

TERTIARY PHOSPHINE COMPLEXES OF

VANADIUM

A thesis submitted by

FIONNA JANE WELLS, B.Sc.

for the

DEGREE OF DOCTOR OF PHILOSOPHY,

UNIVERSITY OF LONDON

Chemistry Department,

Imperial College of Science and Technology,

London, SW7 2AY.

September, 1987.

TERTIARY PHOSPHINE COMPLEXES OF
VANADIUM

A thesis submitted by

FIONNA JANE WELLS, B.Sc.

for the

DIPLOMA OF IMPERIAL COLLEGE,
UNIVERSITY OF LONDON

Chemistry Department,
Imperial College of Science and Technology,
London, SW7 2AY.

September, 1987.

To Alan and my family.

ABSTRACT

The synthesis, characterisation and reaction chemistry of some tertiary phosphine complexes of vanadium are described.

The reaction of $[V_2(\mu-Cl)_3(thf)_6]_2[Zn_2Cl_6]$ with a variety of tertiary phosphines is discussed.

The reactions of the vanadium(II) phosphine halide, trans- $VCl_2(dmpe)_2$ are described. Replacement of the chloride ligands by anionic and neutral groups leads to other neutral and cationic vanadium(II) complexes respectively, while reaction with sodium amalgam in the presence of carbon monoxide results in the formation of trans- $V(CO)_2(dmpe)_2$. Reduction reactions in the presence of other neutral ligands are discussed.

The reaction of trans- $V(CO)_2(dmpe)_2$ with a variety of coordinating and non-coordinating acids is described, together with other oxidation reactions of the vanadium dicarbonyl complex.

The reaction chemistry of [trans- $V(MeCN)_2(dmpe)_2$] $^{2+}$ and $[V(MeCN)_6]^{2+}$ is discussed, comprising substitution and protonation reactions of the former and substitution reactions of the latter.

The e.s.r. spectra of compounds of the type [trans- $VXX'(dmpe)_2$] $^{z+}$ [$z = 2, X = X' = \textit{t}BuNC, MeCN; z = 1, X = Cl^-, X' = \textit{t}BuNC; z = 0, X = X' = CN^-, NCS^-$] are analysed and correlations between the spin-Hamiltonian parameter, E, and the ligand field strength of X(X') made.

ACKNOWLEDGEMENTS

I would like to thank Professor Sir Geoffrey Wilkinson, F.R.S., for his constant supply of ideas and also for his patience and understanding. I am grateful to the following members (past and present) of the Wilkinson group for their help and friendship during the past three years: Dr. Paul Savage, Dr. John Arnold, Dr. Chris Howard, Dr. Julian Salt, Dr. Pericles Stavropoulos, Cindy Longley, Simon Anderson, Tony Wong and Jon Parr.

I would particularly like to thank Dr. Alan Lindsay for his continuing love and support.

I am indebted to Dr. Mike Hursthouse, Majid Motevalli and Bilquis Hussain for the X-ray crystal structure determinations.

I would also like to thank Dr. Peter Beardwood for help with the e.s.r. interpretations; also Roger Lincoln, Colin Robinson, Dick Sheppard and Miss Sue Johnson for all technical help, and Miss Penny Archdall and Mrs. Liz Mitchell for typing of publications and this thesis.

The Science Research Council is gratefully acknowledged for financial support during the past three years.

CONTENTS

| | Page: |
|--|-------|
| Abstract | 3 |
| Acknowledgements | 4 |
| Contents | 5 |
| List of Figures | 6 |
| List of Tables | 7 |
| List of Schemes | 8 |
| List of Abbreviations | 9 |
| CHAPTER 1 : A General Survey of Vanadium Coordination and Organometallic Chemistry | 11 |
| CHAPTER 2 : Synthesis and Reactions of <u>trans</u> -VCl ₂ (dmpe) ₂ and Related Complexes | 38 |
| 2.1. Introduction | 39 |
| 2.2. Results and Discussion | 40 |
| 2.3. Conclusions | 62 |
| CHAPTER 3 : Reactions of <u>trans</u> -V(CO) ₂ (dmpe) ₂ | 64 |
| 3.1. Introduction | 65 |
| 3.2. Results and Discussion | 65 |
| 3.3. Conclusions | 81 |
| CHAPTER 4 : Reactions of the Cation [<u>trans</u> -V(MeCN) ₂ (dmpe) ₂] ²⁺ | 87 |
| 4.1. Introduction | 88 |
| 4.2. Results and Discussion | 88 |
| EXPERIMENTAL SECTION | 102 |
| Chapter 2 | 105 |
| Chapter 3 | 114 |
| Chapter 4 | 120 |
| REFERENCES | 123 |

