerisation. In the latter case, it could be argued that isomerisation occurs because rhodium in a +III oxidation state in this particular complex is borderline between class 'a' and class 'b'. However, it is impossible to distinguish between steric and electronic effects, particularly when only small energy changes are involved, and the isomerisation may therefore result as a consequence of both these factors.

Finally, it is noted there is a marked ability in both rhodium and iridium complexes to undergo reductive elimination. This behaviour is discussed in greater detail in the following chapter.

Experimental

All solvents used were dried according to the methods described. Chlorotris(triphenylphosphine)rhodium(I) was prepared as previously described. Chlorobis(triphenylphosphine)carbonyliridium(I) was prepared according to the method described in Inorganic Syntheses(154). The organic thiocyanates and isothiocyanates were purchased from Fluka Chemicals. All reactions were performed under a nitrogen atmosphere.

The Preparation of Organic Isothiocyanate Complexes.

Chlorobis(triphenylphosphine)bis(phenylisothiocyanate)rhodium(III)

This complex was prepared according to the method described by Baird and Wilkinson. Yield 0.2g (60%).

Found: 10.8%Rh, 3.9%Cl, 6.3%P, 6.5%S.

$Ph(PPh_3)_2(PhNCS)_2Cl$ requires: 11.05%Rh, 4.05%Cl, 6.55%P, 6.85%S.

Chlorbis(triphenylphosphine)bis(methylisothiocyanate)rhodium(III)

Chlorotris(triphenylphosphine)rhodium(I) (0.5g) was added to methyl isothiocyanate (0.5g) in acetone (50ml.) and the reaction mixture stirred for two hours. The resultant bright yellow solid was filtered, washed thoroughly with hexane and dried under vacuum. Yield 0.3g (69%).

Found: 12.5%Rh, 7.5%P.

$Rh(PPh_3)_2(MeNCS)_2Cl$ requires: 12.7%Rh, 7.6%P.

Chlorobis(triphenylphosphine)bis(benzylisothiocyanate)rhodium(III)

This complex was prepared in the same way as chlorobis(triphenylphosphine)bis(methylisothiocyanate)rhodium(III) using benzyl isothiocyanate. Yield 0.2g (40%).

Found: 10.9%Rh, 6.7%P.

$Rh(PPh_3)_2(PhCH_2NCS)_2Cl$ requires 10.8%Rh, 6.5%P.

Chlorobis(triphenylphosphine)bis(phenylisothiocyanate)iridium(III)

A suspension of chlorobis(triphenylphosphine)carbonyliridium(I)

(0.5g) in phenyl isothiocyanate (4 ml) was heated very gently until all the iridium complex had dissolved. Diethyl ether was then added and yielded a very pale yellow solid, which was filtered and further washed with diethyl ether. Yield 0.4g. (62%).

Found: 18.9%Ir, 3.7%Cl, 6.2%P, 6.4%S.

$Ir(PPh_3)_2(PhNCS)_2Cl$ requires 18.9%Ir, 3.5%Cl, 6.1%P, 6.3%S.

Chlorobis(triphenylphosphine)bis(benzylisothiocyanate)iridium(III)

This complex was prepared in the same way as chlorobis(triphenylphosphine)bisphenylisothiocyanate)iridium(III) using benzyl isothiocyanate. Yield 0.4g (61%).

Found: 18.8%Ir, 3.0%Cl, 5.6%P, 6.4%S.

$Ir(PPh_3)_2(PhCH_2NCS)_2Cl$ requires 18.5%Ir, 3.4%Cl, 5.9%P, 6.2%S.

N-thiocyanatobis(triphenylphosphine)bis(methylisothiocyanate)iridium(III)

This complex was also prepared in the same way as chlorbis(triphenylphosphine)bis(phenyl isothiocyanate)iridium(III) using methyl isothiocyanate. Yield 0.35g. (60%).

Found: 20.8%Ir, 6.5%P, 10.3%P.

$Ir(PPh_3)_2(MeNCS)_2NCS.\frac{1}{2}MeCl$ requires 21.0%Ir, 6.7%P, 10.5%S.

The Preparation of Organic Thiocyanate Complexes.

S-thiocyanatochlorobis(triphenylphosphine)(methylthiocyanate)methylrhodium(III)

Chlorotris(triphenylphosphine)rhodium(I) (0.5g) was added to cyclohexane (100 ml.) containing methylthiocyanate (1g), and the reaction mixture stirred for two hours. The resultant pink solid was filtered, washed with hexane and dried under vacuum. Yield 0.3g (69%).

Found: 12.7%Rh, 4.5%Cl, 7.5%P, 7.7%S.

$Rh(PPh_3)_2$(MeSCN)(Me(SCN)Cl requires 12.7%Rh, 4.4%Cl, 7.6%P, 7.9%S.

Bis-S-thiocyanato-bis(triphenylphosphine)(methylthiocyanate)methylrhodium(III)

N-thiocyanatotris(triphenylphosphine)rhodium(I) (0.5g) was added to cyclohexane (100 ml.) containing methyl thiocyanate (1.0g) and the reaction mixture stirred for two hours. The resultant pink solid was filtered, washed with cyclohexane and dried under vacuum. Yield 0.25g (55%).

Found: 12.3%Rh, 7.3%P, 11.2%S.

$Rh(PPh_3)_2$(MeSCN)$(Me(SCN)_2$ requires 12.4%Rh, 7.5%P, 11.5%S.

S-thiocyanatochlorobis(triphenylphosphine)(benzylthiocyanate)benzylrhodium(III)

Chlorotris(triphenylphosphine)rhodium(I) (0.5g) was added to acetone (50 ml.) containing benzyl thiocyanate (1.0g), and the reaction mixture stirred for two hours. The resultant pink solid was filtered, washed with cyclohexane and dried under vacuum. Yield 0.3g (60%).

Found: 11.1%Rh, 6.6%P, 6.9%S.

$Rh(PPh_3)_2(PhCH_2SCN)(PhCH_2)$(SCN)Cl requires 10.8%Rh, 6.5%P, 6.7%S.

Bis-N-thiocyanato-bis(triphenylphosphine)methyliridium(III)

A suspension of chlorbis(triphenylphosphine)carbonyliridium (0.5g) in methyl thiocyanate (4 ml.) was gently heated until all the iridium complex had dissolved. Diethyl ether was then added which yielded a white precipitate which was filtered, washed with diethylether and dried under vacuum. Yield 0.2g (43%).

Found: 25.4%Ir, 2.25%Cl, 6.8%P, 6.8%S.

$Ir(PPh_3)_2(Me)_2(NCS)_2.\frac{1}{2}MeCl$ requires 22.0%Ir, 2.05%Cl, 7.2%P, 7.4%S.

BisN-thiocyanatobenzyltriphenylphosphineiridium(III)

The complex was prepared in the same way as bis-N-thiocyanato-bis-(triphenylphosphine)methyliridium(I) using benzyl thiocyanate. Yield 0.3g (70%).

Found: 28.5%Ir, 2.3%Cl, 4.1%P, 9.4%S.

$Ir(PPh_3)(PhCH_2)(NCS)_2.\frac{1}{2}PhCH_2Cl$ requires 28.0%Ir, 2.6%Cl, 4.5%P, 9.4%S.

Analyses

Analyses were performed as previously described.

Physical measurements

Infrared and n.m.r. spectra were recorded as described in previous chapters.

CHAPTER 9

THE REACTION OF ALLYL THIOCYANATE AND ISOTHIOCYANATE WITH TRANS-M$(PPh_3)_2(CO)Cl$ [where M=Rh, Ir] and $Rh(PPh_3)_3Cl$

THE REACTION OF ALLYL THIOCYANATE AND ISOTHIOCYANATE WITH TRANS-$M(PPh_3)_2(CO)Cl$ [where M=Rh,Ir] and $Rh(PPh_3)_3Cl$

Oxidative addition reactions of complexes of the type trans-$M(L)_2(CO)X$ [where M=Rh,Ir,L=tertiary phosphine and X=halide] involving allyl halides have been extensively studied(149,155,156). Many complexes have been characterised and it has been possible from infrared and n.m.r. spectral studies to determine whether they contain σ- or π-allyl species. The purpose of this investigation into the reactions of allyl thiocyanates and isothiocyanates is not only to study the mode of co-ordination of the thiocyanate group but also to determine the nature of the allylic species which occur in the isolated products. The results will be discussed in the following manner:

a) The reaction of allyl thiocyanate and isothiocyanate with:
   (i) trans-$Ir(PPh_3)_2(CO)Cl$
   (ii) trans-$Rh(PPh_3)_2(CO)Cl$.

b) The reaction of allyl isothiocyanate with $Rh(PPh_3)_3Cl$.

Results

(a)(i) The Reaction of C_3H_5SCN and C_3H_5NCS with trans-$Ir(PPh_3)_2(CO)Cl$

On heating a mixture of trans-$Ir(PPh_3)_2(CO)Cl$ and C_3H_5SCN for a few minutes and adding a little ethyl alcohol a white precipitate develops. Recrystallised from dichloromethane-ethyl alcohol, the compound

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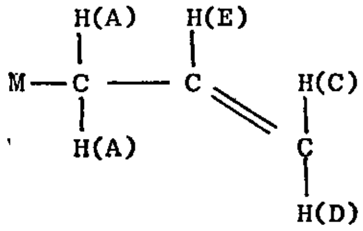
In this chapter the compounds have been numbered, and the letter A has been used to indicate the formation of an adduct, usually between the complex (designated B) and half a mole of allyl chloride or thiocyanate.

analyses as $Ir(PPh_3)_2(CO)(C_3H_5)(NCS)_2.\frac{1}{2}C_3H_5Cl$(1A). Thermogravimetric analysis shows that the half mole of allyl chloride is removed quantitatively on heating at 100°C to give the complex (1B). This and the presence of two thiocyanate groups in (1B) indicate that the reaction is not one simple oxidative addition, resulting in the cleavage of the C_3H_5-SCN bond, but one which also involves the reductive elimination of C_3H_5Cl and further oxidative addition of C_3H_5SCN. In addition to bands due to triphenylphosphine, the infrared spectrum of (1B) exhibits a CN stretching frequency at $2100cm^{-1}$ ($A=16.4x10^4M^{-1}cm^{-2}$; 8.2/NCS in $CHCl_3$) and a CS frequency at $860cm^{-1}$; the integrated intensity is too high for one thiocyanate group and is consistent with two terminal thiocyanate groups co-ordinated to iridium through the nitrogen atom. The weak band at $1620cm^{-1}$ is assigned to the C=C stretching frequency of the σ-allyl group co-ordinated to iridium, while the band at $2070cm^{-1}$ is due to the CO stretching frequency of the carbonyl group shifted to higher wavenumbers on change in oxidation state from +I to +III. Furthermore, the n.m.r. spectrum of the complex (1B) is consistent with a σ-allyl group co-ordinated to iridium(155) (Table 9.1.). The spectrum resembles that for σ-$C_3H_5Mn(CO)_5$(157), the only difference being that the non-equivalent vinyl CH_2 protons (C and D) in the iridium complex are clearly split into doublets (τ6.12 and 5.7), whereas in σ-$C_3H_5Mn(CO)_5$, the vinyl CH_2 protons are non-equivalent and each is split by the vinyl CH into doublets; these doublets overlap to give an observed three line pattern. In addition, the phenyl proton resonances in the n.m.r. spectrum are split into two sets of peaks at τ2.28 and 2.5 (relative area 2:3 respectively) and are very similar to the splitting pattern observed in

N.m.r. Spectral Data for Ir$(PPh_3)_2$(CO)(σ-C_3H_5)$(NCS)_2$(IB)



		τ	multiplicity	relative area	assignment
Ir$(PPh_3)_2$(CO)(σ-C_3H_5)$(NCS)_2$(I)		7.62	2	2	A
		(J_{AE} 8.0)			
		6.12	2	1	D
	allylic resonances	(J_{ED} 15.0)			
		5.7	2	1	C
		(J_{EC} 9.0)			
		4.65	m	1	E
	phenyl	2.28	m	12	
		2.5	m	18	
Mn(σ-C_3H_5)$(CO)_5$$^{(a)}$		8.23			A
		(J_{AE} 9.0)	2	2	
	observed triplet	5.47 5.23 4.93	(J_{EC} 10.0) (J_{ED} 15.0)	2	C D
			m	1	E
C_3H_5Cl		5.95	2	2	A
		(J_{AE} 9.0)			
	observed triplet	4.85 4.76 4.58	(J_{EC} 9.0) (J_{ED} 16.0)	2	C D
		4.1	m	1	E

m = multiplet

J = Hz

(a) from the results McClellan et al.(157)

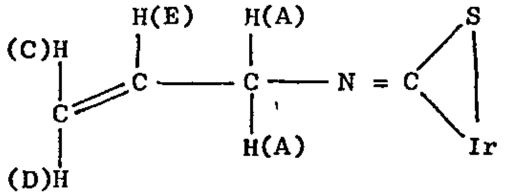
Table 9.1.

the n.m.r. spectrum of trans-Rh$(PPh_3)_2$(CO)X [where X = Cl or NCS] (see Chapter 3), suggesting a structure in which the phosphines are trans to one another. The n.m.r. spectrum of the complex, on addition of Eu$(fod)_3$, shows no induced shifts in either the phenyl or allyl resonances, providing further evidence that the thiocyanate co-ordination is through nitrogen in the complex (see Chapter 7).

The reaction of C_3H_5NCS with trans-Ir$(PPh_3)_2$(CO)Cl also gives a product which analyses as Ir$(PPh_3)_2$(CO)(C_3H_5NCS)NCS.½C_3H_5Cl(2A) (the ½C_3H_5Cl is removed on heating to give the complex (2B). The infrared spectrum of the complex (2B) exhibits bands at 1643 and 1587cm^{-1} which can be attributed to ν(C=C) and ν(CN) of allyl isothiocyanate co-ordinated to iridium through iridium-sulphur and iridium-carbon bonds, similar to those found for PhNCS in Rh$(PPh_3)_2$$(PhNCS)_2$Cl(142). In addition, the band at 2110cm^{-1} (A=12.8x10^{4}M^{-1}cm^{-2} in $CHCl_3$) is assigned to the CN stretching frequency for a terminal N-bonded thiocyanate group, while the band at 2050cm^{-1} is due to the CO stretching frequency of the carbonyl group.

In support of allyl isothiocyanate being co-ordinated to iridium via bonds with both carbon and sulphur, the allyl resonances in the n.m.r. spectrum of the complex(2B), measured in $CDCl_3$, (Table 9.2.) are shifted only slightly relative to the allyl resonances for free C_3H_5NCS. Only one complex peak is observed for the phenyl resonances suggesting that the phosphine ligands are not disposed in the same way to the carbonyl group, as found in the C_3H_5SCN complex. However, the

N.m.r. Spectral Data for $Ir(PPh_3)_2(CO)(C_3H_5NCS)NCS$ (2B)



	τ	multiplicity	relative area	assignment
$Ir(PPh_3)_2(CO)(C_3H_5NCS)NCS$	6.32	a	2	A,
	4.7	m	3	C,D,E
	2.65			phenyl protons
C_3H_5NCS	5.83	2	2	A,B
	(J_{AE} = 8.0)			
	4.6	3	2	C,D
	4.2	m	1	E

a= Broad unresolved singlet.

m= multiplet

J= Hz

Table 9.2.

lack of evidence precludes further structural assignements for the positions of the phosphines, thiocyanate and carbonyl groups and.hence.the geometric configuration can only be arbitrarily assigned.

(a)(ii) The reaction of C_3H_5SCN and C_3H_5NCS with trans-Rh$(PPh_3)_2$(CO)Cl

Analytical and infrared spectral data show that the product obtained from gently heating a mixture of C_3H_5SCN and trans-Rh$(PPh_3)_2$(CO)Cl is the rhodium(I)-complex trans-Rh$(PPh_3)_2$(CO)NCS. Similarly, the reaction of C_3H_5NCS with trans-Rh$(PPh_3)_2$(CO)Cl in acetonitrile gives the same product. On the other hand, gently heating a mixture of C_3H_5NCS with trans-Rh$(PPh_3)_2$(CO)Cl gives a product for which the analyses are not completely satisfactory,but do indicate that the adduct may possibly be formulated as Rh$(PPh_3)_2(C_3H_5NCS)(C_3H_5)(NCS)_2.\frac{1}{2}C_3H_5Cl$ (3A). The infrared spectrum of the adduct (3A) exhibits a very strong CN stretching frequency at 2110cm^{-1} and CS frequency at 830cm^{-1} indicative of N-thiocyanate co-ordination, whilst the band at 1620cm^{-1} can be attributed to ν(C=C) of a σ-allyl group co-ordinated to rhodium. In addition, the absence of any band in the region 2080-1950cm^{-1} shows that carbon monoxide has been displaced. There is no frequency which can be assigned to ν(CN) for an additional allyl isothiocyanate probably acting as a unidentate ligand, and it is suggested that the observed band at 2110cm^{-1} which is due to ν(CN) for the co-ordinated thiocyanate group includes such a frequency. The band at 1643cm^{-1} can be assigned to ν(C=C) of either allyl isothiocyanate or allyl chloride.