LIST OF FIGURES

| | | Page: |
|---------------|--|-------|
| Figure 2.1(a) | Molecular structure of [<u>trans</u> - -V(MeCN) ₂ (dmpe) ₂][BPh ₄] ₂ | 47 |
| 2.1(b) | Molecular structure of [<u>trans</u> - -V(MeCN) ₂ (dmpe) ₂][BPh ₄] ₂ | 48 |
| 2.2. | The e.s.r. spectrum of <u>trans</u> -V(CO) ₂ (dmpe) ₂ in toluene at 77 K | 55 |
| 2.3. | Molecular structure of <u>trans</u> -V(CO) ₂ (dmpe) ₂ | 56 |
| 2.4. | The e.s.r. spectrum of Na[VCl(CO) ₄ (PMe ₃) ₂] in thf at 77 K | 59 |
| 3.1. | Molecular structure of <u>cis</u> -V(CO) ₂ (dmpe) ₂ (O ₂ CET) | 67 |
| 3.2. | ⁵¹ V-{ ¹ H} n.m.r. spectrum of <u>cis</u> - -V(CO) ₂ (dmpe) ₂ (NH ₂ SO ₃) in C ₆ D ₆ at 298 K | 71 |
| 3.3. | Molecular structure of [<u>cis</u> - -V(CO) ₂ (dmpe) ₂ (MeCN)][BPh ₄] | 75 |
| 3.4. | Stirred and Unstirred Voltammetry of <u>t</u> -V(CO) ₂ (dmpe) ₂ in 0.2 M ^t Bu ₄ N ⁺ PF ₆ ⁻ , CH ₂ Cl ₂ | 80 |
| 4.1. | E.s.r. spectra (experimental and simulated) of [V(MeCN) ₆][BPh ₄] ₂ | 91 |
| 4.2. | Molecular structure of the cation [<u>trans</u> - -V(^t BuNC) ₂ (dmpe) ₂] ²⁺ | 94 |
| 4.3. | E.s.r. spectra of [<u>trans</u> -VXX'(dmpe) ₂] ^{Z+} (z = 0, 1, 2) | 97 |
| 4.4. | Cyclic voltammogram of [<u>trans</u> -V(^t BuNC) ₂ (dmpe) ₂] ²⁺ in 0.2 M ^t Bu ₄ N ⁺ PF ₆ ⁻ in MeCN | 101 |

LIST OF TABLES

| | Page: |
|--|-------|
| Table 1.1. Some peroxo vanadium species | 15 |
| 1.2. Some substitution products of $V(CO)_6$ and $V(CO)_6^-$ | 30 |
| 2.1. Selected bond lengths and angles for [<u>trans</u> - -V(MeCN) ₂ (dmpe) ₂][BPh ₄] ₂ | 49 |
| 2.2. Selected bond lengths and angles for <u>trans</u> -V(CO) ₂ (dmpe) ₂ | 57 |
| 3.1. Selected bond lengths and angles for <u>cis</u> -V(CO) ₂ (dmpe) ₂ (O ₂ CEt) | 68 |
| 3.2. Selected bond lengths and angles for [<u>cis</u> -V(CO) ₂ (dmpe) ₂ (MeCN)][BPh ₄] | 76 |
| 3.3. I.R. spectra for <u>cis</u> -V(CO) ₂ (dmpe) ₂ X complexes | 84 |
| 3.4. ¹ H, ³¹ P and ⁵¹ V n.m.r. data for <u>cis</u> -V(CO) ₂ (dmpe) ₂ X complexes | 85 |
| 3.5. Analytical and spectroscopic data for salts of the [V ₂ H ₂ (CO) ₄ (dmpe) ₄] ²⁺ ion | 86 |
| 4.1. Selected bond lengths and angles for [<u>trans</u> - -V(^t BuNC) ₂ (dmpe) ₂][PF ₆] ₂ | 95 |

LIST OF SCHEMES

| | Page: |
|--|-------|
| Scheme 1.1. Some reactions of VCl_4 | 17 |
| 1.2. Some reactions of VCl_3 | 21 |
| 1.3. Reaction of $[V_2(\mu-Cl)_3(thf)_6]_2[Zn_2Cl_6]$ with PPh_3 | 26 |
| 1.4. Some reactions of $CpV(CO)_4$ and $[V(CO)_3Cp]^{2-}$ | 33 |
| 1.5. Preparation and interconversions of low oxidation state bipy complexes | 34 |
| 1.6. Preparation of dinitrosyl complexes | 34 |
| 2.1. Reactions of <u>trans</u> - $VCl_2(dmpe)_2$ | 44 |
| 3.1. Reactions of <u>trans</u> - $V(CO)_2(dmpe)_2$ | 82 |

LIST OF ABBREVIATIONS

| | |
|---------|-----------------------------------|
| Å | angstrom unit, 10^{-8} cm |
| atm | $101\ 325\ \text{Nm}^{-2}$ |
| B.M. | Bohr Magnetons |
| bipy | bipyridyl |
| Cp | cyclopentadienyl |
| dipic | dipicoline |
| dmpe | 1,2-bis(dimethylphosphino)ethane |
| dmpm | 1,2-bis(dimethylphosphino)methane |
| dppm | 1,2-bis(diphenylphosphino)methane |
| dppe | 1,2-bis(diphenylphosphino)ethane |
| diars | diarsine |
| diphos | diphosphine (normally dppe) |
| dmso | dimethyl sulphoxide |
| edta | ethylenediaminetetraacetate |
| e.s.r. | electron spin resonance |
| g.l.c. | gas-liquid chromatography |
| h ν | photolysis |
| Hz | Hertz, sec^{-1} |
| ind | indenyl |
| i.r. | infrared |
| J | coupling constant |
| mes | mesityl |
| mT | millitesla, 10 gauss |
| NaNp | sodium naphthalenide |
| n.m.r. | nuclear magnetic resonance |

| | |
|----------------------|--|
| oep | 2,3,7,8,12,13,17,18-octaethylporphyrin |
| p.p.m. | parts per million |
| phen | phenanthroline |
| py | pyridine |
| tar | tartrate |
| TCNE | tetracyanoethylene |
| thf | tetrahydrofuran |
| terpy | terpyridyl |
| triphos | triposphine |
| V | Volts |
| Δ | heat <u>or</u> difference |
| μ_{eff} | effective magnetic moment |
| Λ_{M} | molar conductivity |
| ν | frequency in cm^{-1} |

CHAPTER 1

A GENERAL SURVEY OF VANADIUM
COORDINATION AND ORGANOMETALLIC CHEMISTRY

1.1. INTRODUCTION

The work presented in this thesis is concerned with the chemistry of vanadium in its lower oxidation states : primarily with complexes stabilised by the basic phosphine, [1,2-bis(dimethylphosphino)ethane], (dmpe). However, before discussing these compounds in detail, it is appropriate to put this work in perspective by presenting a brief outline of the coordination and organometallic chemistry of vanadium, with special emphasis on the less common oxidation states 0, +1 and +2. This chapter will also include a short section on dmpe and its characteristics.

1.2. OXIDATION STATES OF VANADIUM

Vanadium was discovered in 1831 by N.G. Sefström who isolated and characterised the oxide. The element was named after Vanadis, a goddess from Scandanavian mythology. Vanadium complexes are known in formal oxidation states ranging from -3 to +5, with the most common states being +4 and +5. The chemistry of the higher oxidation states is dominated by the tendency of vanadium to bind strongly to oxygen and the majority of complexes in these oxidation states contain the entities VO^{2+} or VO^{3+} . Oxidation state -3 has only been observed in organometallic compounds e.g., $[V(CO)_5]^{3-}$ and will not be discussed further: there are no reports of vanadium in oxidation state -2.