(b) The Reaction of C_3H_5NCS with $Rh(PPh_3)_3Cl$

The reductive elimination of allyl chloride also occurs when C_3H_5NCS is reacted with $Rh(PPh_3)_3Cl$. Stirring a mixture of C_3H_5NCS and $Rh(PPh_3)_3Cl$ (mole ratio 4:1 respectively) in acetonitrile results in a pink adduct which analyses as $Rh(PPh_3)_2(C_3H_5NCS)CNS.\frac{1}{2}C_3H_5Cl$ (4A). The half molecule of allyl chloride is removed quantitatively on heating the adduct at 120°C. to give (4B). The complex (4B) is stable, both in air or when exposed to CO, either as a solid or in solution. The bands at 1600 and $1643cm^{-1}$ in its infrared spectrum are similar to those for the allyl isothiocyanate-iridium(III) complex (2B) and can be attributed to the CN stretching frequency and $\nu(C=C)$ of the allyl group for allyl isothiocyanate co-ordinated to rhodium in a "π-bonded" fashion through the C-S bond. Two CN stretching frequencies are observed at 2130 and $2110cm^{-1}$ with an overall integrated intensity of $3.4x10^4M^{-1}cm^{-1}$ measured in KBr; in chloroform solution only one band appears at $2120cm^{-1}$ ($A=2.3x10^4M^{-1}cm^{-2}$). This evidence suggests that while the thiocyanate group is co-ordinated through the sulphur atom in solution, in the solid state a mixture of isomers is found: a band at $830cm^{-1}$ observed in the infrared mull spectrum can be attributed to the CS stretching frequency for an N-bonded thiocyanate. There is no band in the region $2200-2150cm^{-1}$ which can be associated with bridging thiocyanate.

The n.m.r. spectrum of the pink complex (4B) measured in $CDCl_3$ (See Fig..9.4.) closely resembles that of the C_3H_5NCS-iridium(III) adduct except that two resonances at $\tau5.85$ and $\tau6.3$ in the former are

Infrared Spectral Data(cm^{-1}) for the Products from the Reaction of C_3H_5NCS with $Rh(PPh_3)_3Cl$

Complex	ν(CN)	ν(CS)	ν(C=C)	A(x10^{-4}M^{-1}cm^{-2})
pink (4B)	(a)2130m,2110m,1600mb	830w	1643	3.4
	(b)2120,1600mb		1643	2.3
yellow (5B)	(a)2130s,sp 2110s,b	830m	1643	1.5 and 6.7
	(b)2120		1643	8.4

(a) KBr disc

(b) Chloroform solution

Table 9.3.

The N.M.R. Spectra of the Products from the Reaction of $Rh(PPh_3)_3Cl$ with C_3H_5NCS

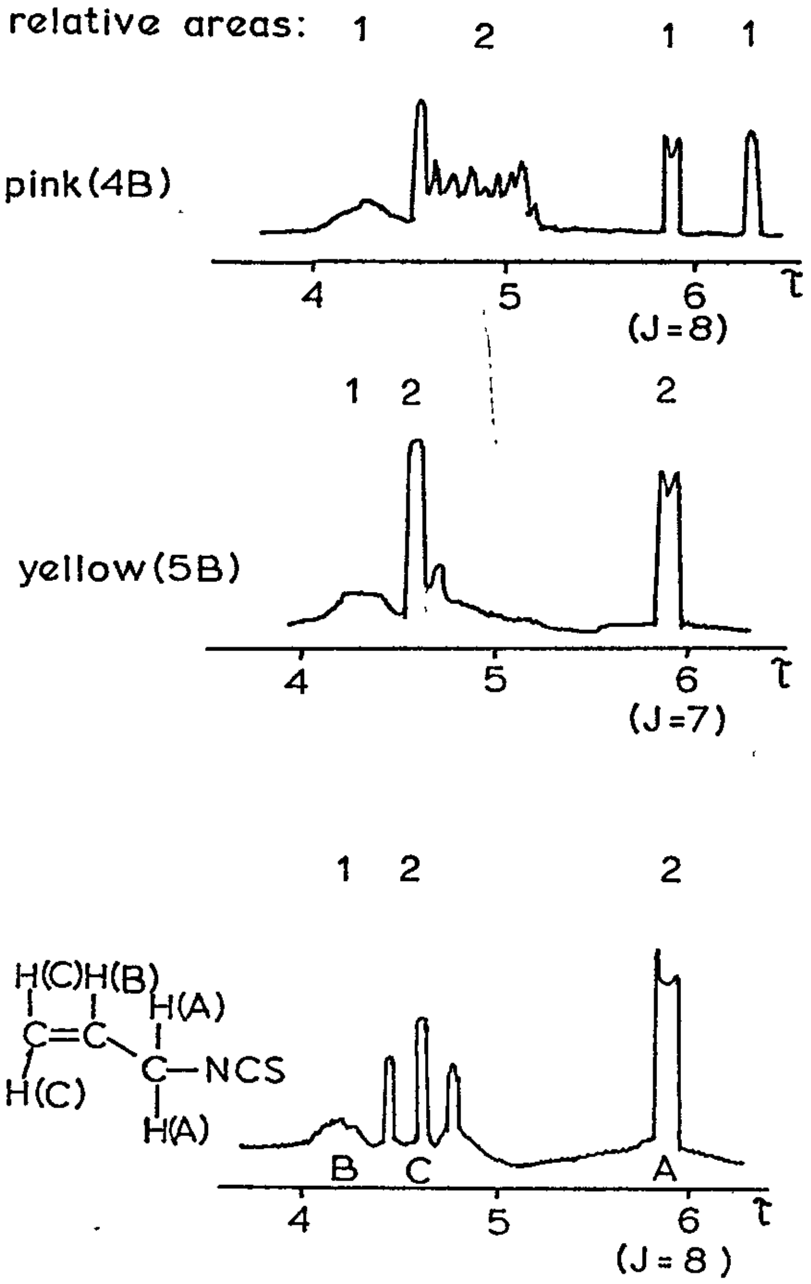


Fig 9.4

observed for the aliphatic protons A. The peak at τ5.85 is similar to that observed in free C_3H_5NCS (Fig. 9.4), and since the other peaks for free C_3H_5NCS overlap with those for the complex and cannot be distinguished, it could be argued that dissociation occurs in solution. However, this seems unlikely since any dissociated species would be expected to react with carbon monoxide. It appears, therefore, that the protons A are non-equivalent, possibly due to their geometric position in relation to the other ligands.

The analytical and spectral data thus suggest that the complex (4B) may be formulated as a five co-ordinate species $Rh(PPh_3)_2(C_3H_5NCS)SCN$ with a "π-bonded" organic thiocyanate group. It is difficult to understand why the complex does not react with carbon monoxide to give the normal six co-ordinate rhodium(III) complex unless the allylic residue partially lies over the sixth co-ordination position without actually taking part in any chemical bonding.

When excess C_3H_5NCS is reacted with $Rh(PPh_3)_3Cl$ in acetonitrile, a yellow complex is obtained which also analyses as $Rh(PPh_3)_2(C_3H_5NCS)$-$(CNS).\frac{1}{2}C_3H_5Cl$ (5A). Similarly, treatment of $Rh(PPh_3)_3NCS$ with C_3H_5NCS gives a yellow product which analyses as $Rh(PPh_3)_2(C_3H_5NCS)(CNS).\frac{1}{2}C_3H_5NCS$ (5A). The half molecules of either allyl chloride or allyl isothiocyanate can be removed quantitatively on heating the adducts at 120°C for 12 hours to give products which are identical in their reactivity and spectra. They are very air stable and do not react with CO. Their infrared and n.m.r. spectra indicate that the yellow product (5B) is not a rhodium (III) complex but a rhodium(I) complex which may be formulated $Rh(PPh_3)_2(C_3H_5NCS)NCS$, where C_3H_5NCS is acting as a unidentate ligand similar to the thiocyanate complexes described in Chapters 2 and 3. In the infrared spectrum, there is no band at ~$1600cm^{-1}$ which could be associated with C_3H_5NCS co-ordinated to rhodium in the "π-bonded" manner. The band at $1643cm^{-1}$, however, which can be clearly assigned to the ν(C=C) of the allyl group, is not consistent with a σ-allyl group co-ordinated to rhodium (a band in the region $1620-1610cm^{-1}$(149) might have been expected) but rather the C=C stretching frequency associated with allyl isothiocyanate (cf $1643cm^{-1}$ band observed in the pink C_3H_5NCS-Rh(III) complex (4B). Similarly, the allyl resonances in the n.m.r. spectrum of the yellow complex (5B) measured in $CDCl_3$ (Table 9.4.) are altered very little compared with those in the spectrum of free allyl isothiocyanate and remain unchanged when measured at -50°C. The n.m.r. spectrum recorded in the range 0-30 τ shows no resonances other than those attributable to phenyl and allyl groups.

From this evidence it is clear that although two CN stretching frequencies are observed at 2130 and $2110cm^{-1}$ (Table 9.3.) in the infrared KBr spectrum, these cannot both be associated with terminal thiocyanate groups and one must be due to C_3H_5NCS. By comparison with other organic isothiocyanate-rhodium complexes described previously, it might have been expected that the CN stretching frequency of C_3H_5NCS acting as a conventional ligand would have been shifted considerably to higher wavenumbers. The only available comparison in the literature is with the organic thiocyanate system in which Goodall(119) has observed that the corresponding frequency of $C_2H_4(SCN)_2$ is altered very little when co-ordinated to $RhCl_3$ and suggested, on this basis, that co-ordination occurred through the sulphur atom. It is possible, therefore, that the CN stretching frequency in allyl isothiocyanate behaves similarly (ν(CN) occurs at 2100cm^{-1} in free C_3H_5NCS). This would then explain the absence of a ν(CN) band at higher wavenumbers in the spectrum of the complex which appears to be $Rh(PPh_3)_2(C_3H_5NCS)(\sigma\text{-}C_3H_5)(NCS)_2.\frac{1}{2}C_3H_5Cl$ (3A) and where the band at 2110cm^{-1} has been assigned to both donor C_3H_5NCS and the co-ordinated thiocyanate group. The presence of a band at 830cm^{-1} which can be attributed to the CS stretching frequency for N co-ordination implies that the thiocyanate group is N-bonded, in keeping with the position of ν(CN). There is no band in the region 750-650cm^{-1} which can be assigned to the CS stretching frequency for allyl isothiocyanate acting as a conventional ligand (ν(CS) for C_3H_5NCS occurs at 696 and 711cm^{-1} in the free ligand) and is probably masked by the large number of phosphine bands which vibrate in this frequency range.

In support of the formulation that the yellow complex (5B) is a four co-ordinate rhodium(I) complex, the U.V. spectrum measured in chloroform is very similar to that found for $Rh(PPh_3)_3Cl$, whereas the pink rhodium(III) complex (4B) shows an additional band at 510nm.

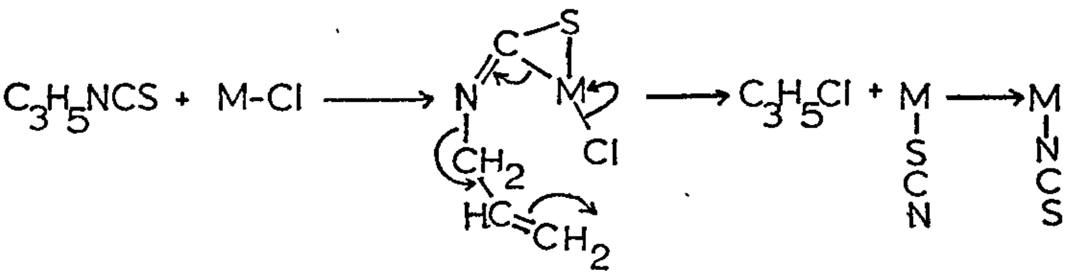
Thus, the yellow complex (5B) is formulated as $Rh(PPh_3)_2(C_3H_5NCS)NCS$ but, unlike the other rhodium(I)-thiocyanate complexes previously described, this complex is not air-sensitive and does not react with carbon monoxide. Such behaviour may be attributed to the nature of the

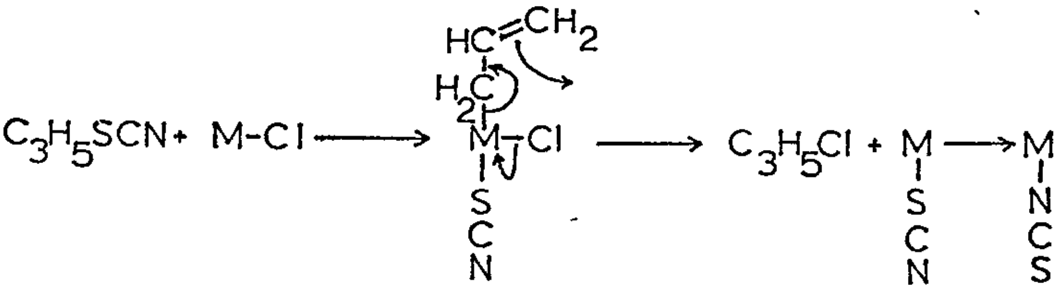
C_3H_5NCS ligand which, on reaction with trans-Rh$(PPh_3)_2$(CO)Cl, can give a rhodium(III)-adduct (3A) containing no carbon monoxide unlike the comparable reaction with trans-Ir$(PPh_3)_2$(CO)Cl. Furthermore, the fact that Rh$(PPh_3)_2(C_3H_5NCS)$NCS is N-bonded implies an interaction which is out of the ordinary between C_3H_5NCS as a ligand and rhodium(I).

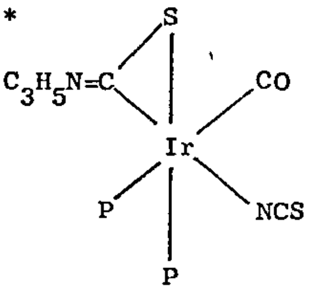
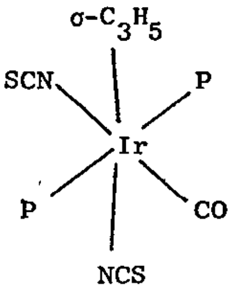
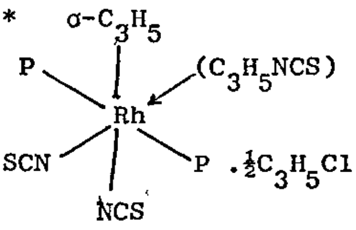
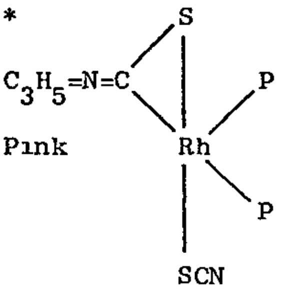
Discussion

The reactions of C_3H_5NCS or C_3H_5SCN with rhodium(I) or iridium(I) complexes are summarised in Table 9.5.

The results are interesting in two aspects. Firstly, in all cases the reactions involve the replacement of the chloride ion by the thiocyanate group. It has been suggested that such a replacement probably involves, first the oxidative addition of C_3H_5NCS or C_3H_5SCN, followed by the reductive elimination of C_3H_5Cl: evidence for the formation of the latter is provided by thermogravimetric analysis which shows that weight losses on heating these adducts is initially equivalent to $\frac{1}{2}C_3H_5Cl$. Such behaviour can be attributed to the ability of the allyl group to undergo rearrangement. Possible mechanisms are:





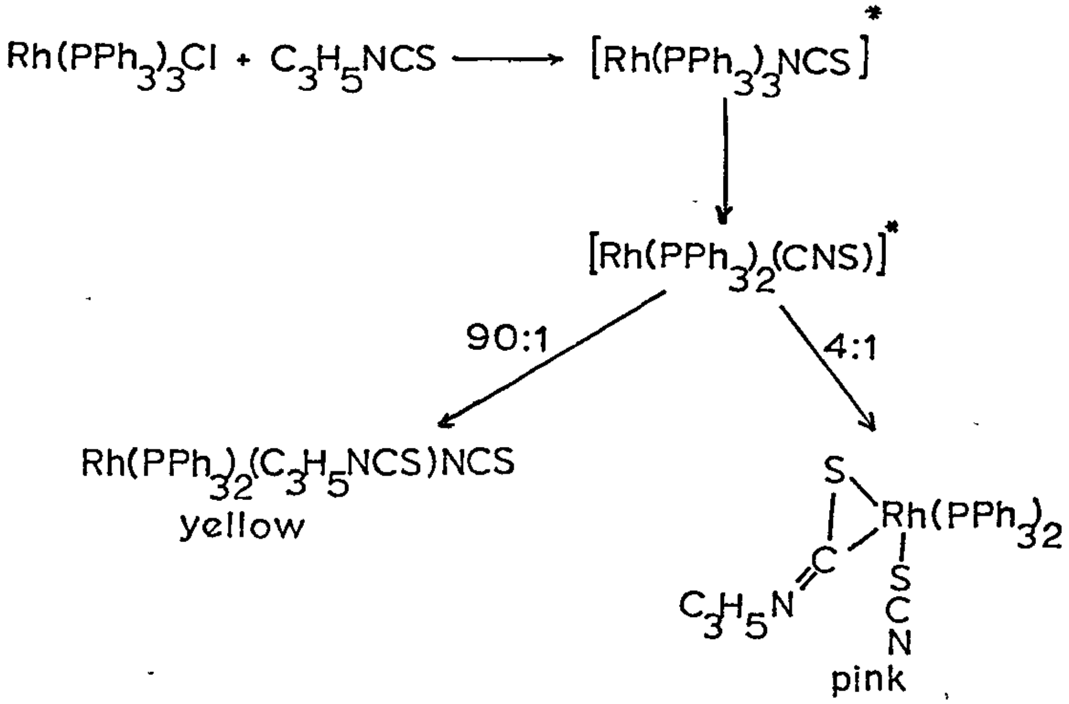
	C_3H_5NCS	C_3H_5SCN
$Ir(PPh_3)_2(CO)Cl$	*  2B	 1B
$Rh(PPh_3)_2(CO)Cl$	$Rh(PPh_3)_2(CO)NCS$	$Rh(PPh_3)_2(CO)NCS$
$Rh(PPh_3)_2(CO)Cl$	*  3A	--
$Rh(PPh_3)_3Cl$	*  Pink 4B yellow $Rh(PPh_3)_2(C_3H_5NCS)NCS$ 5B	--

*The geometric configuration has been arbitrarilly assigned.
P deonotes PPh_3
B, the $\frac{1}{2}C_3H_5Cl$ has been removed by heating.