1.2.1. Oxidation State +5 (d^0)

The +5 oxidation state is one of the most stable for vanadium and as such has been extensively studied (1), (2), (3), (4). It is

strongly oxidising and this fact has prevented the isolation of some complexes because the ligands can be oxidised by vanadium(V). However, despite this, a large number of oxo compounds i.e., containing the VO^{3+} or VO^{2+} unit, have been characterised which incorporate halide, peroxide, alkoxide, hydroxamate and aminocarboxylate ligands.

The most important oxyhalide is $VOCl_3$, made by the action of chlorine on $V_2O_5 + C$ at ca. $300^\circ C$. Some or all of the halogens can be replaced by alkoxide groups to give complexes $VOCl_{3-n}(OR)_n$ ($n = 1-3$). The oxy-compound $VO(NPh_2)_3$ has been synthesised from $V(NPh_2)_3$ by oxidation with NO in tetrahydrofuran ⁽⁵⁾. Oxyvanadium carboxylate complexes $VO(O_2CR)_3$ ($R = \text{alkyl}$) can be easily prepared from the reaction of $VOCl_3$ with $Ag[O_2CR]$ in CH_2Cl_2 ⁽⁶⁾.

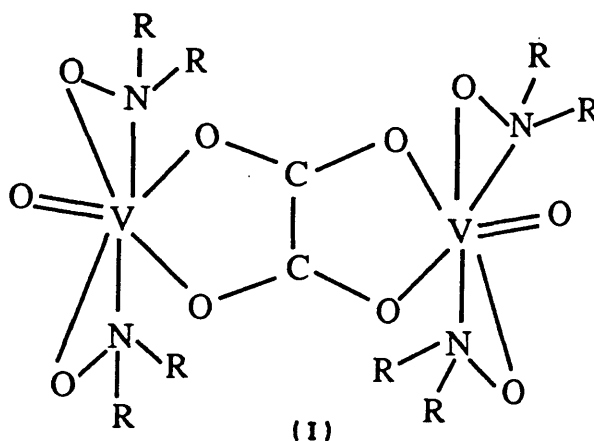
Replacement of the halide ligands can also be effected by the reaction of $VOCl_3$ with MPh_2 ($M = Zn$ or Hg) at $-30^\circ C$ to yield the explosive complex $VOPhCl_2$ ⁽⁷⁾. Analogous alkoxide complexes can be prepared from $VO(OR)_3$ ($R = Pr^i, Bu^t$ or Bu^n) ⁽⁸⁾, which are thermally unstable. The alkoxide ligands in $VO(OCH_2CMe_3)_3$ can also be exchanged for N_3^- by reaction with N_3SiMe_3 to give $VO(OCH_2CMe_3)(N_3)_2$ ⁽⁹⁾.

A variety of oxovanadium compounds containing cyclopentadienyl ligands are known and are of interest because they combine a very hard ligand, oxygen, with an organic ligand which is usually regarded as soft. Reaction of Cp^*VCl_2 ($Cp^* = \eta^5-C_5(CH_3)_5$) with NO yields two products - Cp^*VOCl_2 and $[Cp^*VCl(\mu-O)]_4$ ⁽¹⁰⁾. The former was the first organometallic complex containing a $V=O$ unit to be structurally characterised. Other examples of organometallic compounds containing $V=O$ terminal units are observed in the preparation of VX_3Cp ($X = Cl, Br$) where the ready reaction with oxygen of the trihalide gives

$[\text{VOX}_2\text{Cp}]$ (11).

Peroxo complexes of vanadium containing either the $[\text{VO}(\text{O}_2)]^+$ or $[\text{VO}(\text{O}_2)_x]^-$ moieties can be prepared and these are shown in Table 1.1, together with some other vanadium peroxo species.