Table 9.5.

These mechanisms do suggest that the terminal thiocyanate species are initially S-bonded in which case isomerisation must follow since the majority of the products are N-thiocyanato complexes.

Depending on conditions, reaction of C_3H_5NCS with $Rh(PPh_3)_3Cl$ in acetonitrile can give either a yellow-rhodium(I) or pink-rhodium(III) complex. In either case, the replacement of the chloride ion occurs. Whether the initial reductive elimination of allyl chloride involves the formation of $Rh(PPh_3)_3NCS$ or a dissociated species of the type $Rh(PPh_3)_2(CNS)$ is not certain but displacement of triphenylphosphine must occur at some stage. In order to account for these products one possible mechanism for this reaction is:



* possible intermediates

Thus, while further oxidation occurs when the ratio of C_3H_5NCS to $Rh(PPh_3)_3Cl$ is 4:1, in the presence of excess C_3H_5NCS (mole ratio 90:1) it is possible for C_3H_5NCS to enter a co-ordination site previously occupied by PPh_3 and in so doing would appear to inhibit further oxidative addition: further heating caused no change to the pink product. This could possibly be due to the steric effect of the strongly co-ordinated C_3H_5NCS and the bulky ligands surrounding the metal or to some not understood electronic effects, either of which could affect the rate or driving force of the reaction. Similarly, the reaction of $Rh(PPh_3)_2(CO)Cl$ with C_3H_5NCS in acetonitrile gives $Rh(PPh_3)_2(CO)NCS$ which, after the original reaction, does not procede beyond the rhodium(I) stage. Further oxidative addition does occur, however, when a mixture of trans-$Rh(PPh_3)_2(CO)Cl$ and C_3H_5NCS are gently heated when $Rh(PPh_3)_2(C_3H_5NCS)(\sigma\text{-}C_3H_5)(NCS)_2.\frac{1}{2}C_3H_5Cl$ is obtained. In this instance, whether oxidative addition results because heating provides the necessary thermal energy to overcome the supposed steric or electronic inhibitions can only be a matter of speculation.

Secondly, the mode of co-ordination of the thiocyanate group in these complexes is of interest. As discussed in Chapter 8, Burmeister and Weleski explained S-co-ordination in complexes like $Ir(PPh_3)_2(CO)(SCN)_3$ on the basis of the π-bonding hypothesis(9) and the arguments of Gray and Gutterman(27). It was pointed out, however, that although such argument could be applied to the co-ordination behaviour of the thiocyanate group in rhodium(III) complexes isolated from the oxidative addition reactions of organic thiocyanates and isothiocyanates, the co-ordination behaviour could equally be explained if rhodium in a +III oxidation state is regarded as a class 'a' metal rather than class 'b'. In the case of the iridium(III) complexes described here the results are not in accord with either of these explanations (thiocyanate coordination is through nitrogen in these complexes) and the compounds point again to the dangers of applying such arguments to explain effects which may arise from very small thermodynamic differences (see Chapters 3 and 8).

Experimental

Allyl isothiocyanate was purchased commercially from Fluka Chemicals. Allyl thiocyanate was prepared according to the method described by Emerson(158). $Rh(PPh_3)_3Cl$ was prepared as previously described and trans-$M(PPh_3)_2(CO)Cl$, where M=Rh or Ir, were prepared according to the methods described in Inorganic Synthesis(154). All reactions were performed under nitrogen.

Bis-N-thiocyanatobis(triphenylphosphine)(σ-allyl)(carbonyl)iridium(III)

A suspension of trans-$Ir(PPh_3)_2(CO)Cl$ (0.5g) in allyl thiocyanate (4ml) was heated until all the complex dissolved. Ethyl alcohol was then added, and a white solid precipitated, which was recrystallised from CH_2Cl_2-EtOH Yield 0.35g (60%)

Found: 20.3% Ir, 1.6%Cl, 7.2P%, 7.0%S.

$Ir(PPh_3)_2(\sigma\text{-}C_3H_5)(CO)NCS)_2.\frac{1}{2}C_3H_5Cl$ requires 20.4%Ir, 1.9%Cl, 6.7%P, 6.8%S.

% wt. loss from T.G.A. = 4.2%. Calculated weight loss for $\frac{1}{2}C_3H_5Cl$ = 4.0%.

N-thiocyanateobis(triphenylphosphine)(allylisothiocyanate)(carbonyl) iridium(III)

A suspension of trans-Ir$(PPh_3)_2$(CO)Cl (0.5g) in allyl isothiocyanate (4 ml) was heated until all the complex dissolved. Addition of diethyl ether to the reaction mixture gave a white precipitate which was filtered, washed with ether and dried under vacuum. Yield 0.4g (67%).

Found: 20.0%Ir, 2.2%Cl, 6.6%P, 6.7%S.

Ir$(PPh_3)_2(C_3H_5NCS)$(CO)NCS.$\frac{1}{2}C_3H_5Cl$ requires 20.4%Ir, 1.9%Cl, 6.7%P, 6.8%S.

% weight loss from T.G.A. = 4.3%. Calculated weight loss for $\frac{1}{2}C_3H_5Cl$ = 4.0%.

The Reaction of C_3H_5SCN with trans-Rh$(PPh_3)_2$(CO)Cl

A suspension of trans-Rh$(PPh_3)_2$(CO)Cl (0.5g) in allyl thiocyanate (4 ml) was gently heated for 15 minutes. Addition of ethyl alcohol gave a yellow complex. Yield 0.3g (60%).

Found: 14.6%Rh, 8.8%P, 4.4%S, 0.0%Cl.

Rh$(PPh_3)_2$(CO)NCS requires: 14.5%Rh, 8.7%P, 4.5%S.

The Reaction of C_3H_5NCS with trans-Rh$(PPh_3)_2$(CO)Cl

(a) To a solution of allyl isothiocyanate (4 ml) in acetonitrile (50 ml) was added trans-Rh$(PPh_3)_2$(CO)Cl. The resultant yellow solution was taken to near dryness and ethyl alcohol (100ml) added to give a pale yellow precipitate. Yield 0.25g (50%).

Found: 14.4%Rh, 8.4%P, 4.2%S, 0.0%Cl.

Rh$(PPh_3)_2$(CO)NCS requires: 14.5%Rh, 8.7%P, 4.5%S.

(b) A suspension of trans $Rh(PPh_3)_2(CO)Cl$ (0.5g) in allyl isothiocyanate was gently heated for 30 minutes. Addition of diethyl ether gave a yellow product. Yield 0.2g (35%).

Found: 10.5%Rh, 1.7%Cl, 6.6%P, 9.9%S.

$Rh(PPh_3)_2(C_3H_5NCS)(\sigma\text{-}C_3H_5)(NCS)_2.\frac{1}{2}C_3H_5Cl$ requires: 11.2%Rh, 1.9%Cl, 6.8%P, 10.4%S.

S-thiocyanato-bis(triphenylphosphine)(allylisothiocyanate)rhodium(III)

To a solution of allyl isothiocyanate (0.21g, 21.6mmole) in acetonitrile (40 ml) was added $Rh(PPh_3)_3Cl$ (0.5g 5.4mmole) and the reaction mixture stirred for two hours. The resultant pink precipitate was filtered, washed with hexane and dried under vacuum. Yield 0.3g (70%).

Found: 12.8%Rh, 2.6%Cl, 7.6%P, 8.0%S, 62.0%C, 4.6%H, 3.4%N

$Rh(PPh_3)_2(C_3H_5NCS)SCN.\frac{1}{2}C_3H_5Cl$ requires: 12.6%Rh, 2.29%Cl, 7.6%P, 7.8%S, 61.9%C, 4.5%H, 3.4%N.

% weight loss from T.G.A. = 4.4%. Calculated weight loss for $\frac{1}{2}C_3H_5Cl$ = 4.6%.

Found: 62.6%C, 4.9%H, 3.7%N, 0.0%Cl.

$Rh(PPh_3)_2(C_3H_5NCS)SCN$ requires: 62.7%C, 4.5%H, 3.6%N.

Thiocyanatobis(triphenylphosphine)(allylisothiocyanate)rhodium(I)

To a solution of allyl isothiocyanate (5g, 500mmole) in acetonitrile (40ml) was added $Rh(PPh_3)_3Cl$ (0.5g 5.4mmole) and the reaction mixture stirred for two hours. The resultant yellow precipitate was filtered, washed with hexane, and dried under vacuum. Yield 0.25g (58%).

Found: 62.0%C, 4.6%H, 3.4%N,

$Rh(PPh_3)_2(C_3H_5NCS)NCS.\frac{1}{2}C_3H_5Cl$ requires: 61.9%C, 4.5%H, 3.4%N.

% weight loss from T.G.A. = 4.2%. Calculated weight loss for $\frac{1}{2}C_3H_5Cl$ = 4.6%.

Found: 62.2%C, 4.9%H, 4.3%N, 0.0%Cl

$Rh(PPh_3)_2(C_3H_5NCS)NCS$ requires 62.7%C, 4.5%H, 3.6%N.

The complex was similarly prepared using $Rh(PPh_3)_3NCS$

Found: 62.0%C, 4.3%H, 4.2%N

$Rh(PPh_3)_2(C_3H_5NCS)NCS.\frac{1}{2}C_3H_5NCS$ requires 61.2%C, 4.4%H, 4.3%N.

% weight loss from T.G.A. = 5.6%. Calculated weight loss for $\frac{1}{2}C_3H_5NCS$ = 5.9%.

Found: 62.4%C, 4.8%H, 4.1%n.

$Rh(PPh_3)_2(C_3H_5NCS)NCS$ requires 62.7%, 4.5%H, 3.6%N.

Attempted Preparations:

Reaction of C_3H_5SCN with $Rh(PPh_3)_3Cl$

Heating mixtures of C_3H_5SCN with $Rh(PPh_3)_3Cl$ gave a complex whose infrared spectrum showed bands due to phosphineoxide and indicated a mixture of products which have not been identified. Similarly, stirring a mixture of C_3H_5SCN and $Rh(PPh_3)_3Cl$ in acetonitrile gave a mixture of products.

Reaction of $Rh(PPh_3)_2(C_3H_5NCS)NCS$ (yellow)

Heating a mixture of $Rh(PPh_3)_2(C_3H_5NCS)NCS$ and C_3H_5NCS in acetonitrile gave a product whose infrared spectrum showed that it was a mixture of products which could not be identified.

Analyses

The complexes were analysed by the methods previously described.

Physical measurements

Infrared, n.m.r., and U.V. measurements were made as described in previous chapters.

CHAPTER 10

THE PREPARATION OF THE LINKAGE ISOMERS N- AND O-CYANATO-TRIS(TRIPHENYLPHOSPHINE)RHODIUM(I) FROM THE REACTION OF ETHYL CYANATE WITH TRIS(TRIPHENYLPHOSPHINE)CHLORORHODIUM(I)

THE PREPARATION OF THE LINKAGE ISOMERS N- AND O-CYANATO-TRIS(TRIPHENYLPHOSPHINE)RHODIUM(I) FROM THE REACTION OF ETHYL CYANATE WITH TRIS(TRIPHENYLPHOSPHINE)CHLORORHODIUM(I)

In this chapter is described the reaction of ethyl cyanate with $Rh(PPh_3)_3Cl$. The oxidative addition of organic cyanates have not been studied previously. Therefore it was of considerable interest to investigate the reaction of organic cyanates with $Rh(PPh_3)_3Cl$ in the hope of preparing a series of O-cyanate-complexes.

Resulsts and Discussion

Treatment of $Rh(PPh_3)_3Cl$ with ethyl cyanate in MeCN yields a yellow product whereas in MeCN/EtOH an orange solid is isolated. Both products gave identical analyses which together with their infrared spectra identified them as the linkage isomers $Rh(PPh_3)_3NCO$ and $Rh(PPh_3)_3OCN$ respectively, (see Chapter 5). This parallels the behaviour, for example of the interaction of C_3H_5NCS or C_3H_5SCN with trans-$Rh(PPh_3)_2(CO)Cl$ to give trans-$Rh(PPh_3)_2(CO)NCS$ where it was suggested that oxidative addition occurs, followed by the reductive elimination of allyl chloride. It is interesting to note that the isomers were isolated from these reactions using the same solvent conditions which prevailed during the reaction of $Rh(PPh_3)_3Cl$ with Ph_4AsOCN.

Experimental

Ethyl cyanate was prepared according to the method of Jensen, Due and Holm(136). Tris(triphenylphosphine)chlororhodium(I) was prepared as previously described. The reactions were performed under nitrogen.

N-Cyanatotris(triphenylphosphine)rhodium(I)

Tris(triphenylphosphine)chlororhodium(I) (0.5g) was added to acetonitrile (50 ml.) containing ethyl cyanate (1 ml) and the reaction mixture stirred for one hour. The complex precipitated as a bright yellow solid which was filtered and dried thoroughly under nitrogen. Yield 0.35g (70%).

Ph$(PPh_3)_3$NCO requires 11.0%Rh, 10.0%P.

Found: 10.9%Rh, 10.1%P.

Infrared spectrum: 2230(ν(CN)): 1330(ν(CO)); 592mw(δ(NCO)).

O-Cyanatotris(triphenylphosphine)rhodium(I)

Tris(triphenylphosphine)chlororhodium(I) (0.5g) was added to acetonitrile (10 ml.) - ethanol (50 ml.) containing ethyl cyanate (1 ml) and the reaction mixture stirred for two hours. The complex precipitated as a bright orange solid, which was filtered and dried thoroughly under vacuum. Yield 0.3g (60%).

Rh$(PPh_3)_3$OCN requires: 11.0%Rh, 10.0%P.

Found: 11.0%Rh, 9.9%P.

Infrared spectrum: 2215s(ν(CN)); 1318w(ν(CO)); 607w,590mw(δ(NCO)).

Physical measurements

Infrared spectra were recorded as previously described. The products were analysed for rhodium and phosphorus by X-ray fluorescence spectroscopy.

CHAPTER 11

THE CRYSTAL AND MOLECULAR STRUCTURES OF DI-ISOCYANATO-BIS(π-CYCLOPENTADIENYL)TITANIUM

THE CRYSTAL AND MOLECULAR STRUCTURES OF DI-ISOCYANATO-BIS(π-CYCLOPENTADIENYL)TITANIUM

The metallocenes $(\pi\text{-cp})_2M(OCN)_2$ where [M=Ti,Zr, and Hf] are some of the few compounds where the cyanate group is considered to be O-bonded (44). Burmeister et al. assigned O-cyanate co-ordination in the zirconium and hafnium analogue on the basis of their CO stretching frequencies. In O-cyanato complexes there is ample opportunity for the phenomenon of Fermi resonance to occur between ν(CO) and 2δ(NCO), and in $(\pi\text{-cp})_2M(OCN)_2$,[M=Zr,Hf]: the bands at 1254 and 1070cm^{-1} were assigned on this basis following the arguments initially applied by Bailey and Kozack in assigning O-bonding in hexa-O-cyanates of Mo(III), Re(IV) and Re(V)(37). In the case of $(\pi\text{-cp})_2Ti(CNO)_2$*, it was argued that the band at 1132cm^{-1} is one component of such a pair of bands, and this was supported by mass spectral data which indicated that all three compounds had very similar fragmentation patterns. Recently, however, Burmeister et al. have re-examined the titanium and zirconium compounds and concluded from dipole-moment measurements that they should be formulated as $(\pi\text{-cp})_2Ti(NCO)_2$ and $(\pi\text{-cp})_2Zr(OCN)_2$(67). This conflicts with ^{14}N n.m.r. measurements on the former which show a downfield shift relative to the free cyanate ion; such a shift has been taken as being indicative of O-bonding(66).