The hydroxylamido complex $\text{O}[\text{VO}(\text{Et}_2\text{NO})_2]_2$ can be prepared from NH_4VO_3 and Et_2NOH in aqueous solution (18) and has been shown to have a peroxo-type structure. This is consistent with the fact that hydroxylamine and hydrogen peroxide are isoelectronic. This fact is also used to propose a structure for $[\text{VO}(\text{Et}_2\text{NO})_2(\text{C}_2\text{O}_4)]$ (I) which is the product from the reaction of $\text{O}[\text{VO}(\text{Et}_2\text{NO})_2]_2$ with oxalic acid (18).



Strong acidification of vanadates leads to the formation of the ion, cis- $[\text{VO}_2(\text{H}_2\text{O})_4]^+$. Other dioxyvanadium complexes can be obtained by displacement of the water molecules e.g., $[\text{VO}_2\text{Cl}_4]^{3-}$, $[\text{VO}_2(\text{edta})]^{3-}$ and $[\text{VO}_2(\text{C}_2\text{O}_4)_2]^{3-}$. In common with other d^0 systems, a cis arrangement is favoured for the $\text{V}=\text{O}$ units as this allows better $\text{Opr} \rightarrow \text{Mdr}$ bonding than a linear arrangement would.

Finally, in this brief survey of vanadium(V) chemistry, it is possible to transform the $\text{V}=\text{O}$ unit into $\text{V}=\text{NR}$, as in the reaction of VOCl_3 with phenylisocyanate where the product is $\text{PhN}=\text{VCl}_3$ (19). The

TABLE 1.1 SOME PEROXO VANADIUM SPECIES

| $[\text{VO}(\text{O}_2)]^+$ | $[\text{VO}(\text{O}_2)_x]^-$ | $\text{V}(\text{O}_2)_x$ |
|--|--|---|
| $\text{M}_3[\text{VO}(\text{O}_2)(\text{edta})] \cdot x\text{H}_2\text{O}$ (12) (M = K, Na or NH_4 ; x = 2 or 3) | $\text{K}[\text{VO}(\text{O}_2)_2(\text{H}_2\text{O})]$ (14) | $[\text{V}(\text{O}_2)_3\text{Cl}]^{2-}$ (16) |
| $\text{VO}(\text{O}_2)(\text{OR})$ (13) | $[\text{VO}(\text{O}_2)_2(\text{NH}_3)]^-$ (15) | $[\text{V}(\text{O}_2)(\text{tar})]^-$ (17) |
| $[\text{VO}(\text{O}_2)(\text{dipic})(\text{H}_2\text{O})]^-$ | $\text{K}_2[\text{VO}(\text{O}_2)(\text{C}_2\text{O}_4)_2]$ (14) | |
| | $\text{K}_3[\text{VO}(\text{O}_2)_2(\text{C}_2\text{O}_4)]$ (14) | |
| | $\text{K}_3[\text{VO}(\text{O}_2)_2(\text{CO}_3)]$ (14) | |

tert-butyl analogue can also be synthesised ⁽²⁰⁾.

1.2.2. Oxidation State +4 (d^1)

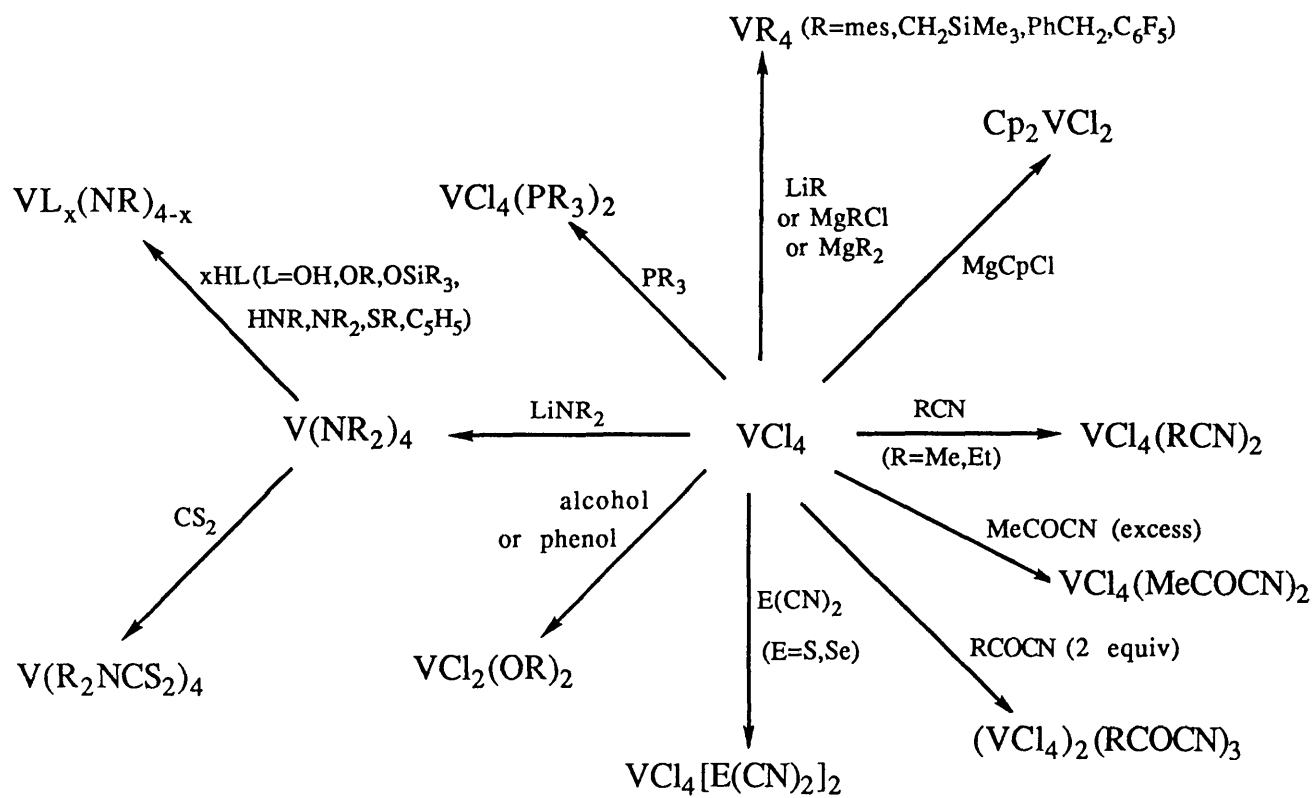
Although vanadium(IV) chemistry is, like vanadium(V), dominated by oxygen compounds containing the VO^{2+} unit, the halide, VCl_4 , undergoes several reactions which result in non-oxygen-containing products. Some of these reactions are summarised in Scheme 1.1.

Another group of vanadium(IV) complexes which do not incorporate the VO^{2+} unit, are those of general formula Cp_2VX_2 , where X represents a variety of anionic and dianionic ligands ⁽⁴⁾. The most synthetically useful of these is VCl_2Cp_2 , which is prepared from VCl_4 and $MgCpCl$. Either one or both of the chlorides can be replaced by alkyl ligands ⁽⁴⁾ to yield $VClRCp_2$ ($R = Me, CH_2SiMe_3$) and VR_2Cp_2 ($R = Me, Et, CH_2SiMe_3$). Original difficulties in synthesising these complexes were thought to be due to steric effects resulting from the relatively small size of the vanadium atom, thus leading to $VRCp_2$ ⁽²¹⁾. However, it is now obvious that the type of alkylating agent and the solvent used are critical to the success of these reactions. Analogous aryl complexes have not been isolated, but VCl_2Cp_2 reacts with dilithio salts of biphenyl and substituted biphenyls to give metallocycles ⁽²²⁾. The chlorides of Cp_2VCl_2 can be replaced by numerous other species such as $SiCl_3^-$, E_5^{2-} ($E = S, Se$), SR^- , $\bar{C}\equiv CR$.