Therefore, an X-ray crystallographic investigation of $(\pi\text{-cp})_2Ti(CNO)_2$

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*'CNO' is used to indicate that the mode of co-ordination of the cyanate is unspecified.

has been carried out in order to resolve the mode of co-ordination in this complex.

Experimental

Crystallographic Measurements

Preparation of Crystals

$(\pi\text{-cp})_2Ti(CNO)_2$ was prepared as described by Burmeister et al.(44). Suitable single crystals were obtained by slow cooling of a chloroform solution.

Density Determination

The density of the complex was determined by the method of flotation in an aqueous solution of potassium iodide. The concentration of potassium iodide was adjusted until crystals neither floated nor sank in the liquid; the density of the liquid was then measured using a Westphal balance and found to be $1.57g/cm^3$.

X-ray Photography

Oscillation and Weissenberg photographs were obtained using Ilford Industrial 'G' film and Cu-Kα radiation. From the symmetry on X-ray photographs, it was seen that the crystals belong to the orthorhombic system. The unit cell dimensions were determined initially from equi-inclination Weissenberg photographs (okl, Ikl, hko) and were subsequently determined accurately on a Hilger-Watts four circle automatic diffractometer, equipped with a scintillation counter using Mo-Kα radiation with a graphite monochromater, by taking the best least squares fit from twelve chosen reflections. The following values were obtained:-

$$a = 9.689 \pm 0.003\ \text{Å}$$
$$b = 13.265 \pm 0.004\ \text{Å}$$
$$c = 17.500 \pm 0.006\ \text{Å}$$

The number of molecules of complex in the unit cell was calculated using the formula

$$Z = \frac{NoDV}{M}$$

where Z is the number of molecules, No Avogadro's number, D the density, V the unit cell volume and M the molecular weight. Substituting the appropriate values gave Z = 8.

Space Group

The Weissenberg photographs showed the following systematic absences:

okl when $k = 2n + 1$

hol when $l = 2n + 1$

hko when $h = 2n + 1$

hoo when $(h = 2n + 1)$

oko when $(k = 2n + 1)$

ool when $(l = 2n + 1)$.

This is unambiguously consistent with a space group of Pbca, (D_{2h}^{15}), No. 61. From international tables it was seen that the eight molecules of the complex must lie in the general positions x, y, z; $\bar{x}$, $\bar{y}$, $\bar{z}$; $\frac{1}{2}$ + x, $\frac{1}{2}$ - y, $\bar{z}$; $\frac{1}{2}$ - x, $\frac{1}{2}$ + y, z; $\bar{x}$, $\frac{1}{2}$ + y, $\frac{1}{2}$ - z; x, $\frac{1}{2}$ - y, $\frac{1}{2}$ + z; $\frac{1}{2}$ - x, $\bar{y}$, $\frac{1}{2}$ + z; $\frac{1}{2}$ + x, y, $\frac{1}{2}$ - z.

The crystal data are summarised below:

$C_{12}H_{10}N_2O_2Ti$, M = 262.3, Orthorhombic,

a = 9.6890 ± 0.0014, b = 13.2645 ± 0.0020, c = 17.5001 ± 0.0031

Å, U = 2249.18 $Å^3$, DM = 1.57g cm^{-3} Z = 8 Dc = 1.55

F(000) = 1024, Space group Pbca Mo-Kα radiation

λ = 0.7107 Å, μ (Mo-Kα) = 7.6cm^{-1}.

Data Collection

The intensity data for 2338 observed reflections up to θ(Mo-Kα)$\leq 30^{\circ}$ were collected on the Hilger-Watts four circle diffractometer. Using a 2θ scan technique, each reflection was measured in 20 steps of 0.03° counting for 1 second. Stationary background counts were taken for 5 seconds at each end of the scale range. The intensities of three standard reflections were periodically monitored and the results used to ensure that all the reflections were on a common scale. The changes in the standard intensities during the data collection were small (1-3%). The intensities of the 2338 reflections were corrected for Lorentzpolarization effects, but not for absorption nor extinction. A set of $[Fo]$ values on a relative scale was thus obtained.

Solution and Refinement of the Structure

The position of a titanium atom was found from a three-dimensional Patterson map. A three-dimensional electron density synthesis, phased by the titanium (R = 0.395), $\left[R = \sum(|Fo| - |Fc|)/\sum |Fo|\right]$ revealed the positions of the carbon atoms of the cyclopentadienyl rings and the two atoms of the cyanate groups which are co-ordinated to the titanium. These atoms were initially considered to be oxygens i.e. it was assumed that the cyanate groups were O-bonded to titanium.

The structure was refined by conventional full matrix least-square and block-diagonal methods. The function minimized was $\Sigma w(|Fo| - |Fc|)^2$ where $|Fo|$ is the observed and $|Fc|$ is the calculated struture amplitude. Scattering factors for titanium were those from international tables(159) and those for carbon, nitrogen and oxygen from Cramer and Mann(160).

Three cycles of isotropic least-squares refinement using unit weights of the positional and isotropic thermal parameters of the titanium, carbon and oxygen atoms reduced R, to 0.265. A second electron density map revealed the positions of the remaining four atoms of the cyanate groups i.e. one nitrogen and carbon per cyanate. Three further rounds of least-square calculations lowered R to 0.116. At this stage a Hughes' weighting scheme was employed of the form $(A/|Fo|)^2$, where

A = 25.0,and the titanium atom was assigned an anisotropic temperature factor. Three cycles of least-square refinement caused R to converge to 0.108 .

An examination of isotropic thermal parameters for the oxygen and nitrogen showed that these atoms might have been positioned incorrectly (Table 11.1.). Their thermal parameters were found to be very similar, which seemed surprising since it would have been predicted that the atom co-ordinated to titanium would have less thermal motion than the terminal atom of the cyanate group. Reversing the positions of the nitrogen and oxygen atoms, i.e. Ti-NCO, reduced R to 0.101 and isotropic thermal parameter for the atoms of each cyanate were now found to be of the right order to account for thermal vibration (see Table 11.1.).

All the nitrogen, oxygen and carbon atoms were allowed to adopt anisotropic temperature factors, and after three rounds of block diagonal least-square refinement R was reduced to 0.054. A final two rounds of full matrix least-square calculations gave a value for R of 0.053 . A difference map showed no irregularities, except in revealing the position of the hydrogen atoms which have not been placed.

An identical refinement of the structure considering the cyanate group to be O-bonded to titanium only gave a final value for R of 0.065 further confirming that the cyanate groups are N-bonded. The achievement of a reasonably good refinement for the O-bonded case has probably resulted because of the small differences in electron density between

Isotropic Thermal Parameters(a) for the Cyanate Groups when considered to be either O- or N-bonded to Titanium

O-bonded (R = 0.108)		N-Bonded (R = 0.101)	
Atom	B($\AA^2$)	Atom	B($\AA^2$)
N_1	4.94	N_1	3.86
N_2	4.81	N_2	3.73
C_{11}	3.53	C_{11}	3.59
C_{12}	3.56	C_{12}	3.60
O_1	5.03	O_1	6.31
O_2	5.24	O_2	6.27

Bond lengths Å Calculated for the cyanate Groups when considered to be O- or N-bonded to Titanium

O-bonded (R = 0.065)		N-bonded (R = 0.053)	
Atoms		Atoms	
Ti - O_1	2.016(4)	Ti - N_1	2.018(3)
Ti - O_2	2.004(4)	Ti - N_2	2.007(3)
O_1 - C_{11}	1.164(6)	N_1 - C_{11}	1.151(5)
O_2 - C_{12}	1.172(6)	N_2 - C_{11}	1.157(5)
C_{11}- N_1	1.183(6)	C_{11}- O_1	1.192(5)
C_{12}- N_2	1.171(6)	C_{12}- O_2	1.184(5)

(a) Numbers in parentheses are the estimated standard deviations occurring in the last digits.

Table 11.1.

the oxygen and nitrogen atoms. Table 11.1. lists bond lengths for the cyanate group for the refined O-bonded situation and these compare favourably with bond lengths determined for the N-bonded case. Therefore the cyanate groups could mistakenly be taken to be O-co-ordinated to titanium if a structure analysis had not been performed considering both N- and O-bonded cases.

The intensity data were collected by Professor T.J. King at the University of Nottingham. The X-ray 72 system set of programmes, compiled by J.M. Stewart, G.J. Kruger, H.L. Ammon, C. Dickinson and S.R. Hall, Computer Science Centre, University of Maryland, and adapted for the ICL 1906A and CDC 7600 computers at Manchester University were used in the structure analysis and interpretation.

Results and Discussion

The final atomic co-ordinates are listed in Table 11.2. and the anisotropic thermal parameter are in Table 11.3. Table 11.4. contains the observed and final structure amplitudes (see Appendix). The molecular structure and atom numbering is shown in Figure 11.5. and Figure 11.6. shows the molecular configuration of the cyanate groups viewed in projection on one of the planes of the cyclopentadienyl rings. Interatomic distances and valency angles are given in Table 11.7. and 11.8. while Table 11.9. gives the equation for the planes through the cyclopentadienyl rings.

Atomic Co-ordinates(a) (as fractions of the cell edges)

Atom	x	y	z
Ti	0.15417(5)	0.37338(3)	0.61097(2)
C_1	-0.02455(38)	0.33807(31)	0.52163(21)
C_2	0.08683(42)	0.27388(31)	0.50412(21)
C_3	0.10937(48)	0.20863(28)	0.56517(25)
C_4	0.00689(45)	0.23092(29)	0.62241(23)
C_5	-0.07433(36)	0.30960(32)	0.59516(23)
C_6	0.24501(46)	0.42743(37)	0.73233(20)
C_7	0.35000(41)	0.43678(32)	0.67934(21)
C_8	0.38185(41)	0.34017(42)	0.65201(25)
C_9	0.29415(57)	0.27191(32)	0.68978(32)
C_{10}	0.20739(47)	0.32677(39)	0.73744(23)
N_1	0.03869(33)	0.49486(21)	0.63796(17)
N_2	0.25276(32)	0.44140(25)	0.52428(16)
C_{11}	-0.03007(41)	0.55843(25)	0.66158(20)
C_{12}	0.30807(38)	0.47519(28)	0.47160(20)
O_1	-0.10016(43)	0.62577(22)	0.68462(23)
O_2	0.36345(38)	0.51131(30)	0.41788(20)

(a) Numbers in parentheses are the estimated standard deviations occurring in the last digits listed.

Table 11.2.

Anisotropic Thermal Parameters$^{(a)}$ (Uij x10^{2})*

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti	3.32(3)	3.19(3)	2.84(2)	-0.01(2)	0.22(2)	-0.09(2)
C_1	4.78(19)	6.59(21)	4.72(18)	-1.03(17)	-1.03(17)	-0.75(17)
C_2	5.85(21)	6.14(23)	4.60(18)	-0.97(18)	0.10(16)	-1.94(17)
C_3	7.03(25)	4.05(18)	7.10(25)	-0.54(17)	-0.62(21)	-1.42(18)
C_4	6.99(24)	4.97(20)	5.87(22)	-2.34(18)	-0.12(19)	-0.02(16)
C_5	3.75(16)	6.78(23)	5.96(21)	-1.22(16)	0.42(15)	-1.01(18)
C_6	6.44(25)	8.77(30)	3.89(18)	0.94(22)	-1.5(17)	-0.70(19)
C_7	5.51(21)	6.80(24)	4.93(19)	-1.86(19)	-1.69(17)	0.84(17)
C_8	4.06(18)	10.79(36)	5.60(23)	1.88(22)	-1.05(16)	-0.91(23)
C_9	8.38(32)	5.20(22)	10.23(37)	0.28(23)	-5.34(30)	1.35(24)
C_{10}	5.93(24)	9.49(32)	5.10(22)	-1.24(25)	-1.45(19)	3.16(22)
N_1	6.03(18)	4.37(14)	4.99(15)	1.25(14)	0.10(14)	-0.61(13)
N_2	5.39(17)	6.11(18)	4.01(13)	-0.65(14)	0.66(13)	0.98(14)
C_{11}	6.17(21)	3.94(15)	4.85(17)	-0.11(15)	0.96(16)	-0.34(14)
C_{12}	4.85(18)	5.47(19)	4.42(17)	-0.31(15)	0.65(14)	0.19(14)
O_1	10.34(26)	4.99(16)	11.08(29)	1.49(16)	4.19(23)	-1.57(17)
O_2	9.19(25)	10.41(27)	6.48(18)	-1.71(20)	2.82(17)	2.71(18)

(a) Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

*The temperature factors are expressed as:

$$\exp\left[-2\pi^{2}(U_{11}h^{2}a^{*2}+U_{22}k^{2}b^{*2}+U_{33}l^{2}c^{*2}+2U_{12}hka^{*}b^{*}+2U_{13}hla^{*}c^{*}+2U_{23}klb^{*}c^{*})\right]$$

where a^{*}, b^{*} and c^{*} are the recipricol lattice parameters.

Table 11.3.

The Arrangement of Atoms in the $(\pi\text{-Cp})_2\text{Ti(NCO)}_2$ Molecule

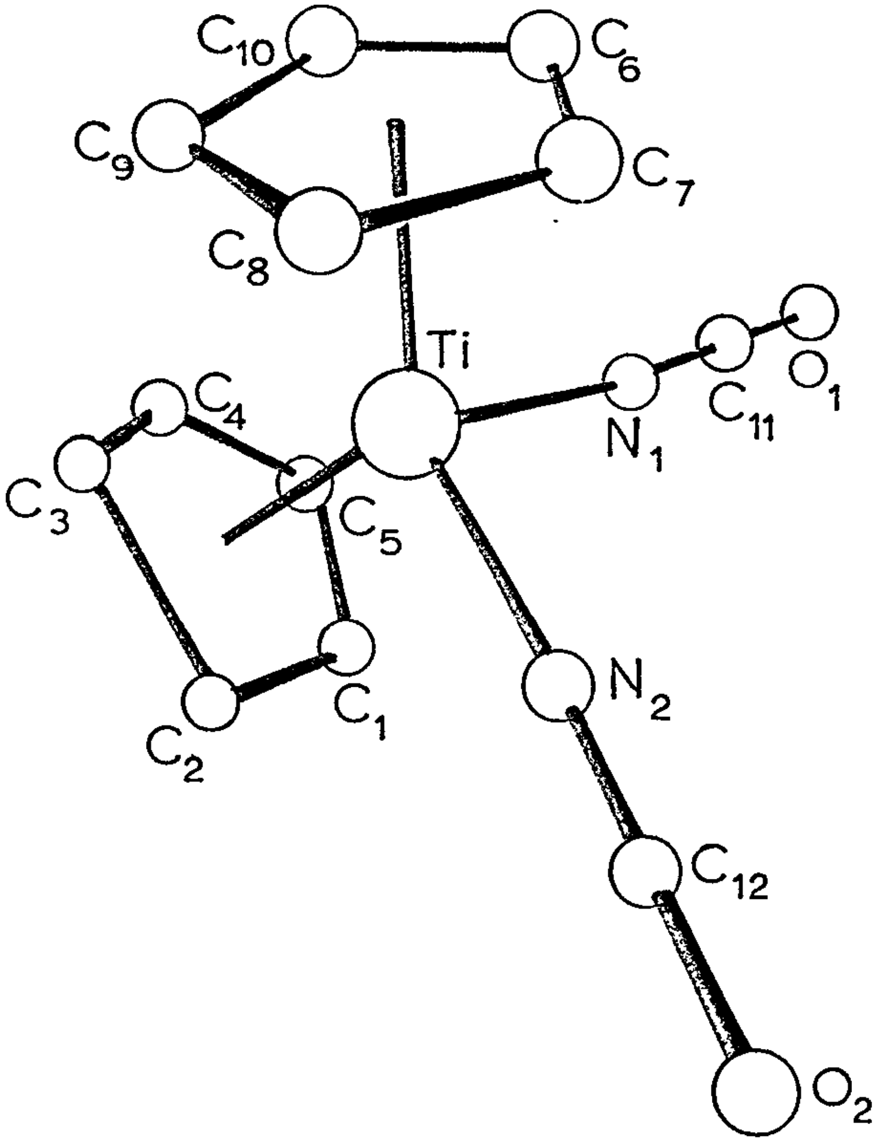

Fig 11.5

The Molecular Configuration of the Cyanate Groups viewed in Projection on one of the Cyclopentadienyl Rings

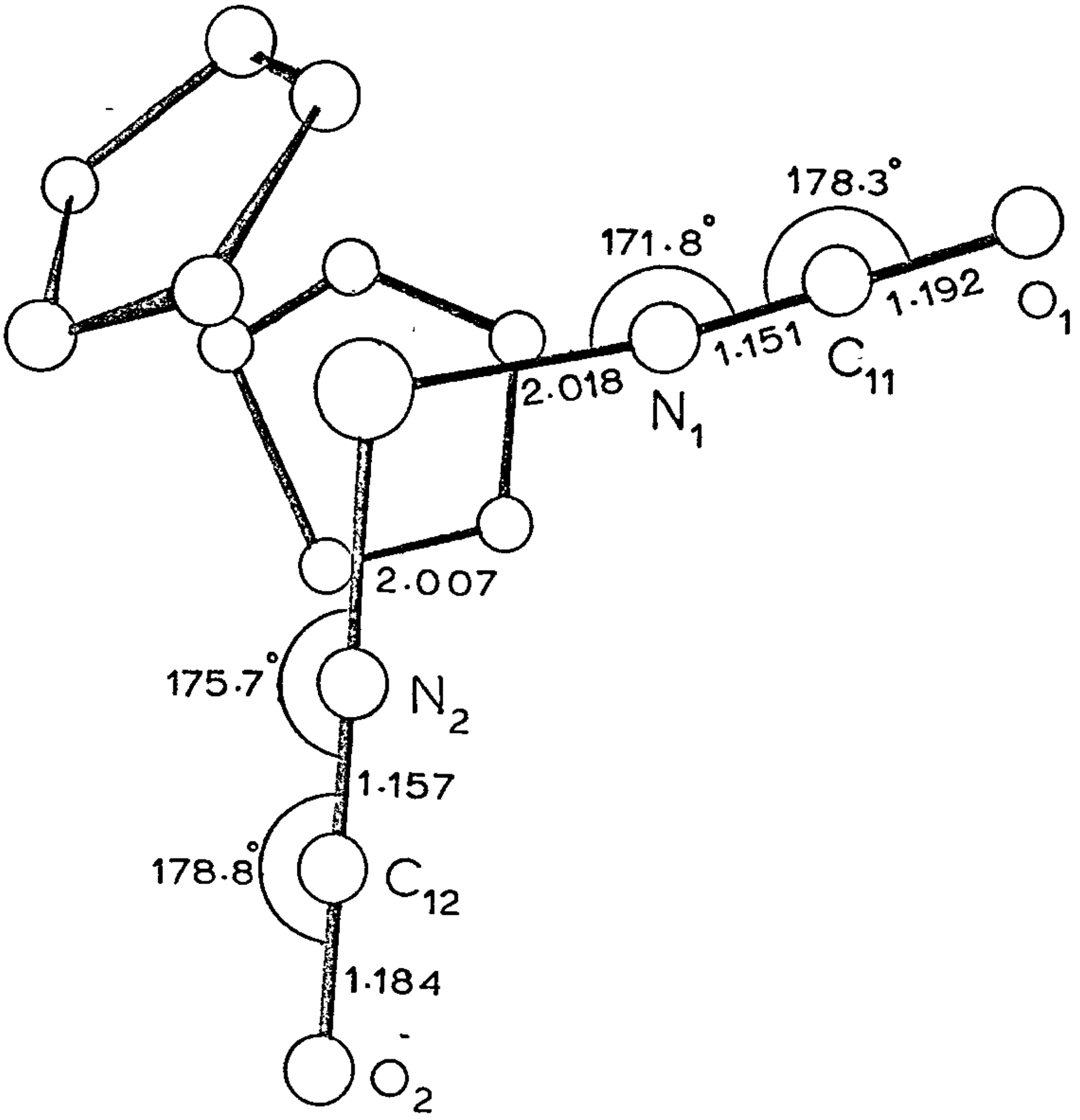

Fig 11.6

Interatomic Distances$^{(a)}$ (Å)

Atoms		Atoms	
Bond Distances			
Ti-C_1	2.380(4)	Ti-N_1	2.018(3)
Ti-C_2	2.380(4)	Ti-N_2	2.007(3)
Ti-C_3	2.368(4)	N_1-C_{11}	1.151(5)
Ti-C_4	2.377(4)	N_2-C_{12}	1.157(5)
Ti-C_5	2.386(4)	C_{11}-O_1	1.192(5)
Ti-c.o.g.$^{(b)}$ (ring A)	2.053	C_{12}-O_2	1.184(5)
Ti-C_6	2.408(4)		
Ti-C_7	2.396(4)	Some Intramolecular non-bonded distances	
Ti-C_8	2.361(4)		
Ti-C_9	2.357(5)	N_1-N_2	2.960(4)
Ti-C_{10}	2.355(4)	N_2-C_2	2.765(5)
Ti-c.o.g.″ (ring B)	2.058	N_2-C_7	2.873(5)
C_1-C_2	1.409(6)	N_2-C_8	2.892(6)
C_2-C_3	1.392(6)	N_1-C_6	2.743(5)
C_3-C_4	1.441(6)	N_1-C_1	2.974(5)
C_4-C_5	1.391(6)	N_1-C_5	2.793(5)
C_1-C_5	1.425(5)	C_3-C_9	2.944(7)
C_6-C_7	1.382(6)		
C_7-C_8	1.402(7)		
C_8-C_9	1.407(7)		
C_9-C_{10}	1.389(7)		
C_6-C_{10}	1.387(7)		

(a) Numbers in parentheses are estimated standard deviations occurring in the last digit listed.

(b) c.o.g. denotes the centre of gravity of the π-C_5H_5 group.

Table 11.7.

Valency Angles$^{(a)}$ (degrees)

Atoms		Atoms	
C_3-Ti-C_9	77.1(2)	N_1-Ti-N_2	94.7(2)
cog′-Ti-cog″	132.8	Ti-N_1-C_{11}	171.8(3)
N_1-Ti-C_5	78.2(1)	Ti-N_2-C_{12}	175.7(3)
N_1-Ti-C_6	76.0(1)	N_1-C_{11}-O_1	178.3(4)
N_2-Ti-C_1	84.7(1)	N_2-C_{12}-O_2	178.8(4)
N_2-Ti-C_2	77.6(1)		
N_2-Ti-C_7	80.9(1)		
N_2-Ti-C_8	82.5(1)		
C_1-C_2-C_3	109.2(3)		
C_2-C_3-C_4	107.3(4)		
C_3-C_4-C_5	107.8(3)		
C_4-C_5-C_1	108.5(3)		
C_5-C_1-C_2	107.2(3)		
C_6-C_7-C_8	107.9(4)		
C_7-C_8-C_9	107.2(4)		
C_8-C_9-C_{10}	108.0(4)		
C_9-C_{10}-C_6	107.9(4)		
C_{10}-C_6-C_7	108.9(4)		

(a) Numbers in parentheses are estimated standard deviations occurring in the last digit listed.

Table 11.8.

Best Weighted Least-Squares Planes$^{(a)}$

Atoms	Plane	P	Q	R	S	$\sigma^{(b)}$
C_1-C_5	A	6.0522	8.7428	7.3295	6.6233	0.006
C_6-C_{10}	B	6.4732	-1.4784	12.8744	10.3694	0.013

(a) The equation of the planes can be expressed as PX+QY+RZ=S in direct space where X, Y, Z are fractional co-ordinates of the atoms in the plane.

(b) σ denotes the standard deviation of the atoms from the plane.

Distances of Atoms from Planes

Atoms	Plane A	Atoms	Plane B
C_1	0.007	C_6	0.013
C_2	-0.008	C_7	-0.004
C_3	0.005	C_8	-0.006
C_4	0.009	C_9	0.013
C_5	0.004	C_{10}	-0.016

The angle between planes A and B = 49.3°

Table 11.9.

The most important result of this investigation is the unequivical demonstration that in the crystalline state the cyanate groups are N-bonded to titanium. The titanium-isocyanate linkages are approximately linear, with Ti-N-C angles of 171.8° and 175.7° and NCO angles of 178.3° and 178.8°. Small deviations in linearity of the M-N-C bond have also been observed in $Me_4NAg(NCO)_2$ where angles of ~170° were found(161). The linearity of the Ti-N-C linkages are consistent with nitrogen atoms being formally regarded as sp hybridised. On the other hand, in HNCO(162) and MeNCO(163), where the nitrogen atoms are considered to be sp^2 hybridised, the molecules are appreciably bent with angles of ca.128° and 140°. If the cyanate group were O-bonded in the titanium complex it might have been expected that the Ti-O-C linkages would be considerably bent because of sp^2 hybridized oxygens, but in the absence of an X-ray determination of any terminal O-bonded cyanate complex this remains a speculation. Furthermore, it is noticeable that the C-N distances are shorter than the C-O distances (Table 11.6.), as might be expected for the linkage Ti-N=C=O, and is consistent with other iso-cyanato species such as $(\pi\text{-}C_5H_5)Cr(NO)_2NCO$ C-N=1.126Å C-O=1.179 Å(164).

The co-ordination about the titanium is that of a distorted tetrahedron: the N_1-Ti-N_2 angle of 94.7° and the (π-C_5H_5 centroid)-Ti-(π-C_5H_5 centroid) angle of 132.8° indicate the extent of this deformation. These angles are not unlike the comparable ones found in similar molecules. For example, it is reported that in $(\pi\text{-}C_5H_5)_2TiS_5$(165) the S-Ti-S angle is 94.6° and the centroid Ti- angle is 133.6°, while in

$(h^5\text{-}C_5H_5)_2Ti(h^1\text{-}C_5H_5)_2$(166) the corresponding angles are 129.9° and 86.3°.

The variations in C-C distances (1.441-1.382Å) and C-C-C angles (109.2-107.2) in cyclopentadienyl rings are similar to those reported in similar systems such as $(h^5\text{-}C_5H_5)_2Ti(h^1\text{-}C_5H_5)_2$(166). The cyclopentadienyl rings are planer, (esd from planes are 0.006 and 0.013Å for ring A and ring B respectively). The symmetrical metal to ring bonding is most clearly evident in the titanium to carbon bond lengths which fall in the narrow range from 2.386-2.368Å in ring A and 2.408-2.355Å in ring B. The titanium atom lies 2.053 and 2.058Å from the mean planes of the cyclopentadienyl rings A and B respectively. These and the Ti-C distances are very similar to those found in other titanium compounds containing π-cyclopentadienyl groups such as $(\pi\text{-}C_5H_5)TiS_5$(165), $[(\pi\text{-}C_5H_5)_2TiAl(C_3H_5)_2]_2$(167), $(\pi\text{-}C_5H_5)_2TiCl_2$(168, 169) and $(h^5C_5H_5)_2Ti(h^1C_5H_5)_2$(166).

The arrangement of molecules in the crystal is shown in Fig. 11.10. (The rings refer to the positions of the central titanium atoms along a in cell fractions). Some intermolecular contacts are listed in Table 11.11. None of these distances are abnormal.

Conclusions

This structure determination has clearly shown that the cyanate group are N-bonded in the complex $(\pi\text{-cp})_2Ti(NCO)_2$ in the solid state.

The Crystal Structure viewed in projection along the a axis

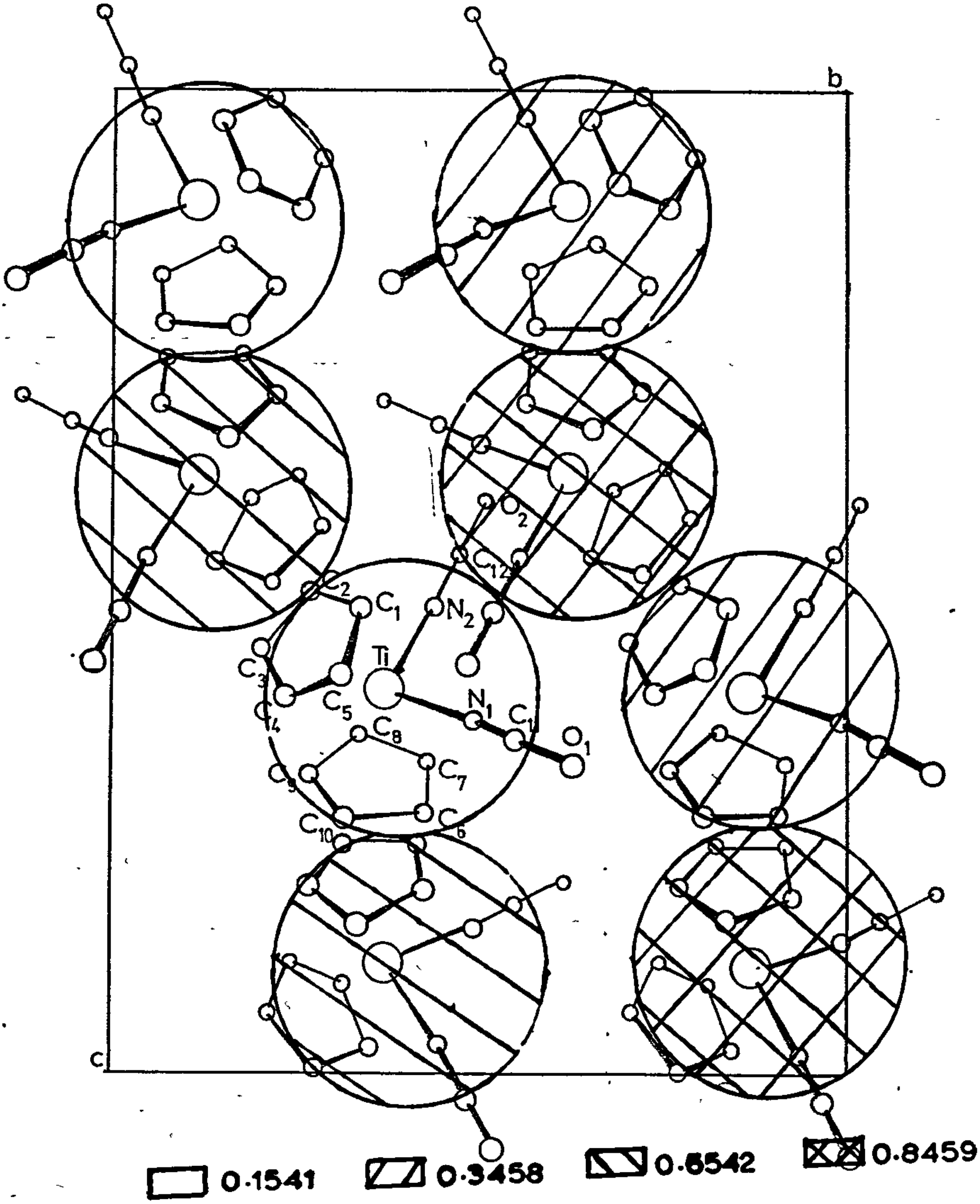

Fig 11.10

Some Intermolecular Distances ($\leqslant 3.6$Å)

Atom 1	Atom 2		
O_1	C_{10}	V	3.17
O_2	C_7	I	3.33
C_6	C_{11}	VI	3.35
C_6	O_1	VI	3.36
C_2	C_8	I	3.39
C_7	C_{11}	VI	3.42
O_1	C_9	V	3.48
C_{11}	C_1	II	3.53
O_1	C_9	IV	3.54
C_2	O_1	II	3.56
N_1	C_1	II	3.57
O_2	C_4	III	3.57
O_1	C_8	IV	3.59
C_{12}	C_{11}	II	3.59
C_{12}	C_3	IV	3.59
O_1	O_2	II	3.61

The Roman numerals refer to the following transformations of the atomic co-ordinates in Atom 2.

I $1-x, 1-y, 1-z$; II $-x, 1-y, 1-z$; III $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$;

IV $\frac{1}{2}-x, \frac{1}{2}+y, z$; V $-x, \frac{1}{2}+y, 1\frac{1}{2}-z$; VI $\frac{1}{2}+x, y, 1\frac{1}{2}-z$.

Table 11.11.

The infrared mull spectrum of the complex does not exhibit a CO stretching frequency in the region 1350-1320cm^{-1}. A band in this region has been used as being diagnostic for N-co-ordination and further demonstrates that assignments of cyanate co-ordination based on this frequency should be treated with caution. Preliminary studies of integrated absorption intensities of the CN stretching frequencies in the solid state (A = 13 and 16x10^{4}M^{-1}cm^{-2}) and in solution compare with those reported by Burmeister(44) and are larger than the value for the free ion, indicating that $(\pi\text{-cp})_2Ti(NCO)_2$ is also N-bonded in solution. The europium shift studies described previously also indicate N-bonding in solution while the zircocene adduct may very well be O-bonded. However, integrated intensities of the CN stretching frequencies reported for the zirocene adduct are also larger than the free ion.(44) Therefore, an X-ray crystal determination of $(\pi\text{-cp})_2Zr(CNO)_2$ and the hafnium analogue is further needed in order to provide confirmation of the mode of co-ordination of the cyanate group in these complexes, and to clarify the suitability of infrared, ^{14}N n.m.r., and europium shift studies in assigning cyanate co-ordination.

CHAPTER 12

A CONVENIENT METHOD FOR THE ANALYSIS OF ORGANOMETALLIC AND RELATED COMPOUNDS

A CONVENIENT METHOD FOR THE ANALYSIS OF ORGANOMETALLIC AND RELATED COMPOUNDS

As a result of investigations into complexes of the type $Rh(PPh_3)_2(L)XCN$ ($X = S$, Se), it was found that satisfactory analysis of carbon, hydrogen and nitrogen by conventional combustion techniques could not be obtained. Therefore a convenient method of analysis by X-ray fluorescence spectrometry has been developed for such compounds, and has been used extensively in the analyses of compounds in these studies.

X-ray fluorescence spectrometry is a well-established technique for elemental analysis. Samples are usually presented as massive solids, powders or pressed discs, or in diluted forms as solutions, or as annealed melts in some suitable substrate. When only a small amount of material is available some form of dilution is desirable to produce a sample of the right dimensions for the spectrometer. Liquid solutions, although ideally homogeneous, are not suitable for light element analysis since the longer wavelengths emitted from such elements are absorbed by the liquid cell window. The use of annealed melts is precluded if loss of material occurs on heating. It has been found that small amounts of sample dispersed in KCl or borax and pressed into discs under constant pressure are in a convenient form for quantitative analysis. The use of KCl discs is restricted to 'heavy' element analysis ($Z>25$), whilst borax discs may be used for all elements above $Z = 13$.

Results and Discussion

The product and residues from the reaction of analytically pure tetramethylammonium thiocyanate with tris(triphenylphosphine)chlororhodium(I) in acetonitrile as shown in Table 12.1 have been analysed by this method. It has been possible to account for the rhodium, phosphorus and, chlorine, and sulphur used to within 5%. Thus the product of the reaction has been identified as $Rh(PPh_3)_2(MeCN)SCN$, whereas attempts to characterise the same compound from C , H and N analyses, obtained by combustion, have generally been unsatisfactory for this and other S- or Se- bonded rhodium complexes (Table 12.2). On the other hand the closely related N-bonded compounds, e.g. the known complexes $Rh(PPh_3)_2(CO)NCX$ (X = S or Se), may be characterised adequately by either method (Chapter 2).

All the compounds described in these studies have been analysed for one or more of the elements listed in Table 12.3. as a percentage by weight and are accurate to within 0.1-0.3%.

The method has also been used successfully in other studies for the determination of titanium, copper, cobalt, the analyses of clay samples, and the sensitivity of the method to chlorine has been considerably improved by using lithium borate rather than sodium borate as the matrix.

Experimental

The analyses were made using a Philips PW1540 vacuum spectrograph

Analytical Results for the Reaction of Me_4NSCN with $Rh(PPh_3)_3Cl$

Weights of starting materials

$Rh(PPh_3)_3Cl$ = 0.2311g

Me_4NSCN = 0.0396g

Weight of product = 0.1590g

Weight of residue = 0.1336g

Element	Total Weight of each element	
	in the starting material	found in product and residue
Rhodium	0.0258g	0.0270g
Phosphorus	0.0233g	0.0228g
Sulphur	0.0096g	0.0098g

Table 12.1.

Analytical Results for Rh(PPh$_3$)$_2$(MeCN)XCN {X = S or Se}

	% Found						% Calculated					
	By X-ray			Combustion								
	Rh	P	S	C	H	N	Rh	P	S	C	H	N
Rh(PPh$_3$)$_2$(MeCN)SCN	14.1	8.7	4.3	54.4	5.2	3.6	14.2	8.7	4.4	64.5	4.5	3.9
Rh(PPh$_3$)$_2$(MeCN)SeCN	13.2	8.0	10.1	47.8	3.7	3.0	13.3	8.0	10.2	57.8	3.9	3.6

Table 12.2.

Condition for the Analysis of Some Elements by X-Ray Fluorescence Spectrometry

Element	Type of Disc	% Element in Disc	Emission Line	Angle 2θ	Accuracy
Rhodium	KCl Borax	0.1 - 1.0	$K\alpha 1$	17.51	±0.1%
Phosphorus	Borax	0.5 - 1.5	$K\alpha 1$	89.50	±0.3%
Sulphur	Borax	0.25- 1.0	$K\alpha 1$	75.85	±0.3%
Chlorine	Borax	0.3 - 1.0	$K\alpha 1$	65.50	±0.3%
Selenium	KCl Borax	0.1 - 1.0	$K\alpha 1$	31.84	±0.1%
Tellurium	KCl Borax	1.0 - 4.0	$K\alpha^{2}1$	25.88	±0.1%
Iridium	KCl Borax	0.1 - 1.0	$L\alpha 1$	39.22	±0.1%

Table 12.3.

attachment with a wide range goniometer PW1050. For light element conditions a penta-erythritol analysing crystal was used together with a gas-flow (90%Ar, 10%CH_4) proportional counter. The argon/methane gas was passed through pyrogallol and concentrated sulphuric acid to remove traces of oxygen and water. For heavy element analysis a LiF(100) crystal was used with a MaI(Tl) scintillation counter. The pulses from either detector were fed via a pulse height analyser to a ratemeter/scaler unit. Heavy elements may be analysed under light element conditions, if an emission of suitable energy exists e.g. the L α line of rhodium.

A typical disc [e.g. for $Rh(PPh_3)_2(MeCN)SCN$] requires 50-100mg of sample pressed with 1.0g of borax at 30 tons for 10 minutes. The percentage weight of each element examined in the sample (e.g. Rh, P, or S) is determined against calibration standards of known composition. (Fig. 12.3 and 12.4). For example standard discs containing between 10 to 100 mg of the known complexes trans-$Rh(PPh_3)_2COCl$ and Me_4MXCN [X = S or Se] have proved very satisfactory in the analysis of rhodium phosphorus, sulphur and chlorine.

A Typical Calibration Graph for the Determination of % Rhodium

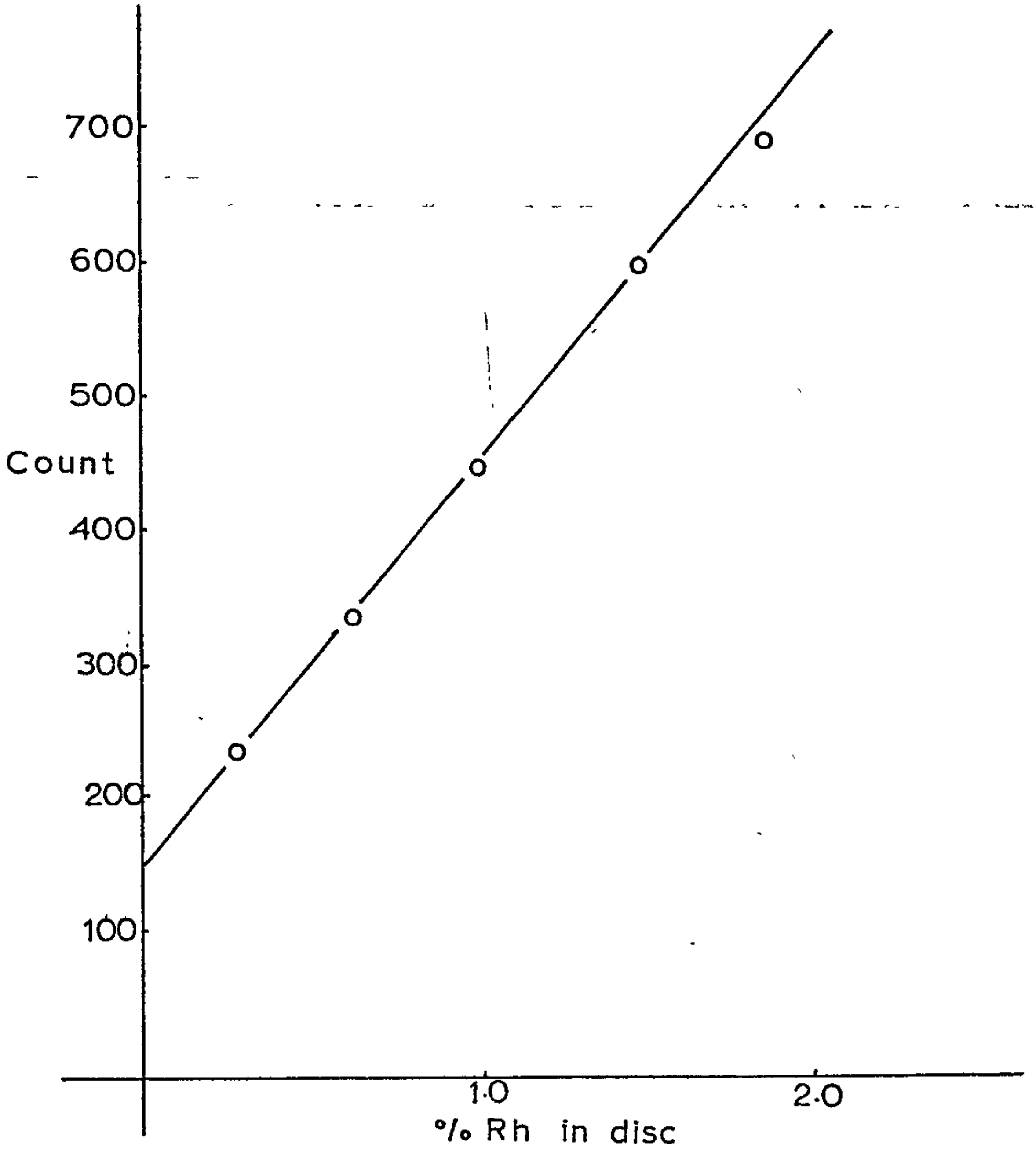

Fig 12.4

A Typical Calibration Graph for the Determination of °/o Phosphorus

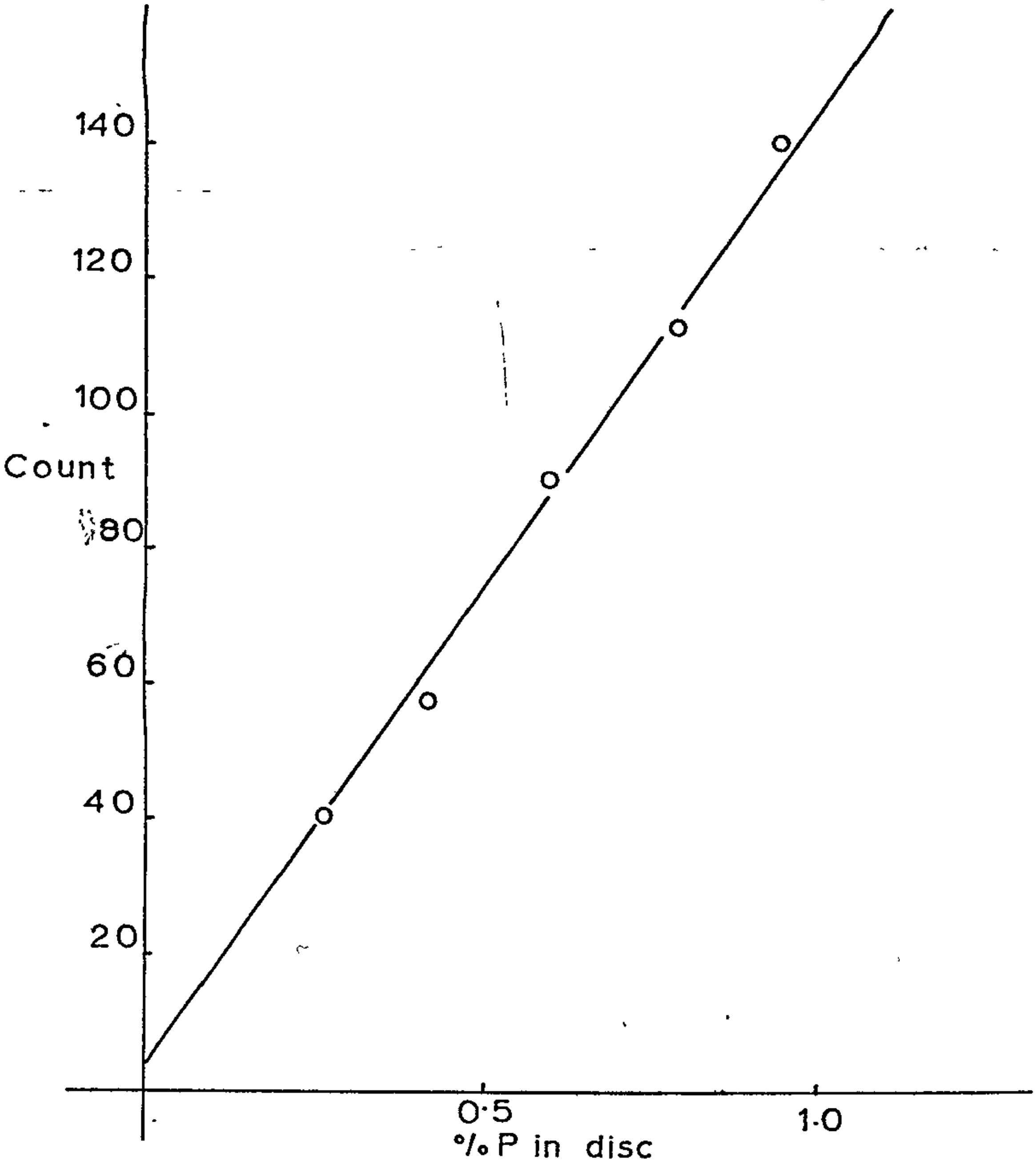

Fig 12.5

APPENDIX

Observed and Measured Structure Amplitudes

Table 11.4.

	Fo	Fc
	0,0,L	
2	527	547
4	1273	1256
6	250	203
8	1021	1002
10	656	684
14	658	644
18	241	245
20	68	80
22	252	242
24	165	171
	0,2,L	
1	1468	1682
2	39	11
3	1100	1105
4	81	115
5	179	205
6	200	195
7	1403	1370
8	142	173
9	506	463
10	367	338
11	881	848
12	34	15
13	465	478
14	68	57
15	320	305
16	216	228
17	227	224
18	182	183
19	209	213
20	131	132
21	225	226
	0,4,L	
0	183	232
1	182	216
2	583	694
3	46	50
4	654	666
5	372	346
6	373	367
7	143	77
8	531	520
9	149	111
10	516	505
11	43	19
12	223	228
13	155	163
14	667	664
15	114	104
17	139	141
18	416	402
19	102	98
20	88	97
21	100	89
22	262	260
24	131	125
	0,6,L	
0	412	348
1	193	195
2	302	328
3	1229	1230
4	431	352
5	337	325
6	400	373
7	964	998
8	157	156
9	305	304
10	134	116
11	469	470
12	37	30
13	61	48
14	51	57
15	390	374
16	129	137
17	268	271
18	152	157
19	204	205
21	255	268
23	112	127
	0,8,L	
0	721	763
1	184	172
2	122	109
3	387	370
4	1024	1045
5	37	51
6	278	262
7	170	175
8	535	508
9	100	94
10	532	528
11	68	75
12	389	382
13	62	76
14	291	278
16	185	187
17	54	55
18	209	211
20	93	90
22	148	146
	0,10,L	
0	117	140
1	122	131
3	470	495
4	101	127
5	372	360
6	282	302
7	578	580
8	59	50
9	148	145
11	300	297
14	165	169
15	216	218
17	192	179
19	100	102
	0,12,L	
0	493	487
2	112	114
3	76	71
4	379	377
5	120	138
6	181	181
7	143	142
8	83	87
10	344	329
11	174	172
12	152	154
13	95	109
14	261	262
16	51	62
17	52	49
18	247	241
	0,14,L	
0	215	224
1	104	99
3	335	340
4	102	98
5	54	47
6	42	35
7	380	384
9	42	41
11	361	354

0,14,L

13	77	61
15	194	196
16	52	40

0,16,L

0	339	320
2	44	41
4	298	312
5	89	94
6	85	75
7	114	107
8	152	146
10	141	143
12	58	61

0,18,L

0	84	57
1	135	124
3	173	174
6	86	78

1,0,L

2	1588	1658
4	560	517
6	377	403
8	351	390
10	782	825
12	301	298
14	91	88
16	478	497
18	179	177
20	231	225
22	173	163
24	167	154

1,1,L

1	744	712
2	935	915
3	771	871
4	1411	1472
5	136	156
6	556	537
7	659	616
8	537	532
9	475	443
10	599	625
11	68	63
12	379	363
13	226	225
14	56	46
15	91	101
16	132	136
17	117	115
18	95	83
19	139	138
20	139	146
22	74	51
23	90	92
24	51	56

1,2,L

1	1359	1579
2	532	528
3	1122	1188
4	259	287
5	80	35
6	194	204
7	331	300
8	185	141
9	776	813
10	225	211
12	41	47
13	434	433
15	414	402
16	69	56
17	333	327
18	48	25
19	116	117
21	78	83
23	225	222

1,3,L

1	883	902
2	611	620
3	613	571
4	442	401
5	58	95
6	342	346
7	394	400
8	320	318
9	621	628
10	363	359
11	507	515
12	184	199
13	314	303
14	98	79
15	250	253
16	138	132
17	100	106
18	52	57
19	47	47
20	64	62
22	60	46
23	90	87
24	76	69

1,4,L

1	670	629
2	874	949
3	314	354
4	965	884
5	254	244
6	812	891
7	39	17
8	598	594
9	46	46
10	517	499
12	371	386
13	106	108
14	43	27
15	147	147
16	380	359
19	109	113
20	179	199
21	61	57
22	58	55

1,5,L

1	415	383
2	371	376
3	405	355
4	238	213
5	361	397
6	119	147
7	343	343
8	186	195
9	45	51
11	115	102
12	261	279
13	220	237
14	95	89
15	95	85
16	196	204
17	130	127
19	86	82
20	121	121
21	130	117
23	101	101

1,6,L

1	396	457
2	230	244
3	648	641
4	177	179
5	1214	1265
6	395	399
7	95	82
9	450	430
11	146	155
12	213	219
13	318	336
14	116	119
15	72	54
16	41	46
17	255	243
18	49	68
19	225	252
21	65	83
23	128	133

1,7,L

1	430	457
2	275	306
3	471	466
5	286	287
6	463	450
7	47	67
8	123	103
9	232	221
10	114	105
11	89	96
12	58	58
13	364	370
14	97	96
16	165	160
17	132	149
20	140	146
21	50	65

1,8,L

1	108	133
2	415	428
3	78	67
4	252	238
5	129	130
6	793	813
7	104	85
8	358	332
9	60	62
10	238	233
11	110	122
12	302	303
13	81	72
14	238	239
15	90	96
16	221	229
18	97	91
20	224	230
22	59	60

1,9,L

1	81	85
2	194	198
3	203	224
4	70	68
5	67	68
6	292	296
7	150	156
9	244	239
10	310	309
12	195	195
13	130	129
14	50	43
16	113	111
17	84	89
19	81	79
20	109	112

1,10,L

1	440	435
2	104	117
3	249	248
4	38	17
5	329	331
7	142	143
9	364	372
10	42	42
11	161	165
12	155	158
13	387	393
14	50	58
15	75	79
17	92	98
19	170	167

1,11,L

1	122	123
2	313	318
3	63	43
4	48	38
6	228	220
8	53	39
9	113	126
11	169	179
13	59	54
15	91	91
16	134	126
17	84	92
19	122	119

1,12,L

1	144	148
2	342	340
3	96	95
4	241	254
5	39	27
6	289	281
8	247	236
10	157	150
11	107	110
12	220	223
14	102	110
16	152	153

1,13,L

1	86	91
2	76	72
3	187	187
4	209	200
5	170	170
6	150	148
7	68	65
8	209	208
9	108	101
10	59	68
11	52	53
12	46	54
13	140	139
14	85	90
15	88	76
16	90	87
17	61	63

1,14,L

1	203	201
2	104	103
3	158	156
4	42	32

1,14,L

5	225	229
9	203	205
13	180	184
15	103	94

1,15,L

1	129	138
2	42	29
3	216	212
4	73	66
5	154	151
6	106	95
7	86	84
8	107	109
9	96	98
10	55	53
12	73	72
13	103	102
14	52	12

1,16,L

2	189	182
4	87	93
5	45	37
6	137	143
7	43	30
8	82	78
9	50	39
10	157	155
12	150	139

1,17,L

1	109	107
2	97	93
3	67	55
6	109	105
8	57	70
10	56	49

1,18,L

1	159	154
3	101	87
4	51	8
5	101	98

2,0,L

0	330	312
2	559	468
4	1135	1088
6	786	695
8	35	75
10	174	195
12	134	128
14	422	424
16	62	54
18	56	62
20	55	65
22	89	75
24	92	96

2,1,L

0	1169	1217
1	129	144
2	413	392
3	1143	1245
4	105	213
5	475	400
6	582	509
7	1238	1244
8	475	514
9	170	153
10	422	449
11	528	522
12	158	157
13	86	82
14	246	240
15	170	167
16	227	236
17	99	104
18	315	318
19	81	92
20	43	49
21	131	129
22	154	149
23	57	69
24	64	45

2,2,L

0	717	712
1	1196	1223
2	1124	1172
3	255	198
4	600	592
5	45	40
6	164	141
7	367	379
8	297	268
9	84	62
10	263	255
11	118	140
13	116	111
14	162	156
15	222	222
16	68	64
17	95	97
19	117	118
20	102	93
21	64	60

2,3,L

0	591	690
1	364	316
2	493	418
3	473	347
4	1092	1065
5	251	226
6	467	468
7	805	845
8	289	301
9	135	140
10	394	395
11	543	532
12	213	212
13	99	101
14	363	375
15	459	466
17	220	225
18	194	185
19	191	186
20	50	58
21	172	173
22	172	167
24	64	57

2,4,L

0	514	543
1	239	220
2	67	79
3	210	190
4	886	859
5	184	134
6	359	352
7	300	294
8	692	687
9	151	145
10	32	5
11	67	54

2,4,L

12	115	113
13	242	249
14	59	47
15	165	166
16	173	162
18	179	178

2,5,L

0	689	762
1	129	149
2	368	369
3	726	674
4	523	544
5	101	98
6	213	215
7	649	665
8	170	203
10	471	461
11	367	359
12	261	265
13	46	49
14	540	563
15	267	282
16	91	99
17	194	199
18	188	191
19	131	128
21	195	187
22	119	117

2,6,L

0	341	329
1	111	98
2	56	59
3	306	312
4	115	130
5	78	82
6	177	168
7	401	389
9	42	76
11	223	209
12	47	40
14	47	47
15	164	155
17	79	76
18	90	94
21	84	86

2,7,L

0	831	846
1	635	672
2	164	158
3	854	883
4	458	440
5	42	64
7	523	552
8	323	330
9	131	128
10	390	396
11	295	295
12	180	177
13	136	141
14	325	317
15	242	249
17	116	119
18	154	160
19	104	111
21	101	103
22	93	102

2,8,L

0	43	22
1	173	145
2	121	125
3	112	89
4	389	384
6	124	118
7	105	104
9	106	119
10	183	186
11	141	134
12	49	45
14	172	173
15	47	41
18	144	139
20	78	72

2,9,L

0	575	582
1	297	305
3	489	500
4	513	532
5	259	269
6	189	197
7	351	340
8	222	224
9	71	75
10	361	360
11	251	245
12	51	64
13	145	142
14	270	269
15	59	56
16	44	43
17	118	116
18	186	185
19	93	73
21	81	75

2,10,L

0	108	113
1	128	127
2	71	49
3	267	271
4	41	19
5	160	158
6	67	67
7	195	199
9	176	175
11	234	224
15	145	151
18	55	57

2,11,L

0	492	503
1	55	58
3	329	332
4	331	331
6	108	97
7	384	389
8	41	38
10	170	164
11	287	295
12	65	61
13	109	101
14	118	103
15	118	126
16	76	82
17	125	126
18	147	132
19	82	88

2,12,L

0	197	191
1	222	227
2	126	129
3	101	97
4	171	181

2,12,L

5	73	71
7	70	73
8	145	141
9	52	67
10	73	69
11	48	53
12	142	138
13	55	49
14	63	67
16	45	10

2,13,L

0	401	403
1	112	98
2	131	119
3	157	144
4	271	260
5	82	81
6	77	95
7	123	120
8	161	156
10	160	145
11	157	152
12	84	80
14	132	147
15	117	123
17	99	91

2,14,L

0	54	47
1	109	95
3	124	116
4	49	43
6	39	49
9	73	77
10	53	56
11	97	95
13	60	67

2,15,L

0	141	144
1	89	94
3	166	165
4	124	125
5	106	97
7	238	232
8	104	98
10	85	96
11	179	168
12	77	75
14	112	119

2,16,L

0	66	51
1	63	50
2	64	68
6	60	53
8	88	80
10	72	77

2,17,L

0	152	154
1	58	54
3	129	133
4	154	159
7	148	138
8	86	79

2,18,L

0	50	52
1	95	66
4	57	35

3,0,L

2	114	120
4	299	295
6	1007	925
8	313	285
10	37	32
12	77	106
14	279	296
18	68	70
20	129	133

3,1,L

1	522	485
2	193	228
3	126	121
4	624	555
5	810	796
6	551	498
7	50	71
8	655	620
9	775	779
10	312	315
12	179	175
13	446	424
14	95	90
15	107	106
16	347	345
17	336	329
19	229	237
20	179	184
21	60	44
22	84	80
23	147	144

3,2,L

1	97	72
2	42	13
3	935	881
4	463	391
5	84	54
6	239	248
7	369	366
8	77	84
9	179	151
10	71	65
11	230	225
12	100	107
13	152	146
14	117	118
15	71	71
17	67	68
18	75	69
19	183	187
20	79	78

3,3,L

1	1006	998
2	973	923
3	856	764
4	204	206
5	892	890
6	765	786
7	106	82
8	296	302
9	597	589
10	516	495
11	45	48
12	390	388
13	357	337
14	117	114
15	224	213
16	300	295
17	207	208

3,3,L

19	76	82
20	208	209
21	52	64
23	103	103

3,4,L

1	63	25
3	456	440
4	230	205
5	425	397
6	288	312
7	314	291
8	292	295
9	131	128
10	77	69
11	105	118.
12	102	81
14	42	18
16	80	100
18	96	87
20	73	71
23	45	21

3,5,L

1	936	1017
2	845	810
3	303	308
4	126	121
5	616	618
6	647	639
7	61	69
8	720	685
9	393	372
10	222	208
11	112	116
12	328	336
13	271	287
14	278	285
15	120	114
16	314	317
17	76	59
18	71	76
19	95	95
20	110	113
21	79	71
22	65	46
23	130	122

3,6,L

1	580	598
2	152	137
3	261	249
4	301	274
5	138	120
6	59	44
7	328	318
8	192	196
9	100	116
10	170	174
12	100	97
13	199	201
15	107	111
21	64	47

3,7,L

1	277	299
2	407	429
3	453	457
4	247	267
5	278	273
6	380	409
7	55	63
8	297	281
9	220	177
10	164	167
11	208	217
12	242	237
13	295	314
14	74	79
15	190	193
16	128	127
17	248	256
19	187	190
20	154	147
21	73	76
22	61	52

3,8,L

2	246	234
3	316	332
4	192	198
5	154	151
6	169	176
7	111	105
9	70	85
10	376	383
11	52	55
12	52	60
14	163	153
16	60	66

3,9,L

1	389	382
2	364	326
3	261	277
4	170	181
5	214	206
6	265	274
7	185	206
8	190	197
9	222	228
10	251	260
11	99	95
12	366	363
13	256	247
14	65	72
15	142	145
16	228	221
17	151	151
19	124	122
20	145	143

3,10,L

1	172	172
2	78	83
6	56	60
7	43	44
8	169	165
9	255	264
11	79	77
15	77	69
17	66	67

3,11,L

1	342	353
2	269	291
3	178	181
4	170	171
5	472	476
6	125	130
7	134	144
8	92	80
9	365	364
10	227	215
12	241	238
13	212	216
14	70	63
15	55	59

3,11,L

16	130	133
17	99	93
19	107	101

3,12,L

1	68	66
4	187	181
5	59	54
6	41	41
8	131	130
11	68	70
13	60	64
16	68	69

3,13,L

1	187	189
2	323	330
3	173	172
4	114	113
5	115	114
6	264	266
7	59	59
8	123	125
9	127	134
10	96	102
11	53	49
12	103	108
13	109	114
14	47	42
15	70	63
16	115	119

3,14,L

1	37	26
2	51	67
3	119	123
6	68	45
13	93	83
15	56	31

3,15,L

1	135	127
2	180	186
5	139	131
6	157	163
8	78	80
9	166	163
10	96	84
11	55	45
12	71	71
13	138	144

3,16,L

6	82	76
8	49	36

3,17,L

1	89	99
2	163	152
4	60	58
5	121	117
6	105	106
8	102	93

3,18,L

1	56	56

4,0,L

0	791	759
2	276	254
4	1297	1286
6	451	444
8	231	220
10	504	532
12	147	151
14	232	238
16	112	134
18	300	299
20	141	146
22	89	104

4,1,L

0	355	336
1	592	552
2	141	92
3	506	537
4	485	510
5	218	206
6	759	729
7	379	357
8	531	544
9	50	53
10	131	131
11	326	342
12	129	131
13	306	297
14	297	284
15	107	108
16	69	85
17	156	151
18	103	105
19	75	75
21	119	124
22	101	111
23	71	79

4,2,L

0	237	229
1	432	387
2	236	202
3	855	884
4	267	221
5	846	805
6	258	297
7	703	713
8	187	173
9	138	141
10	250	235
11	274	260
12	37	35
13	75	68
14	54	56
15	303	302
16	79	75
17	266	267
19	92	88
20	49	38
21	168	175
23	72	69

4,3,L

0	408	387
1	790	802
2	253	239
3	466	454
4	254	273
5	241	212
6	230	242
7	578	589
8	400	390
9	45	62
10	282	277
11	258	242
12	66	72
13	41	43

4,3,L

14	92	106
15	204	202
16	146	151
17	45	41
18	155	162
19	61	69
21	89	92
22	79	84

4,4,L

0	876	922
1	38	17
2	345	328
4	1051	1035
6	84	61
7	221	225
8	444	434
9	235	246
10	308	276
11	170	176
12	384	381
14	365	380
15	64	59
16	60	42
18	215	213
22	140	139

4,5,L

0	1083	1081
1	279	306
2	204	179
3	93	101
4	240	233
5	479	467
6	56	52
7	193	194
8	332	340
10	171	160
11	182	178
12	61	54
13	106	91
14	268	267
15	188	184
18	113	119
19	74	75
21	110	105
22	114	108

4,6,L

0	320	312
1	230	248
2	60	46
3	531	516
4	242	226
5	139	143
6	202	204
7	523	538
9	126	124
11	421	427
15	132	144
16	78	79
17	139	148
19	97	91
21	144	145

4,7,L

0	157	159
1	264	272
2	127	114
3	102	131
4	323	324
6	39	8
7	82	83
8	178	173
9	66	77
10	60	44
11	350	358
12	173	171
13	200	203
14	159	158
15	175	188
17	46	46
18	153	120
19	62	68
21	74	78

4,8,L

0	693	695
1	109	105
2	115	113
3	36	23
4	186	171
5	64	70
6	146	162
8	285	296
9	151	154
10	267	273
11	110	118
12	56	46
13	66	60
14	269	270
16	63	71
18	162	176

4,9,L

0	140	131
1	45	30
2	46	57
3	208	213
4	301	306
6	155	156
7	217	216
8	183	194
9	129	128
10	115	124
11	222	227
12	75	74
14	84	88
15	160	158
16	59	59
17	89	90
18	128	129
19	75	73
20	47	21

4,10,L

0	137	149
1	155	161
2	121	127
3	327	345
4	86	93
5	53	64
7	461	457
8	64	66
9	138	131
11	327	341
12	47	39
13	93	99
15	127	126
17	76	72
19	117	122

4,11,L

0	99	107
1	161	166
3	248	245
4	275	289
5	161	166

4,11,L

6	88	82
7	163	167
8	62	65
9	83	78
10	126	128
11	131	131
13	39	24
14	109	104
15	102	98
17	71	58
18	121	120

4,12,L

0	391	411
1	91	98
2	57	53
3	44	42
4	218	227
5	173	172
6	128	134
7	56	47
8	181	182
10	152	152
12	82	101
14	138	149
16	76	79

4,13,L

0	53	56
1	174	168
2	98	90
3	150	154
4	140	145
5	56	71
6	99	94
7	92	96
8	155	157
10	87	86
11	132	130
12	114	108
14	96	101
15	53	49

4,14,L

1	129	123
3	131	126
5	88	95
7	173	181
11	145	137
13	64	60

4,15,L

0	144	149
1	114	105
2	56	61
3	110	104
4	90	87
5	61	67
6	73	56
7	103	106
8	96	90
9	71	67
10	58	70
11	86	89
12	51	48

4,16,L

0	139	144
1	44	16
4	155	152
6	81	84
8	79	82
10	151	140

4,17,L

0	117	113
4	117	106
6	65	67
7	88	82

5,0,L

2	837	903
6	744	755
8	288	303
12	540	571
14	187	193
16	443	459
18	87	86
20	326	318
22	83	71

5,1,L

1	75	76
2	203	181
3	215	191
4	217	214
5	241	249
6	177	176
7	95	82
8	117	114
9	32	19
10	277	289
11	80	88
13	158	176
16	81	62
17	74	75
18	62	52

5,2,L

1	719	732
2	395	406
3	533	571
4	426	421
5	848	886
6	46	35
7	242	240
9	517	528
10	143	173
11	259	248
13	527	537
14	140	136
15	195	209
16	84	91
17	225	225
19	220	223
20	65	57
21	114	111

5,3,L

1	84	97
2	231	227
3	272	263
5	94	78
6	220	213
7	63	80
9	76	51
10	71	70
11	212	216
12	99	99
15	113	113
18	42	37
22	53	41

5,4,L

1	373	379

5,4,L

2	1102	1126
3	50	35
4	342	351
5	79	88
6	635	645
7	84	105
8	388	379
9	65	86
10	436	442
11	90	89
12	450	439
13	79	87
14	118	110
15	155	153
16	193	195
17	91	92
20	195	200
22	50	60

5,5,L

1	71	66
2	273	244
3	37	43
4	266	271
5	36	33
6	148	120
7	173	187
8	85	91
9	185	182
10	79	75
11	81	90
12	50	53
13	114	119
14	67	66
15	62	53
19	49	51
20	56	37

5,6,L

1	686	707
2	115	103
3	228	210
4	119	106
5	458	472
6	193	173
7	162	146
9	504	490
10	161	166
12	95	95
13	234	240
14	63	62
15	167	175
17	186	182
19	176	178
21	111	120

5,7,L

1	159	159
2	126	133
3	43	28
4	50	37
5	74	77
6	190	191
7	146	153
8	196	194
9	218	221
10	113	117
14	100	102
15	64	73
16	48	56

5,8,L

2	275	258
3	99	93
4	271	269
5	101	91
6	265	268
8	363	352
9	99	90
10	430	437
12	296	309
14	100	103
16	277	273
18	49	33
20	193	194

5,9,L

1	86	98
2	242	243
3	80	81
4	94	95
5	252	259
6	53	44
7	143	139
8	39	36
11	59	54
12	38	44
14	39	32

5,10,L

1	316	307
2	158	177
3	206	205
4	113	125
5	391	385
6	113	120
7	107	104
8	43	39
9	389	384
13	256	244
15	188	179
17	178	182

5,11,L

1	67	73
3	53	46
4	55	59
5	134	136
8	47	53
12	74	63

5,12,L

2	367	386
3	57	54
4	77	93
5	90	90
6	316	306
8	242	239
10	153	159
12	175	168
14	76	78
16	173	172

5,13,L

2	40	36
6	68	76
8	54	58
9	55	55
12	56	51

5,14,L

1	169	172
3	165	163
5	283	270
9	222	230
11	61	64

5,14,L

13	166	159

5,15,L

1	66	75

5,16,L

2	201	206
6	150	159
8	125	132

6,0,L

0	518	483
2	37	42
4	981	936
6	193	183
8	391	377
10	291	285
12	253	239
14	448	455
16	84	92
18	222	222
22	175	180

6,1,L

0	372	354
1	57	41
2	351	335
3	335	321
4	131	140
5	69	65
6	107	94
7	282	260
8	53	48
9	238	230
10	311	314
11	171	168
12	145	128
13	64	75
14	144	149
17	101	102
18	48	54
19	67	67
21	87	81
22	58	57

6,2,L

0	161	182
1	429	426
2	112	103
3	496	489
4	47	50
5	321	305
7	418	408
8	137	129
9	145	156
10	151	138
11	421	409
12	148	145
13	107	108
15	338	355
17	102	98
19	140	142
20	60	59
21	165	164

6,3,L

2	198	173
3	298	285
4	108	110
5	95	111
6	170	179
7	125	111
8	215	205
9	147	141
10	164	152
11	442	458
12	155	160
14	111	106
15	100	99
18	56	56

6,4,L

0	445	449
2	290	282
3	60	66
4	361	342
5	209	221
6	264	266
7	173	169
8	404	413
9	247	242
10	355	339
11	43	38
12	148	138
13	76	79
14	228	226
15	45	52
16	76	72
18	267	263
19	61	62
20	54	63

6,5,L

0	149	168
1	125	133
2	52	47
3	177	188
4	280	286
5	63	53
6	40	24
7	147	156
8	132	127
9	222	228
10	150	151
11	80	83
13	49	55
14	130	145
15	50	29
17	71	70
18	118	119
21	65	59

6,6,L

0	106	120
1	454	459
2	153	153
3	477	466
4	304	300
5	108	94
7	419	429
8	158	145
9	91	94
11	525	515
13	185	174
15	192	196
17	167	160
19	138	134

6,7,L

0	251	258
1	54	51
2	193	215
3	185	175
4	219	221
5	193	192
6	46	33

6,7,L

7	174	179
8	115	113
9	160	148
10	59	59
11	110	113
13	66	76
14	82	80
15	72	78
17	60	44
18	92	102
19	86	85
20	60	51

6,8,L

0	510	530
1	89	90
2	194	202
4	407	416
6	382	372
7	125	126
8	418	423
10	264	254
11	69	61
12	175	166
13	39	21
14	234	236
16	44	29
18	169	167

6,9,L

0	248	259
1	86	96
4	77	64
7	221	214
8	79	87
9	85	98
10	82	92
11	82	77
12	42	25
13	46	65
14	133	134
15	90	91
18	67	70

6,10,L

0	107	109
1	298	295
3	293	285
4	82	92
5	97	93
6	65	52
7	321	320
10	43	47
11	177	181
13	94	81
14	49	17
15	149	154
16	51	32
17	121	119

6,11,L

0	239	244
1	185	190
3	72	73
4	124	114
5	117	110
6	42	51
7	118	113
11	79	91
13	48	6
14	73	76
15	57	63

6,12,L

0	217	208
4	261	257
6	135	135
8	181	180
9	69	78
10	137	132
12	84	90
13	52	40
14	176	157

6,13,L

0	81	83
1	49	46
3	64	65
4	87	88
5	55	71
6	110	105
7	124	116
8	68	55
10	49	52

6,14,L

1	156	156
2	45	30
3	176	160
4	60	70
5	87	83
7	190	184
11	177	178

6,15,L

4	87	91
7	76	86

6,16,L

0	123	135
3	60	54
4	171	157

7,0,L

2	254	246
4	110	111
6	521	495
8	379	366
10	64	78
12	136	148
14	301	309
16	154	161

7,1,L

1	214	210
2	369	348
4	94	99
5	286	263
6	310	281
7	145	153
8	177	172
9	274	284
10	255	242
11	39	40
12	289	278
13	292	286
14	210	217
15	108	103
16	111	115
17	78	82
19	135	131
20	140	142
21	104	94

7,2,L

2	52	62
3	176	167
4	43	29
5	432	427
6	89	92
8	47	51
9	163	145
10	79	80
11	57	60
12	103	118
13	180	185
14	115	120
16	69	94
17	136	128
19	120	109

7,3,L

1	238	228
2	227	226
3	156	157
4	257	239
5	390	359
6	301	303
7	40	43
8	248	254
9	263	241
10	227	228
11	109	114
12	175	168
13	216	222
15	42	36
16	127	124
17	94	99
18	55	62
19	97	90
20	124	131

7,4,L

2	190	180
3	117	117
4	140	139
5	51	57
6	47	63
7	202	203
8	182	182
9	94	81
10	104	104
12	254	245
14	61	66
16	160	159
19	68	47
20	88	109

7,5,L

1	373	400
2	323	319
3	196	182
4	144	135
5	454	457
6	166	155
7	58	48
8	115	122
9	335	334
10	96	96
11	81	79
12	257	266
13	73	73
15	108	108
16	158	145
17	104	110
19	112	115
20	117	133

7,6,L

1	77	88
2	79	85
5	256	259
7	41	56
8	72	59
9	376	375
12	79	86
13	145	143
15	49	56
17	82	80
19	70	70

7,7,L

1	304	317
2	403	428
3	100	93
4	88	75
5	259	260
6	193	203
7	130	129
8	210	215
9	292	294
10	109	106
11	79	63
12	161	160
13	164	167
14	47	32
15	107	99
16	157	158
17	165	165
19	101	105

7,8,L

2	364	374
6	133	138
9	114	99
16	86	89
12	53	60
10	106	106

7,9,L

1	107	105
2	354	347
3	187	195
5	155	148
6	246	256
8	199	219
9	87	95
10	109	107
11	43	34
12	174	173
13	134	135
14	58	55
15	98	92
16	164	172
17	99	88

7,10,L

1	186	177
2	83	85
5	112	109
8	119	115
9	114	106
10	90	88
11	63	59
13	104	106
15	70	68
16	56	59

7,11,L

1	152	161
2	145	155
3	154	155

7,11,L

4	41	23
5	215	220
6	132	130
8	76	81
9	159	154
12	86	73
13	108	100
15	104	107

7,12,L

1	73	73
2	111	107
3	96	92
6	87	86
8	66	62
9	54	55
10	79	81
12	141	131

7,13,L

1	114	116
2	161	164
3	85	79
4	92	81
5	127	122
6	113	97
7	77	79
8	120	119
9	101	103
10	89	94
12	99	95

7,14,L

1	88	87
3	56	61
5	108	98
9	81	89

7,15,L

1	74	88
2	76	73
5	159	144
6	61	68

8,0,L

0	234	241
4	84	79
10	47	48

8,1,L

1	229	229
0	239	258
3	435	428
4	550	559
7	421	418
8	180	192
9	51	44
10	216	210
11	286	280
12	171	181
14	196	190
15	118	117
17	84	88
18	128	129
19	56	39

8,2,L

0	57	52
1	91	73
4	70	78
6	74	81
7	60	63
8	42	52
9	116	113
10	79	79
11	71	62
12	123	126
14	44	38
15	77	70

8,3,L

0	365	371
1	226	247
2	202	205
3	308	313
4	316	301
5	153	167
6	123	127
7	220	223
8	282	286
9	152	155
10	119	114
11	196	197
12	66	65
13	76	78
14	109	93
15	203	198
17	149	131
18	173	181
19	95	77

8,4,L

0	133	131
1	122	134
3	79	77
4	43	20
5	172	177
6	149	149
12	44	30
13	77	72
14	58	58
16	46	45

8,5,L

0	240	243
1	118	129
2	84	90
3	167	165
4	322	328
6	168	173
7	209	208
8	229	226
9	50	55
10	234	228
11	264	258
12	83	79
13	69	72
14	140	151
15	156	154
16	73	75
17	103	103
18	184	171

8,6,L

0	127	122
1	47	55
3	83	79
4	73	65
5	78	78
7	136	139
8	68	78
9	122	130
12	44	50

8,7,L

1	322	324
3	248	250
4	159	155
5	311	286
6	116	115
7	256	257
8	170	163
10	140	135
11	162	152
12	112	112
13	71	76
14	175	172
15	150	153
17	109	102

8,8,L

1	58	63
3	135	129
4	133	135
6	113	120
7	89	77
9	51	39
10	75	83

8,9,L

0	257	270
1	259	270
3	150	153
4	236	237
5	102	98
7	114	101
8	138	143
6	138	145
11	131	136
12	89	84
13	72	68
14	129	125
15	118	109

8,10,L

0	73	77
1	42	42
2	44	29
4	39	30
5	57	59
7	49	56

8,11,L

1	126	120
0	187	200

8,10,L

8	69	73

8,9,L

10	104	105

8,11,L

3	121	114
4	128	137
6	75	75
7	146	152
8	153	153
10	114	105
11	158	146
12	68	67

8,13,L

0	141	151
1	84	80
3	122	117
4	135	143
6	80	75
7	107	113
8	153	147
10	88	79

8,15,L

0	75	90
1	77	89

9,0,L

2	387	392
4	103	99
6	205	204
8	140	145
10	214	222
12	195	191
16	152	156

9,1,L

1	222	224
2	249	252
3	144	132
5	272	282
6	205	206
7	89	81
8	93	90
9	157	149
10	79	78
11	49	51
12	166	163
13	112	106
14	45	45
15	46	26
16	105	91
17	50	34
18	60	60

9,2,L

1	243	235
3	246	247
5	285	285
6	155	148
8	148	144
9	173	172
10	145	143
11	71	62
13	108	104
15	145	150
17	94	92
18	76	72

9,3,L

1	223	225
2	254	245
3	139	147
4	113	111
5	241	240
6	180	181
8	46	56
9	171	159
10	129	137
11	50	55
12	108	94
13	159	154
14	64	50
15	70	58
16	110	110
17	61	54

9,4,L

2	242	249
5	198	203
6	174	177
7	92	84
8	235	235
11	38	18
12	160	159
14	52	39
16	147	147
17	57	56

9,5,L

1	75	63
2	312	319
5	110	107
6	228	235
7	67	63
8	57	58
9	186	182
10	70	73
12	107	105
13	117	108
15	85	89
16	110	113
17	63	73

9,6,L

1	154	154
2	63	75
5	194	198
6	83	97
9	200	205
10	55	44
13	148	147

9,7,L

1	118	117
2	153	151
3	140	129
5	130	136
6	87	67
7	77	77
8	91	105
9	126	128
10	53	56
12	112	111
13	89	89
14	55	36
16	73	81

9,8,L

2	151	155
3	58	71
5	51	35
6	170	172
7	47	48
8	67	79
10	107	106
12	84	71
14	91	82
15	49	33

9,9,L

1	147	151
2	158	158
3	70	82
5	132	128
6	97	84
8	71	61
9	141	135
10	68	66
12	64	66
13	88	97
14	56	32

9,10,L

2	50	32
3	63	55
5	202	202
9	129	130

9,11,L

1	85	99
2	95	111
3	71	58
5	123	119
6	103	95
8	68	71
9	137	142
10	70	68

9,12,L

2	118	122
4	81	84
6	82	73
8	73	75

9,13,L

1	50	37
2	103	105
5	88	87
6	113	101

10,0,L

0	510	306
4	347	337
6	143	156
8	215	205
10	195	199
12	110	111
14	199	200

10,1,L

0	51	68
1	50	46
2	43	41
3	50	60
4	44	19
5	59	56
6	104	109
7	61	55
8	78	69
9	63	73
13	61	47

10,2,L

0	184	206
1	244	243
3	313	303
5	69	64
7	210	216
11	285	280
12	58	44
13	100	111
15	167	167

10,3,L

0	59	37
1	83	71
3	78	81
4	102	99
5	81	66
6	79	81

10,3,L

9	72	72

10,4,L

0	314	322
1	77	83
2	120	122
3	57	63
4	218	213
5	58	63
6	131	126
7	60	64
8	184	188
9	64	45
10	210	212
12	129	125
13	72	63
14	191	199

10,5,L

0	155	155
1	88	70
3	73	82
4	82	70
5	45	52
6	54	62
7	80	85
8	50	49

10,6,L

0	47	33
1	126	139
2	47	29
3	172	173
4	95	99
5	137	131
7	267	259
9	49	44
10	50	43
11	196	196
13	57	49

10,7,L

0	105	108
4	53	54
6	53	51
10	54	60
11	63	52
13	59	46

10,8,L

0	151	157
2	50	45
4	251	245
6	187	183
8	171	175
10	141	135
11	67	45
12	90	89

10,9,L

0	85	81
4	61	55
6	58	68
7	70	74
10	51	54

10,10,L

1	141	142
3	208	216
5	55	43
7	203	197

10,11,L

1	71	62
2	53	33
3	81	60
7	61	65

10,12,L

0	162	153
4	137	141

11,0,L

2	203	208
4	84	86
6	89	87
10	181	184
12	211	227

11,1,L

1	64	66
5	46	52
6	48	30
7	50	50
8	52	48
9	66	67
11	49	43

11,2,L

1	196	211
2	95	102
4	54	6
5	171	169
6	73	61
9	253	249
10	49	12
13	199	194

11,3,L

2	57	60
4	46	35
5	78	83
6	75	62
8	90	82
10	59	54

11,4,L

2	252	252
4	83	81
6	200	199
8	146	159
10	129	123
12	177	177

11,5,L

1	51	38
2	88	100
4	58	26
5	57	64
9	59	63
12	65	58

11,6,L

1	153	162
3	121	123
4	54	52
5	228	227
9	200	201

11,7,L

2	62	70
5	51	15
6	55	27
9	54	57

11,8,L

2	179	185
4	109	110
6	179	182
8	163	158
10	71	86

11,9,L

2	63	61
3	54	57
5	59	69

11,10,L

1	100	111
2	65	64
3	93	96
5	185	187

12,0,L

0	123	126
2	83	75
4	83	79
6	85	86
8	115	119
10	162	173

12,1,L

0	97	107
1	60	88
3	106	105
4	101	86
7	124	134
8	92	104
11	83	68

12,2,L

1	68	78
3	133	137
4	64	56
7	121	123
11	116	121

12,3,L

0	132	135
1	112	101
2	77	61
3	122	129
4	88	96
6	98	105
8	107	113
9	60	49
10	73	84

12,4,L

0	101	112
4	111	127
6	78	72
8	55	59
10	58	71

12,5,L

0	174	177
1	73	76
3	101	93
4	140	126
7	123	112
8	75	79

12,6,L

0	61	70
1	69	50
3	68	71
7	122	120
8	54	41

12,7,L

0	96	83
1	86	81
3	110	103
4	133	132
5	59	49
6	61	67
7	91	87

12,8,L

0	64	65
4	97	96

13,1,L

1	104	108
2	176	173
5	155	120
6	154	149

13,3,L

1	135	133
2	85	94
3	126	127
5	134	145
6	108	104

13,5,L

2	158	145

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