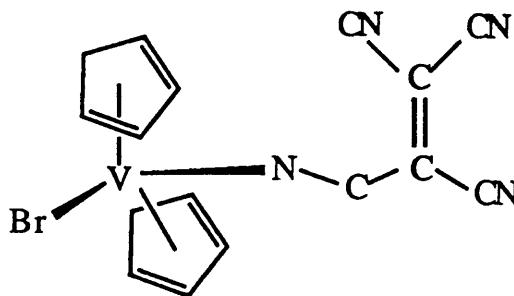
The complex $VX(TCNE)Cp_2$ ($X = Cl, Br$ or I) can be prepared from $VXCp_2$ and TCNE. This is the only example of an N-bonded TCNE ligand (II) and the low values of the $\nu(CN)$ and $\nu(CC)$ absorptions in the IR spectrum suggested that the complex might be regarded as containing $[TCNE]^-$, bonded to vanadium(IV). However since the compound is

SCHEME 1.1.

SOME REACTIONS OF VCl_4



diamagnetic, this is really only a formalism (23).



(II)

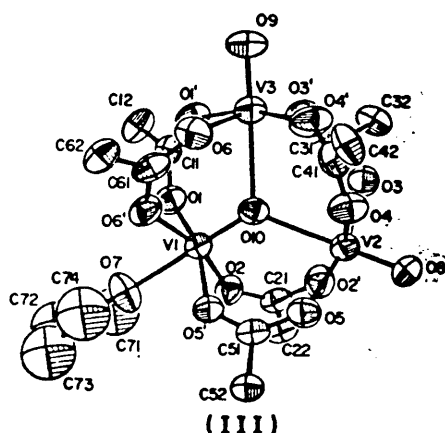
As mentioned earlier, the vast bulk of vanadium(IV) compounds contain the unit VO^{2+} . This is considered the most stable oxycation of the first row transition ions and forms numerous stable anionic, cationic and neutral complexes with all types of ligands. These complexes have several general characteristics : (1) blue in colour, with the exception of certain Schiff bases which can be yellow or maroon; (2) an e.s.r. spectrum with characteristic g values and ^{51}V hyperfine coupling (8 lines); (3) a strong V-O stretching band in the IR in the range $950\text{-}1000\text{ cm}^{-1}$; (4) typically have square pyramidal or bipyramidal structures with the vanadyl oxygen apical. In some cases, five coordinate complexes adopt a trigonal bipyramidal configuration.

These species will be discussed no further here except to mention reactions in which the VO^{2+} unit is destroyed. Complexes $\text{VO}(\text{L})_n$ (L = tetradentate or two bidentate ligands, e.g., acac) react with SOX_2 (X = Cl (24), Br (25)) or PCl_5 (24) to produce $\text{VX}_2(\text{L})_n$. The VBr_2^{2+} unit is also formed in the reaction of $\text{VO}(\text{L})$ (L = Schiff's base) with Ph_3PBr_2 . Treatment of these oxo-Schiff's base species with B_2S_3 results in $\text{VS}(\text{L})$ (26). The thiolate complex $[\text{VS}(\text{SCH}_2\text{CH}_2\text{S})_2]^{2-}$ can be made from $[\text{VO}(\text{SCH}_2\text{CH}_2\text{S})_2]^{2-}$ and $(\text{Me}_3\text{Si})_2\text{S}$ (27). Recently,

the VPh_2^{2+} unit has been prepared from $VO(salen)$ ($salen =$ bis(salicylaldehyde)ethylenediiminato), via $VCl_2(salen)$. Reaction of $VCl_2(salen)$ with phenyl lithium yields $[VPh_2(salen)].MeOH$, the first thermally stable organovanadium(IV) complex (28).

The vanadyl bond can also be cleaved by dithiocarboxylates, RCS_2^- , in water or ethanol to give the eight coordinate air-stable complexes, $V(RCSS)_4$ (29).

Finally, an unusual oxovanadium(IV) complex, $V_3(O)_3(thf)(PhCO_2)_6$ has been prepared from the reaction of $VCl_3(thf)_3$ and sodium benzoate in CH_2Cl_2 (30). This trimeric oxovanadium(IV) structure (III) has the unprecedented feature of a bridging oxovanadium(IV) group, with O(10) serving weakly, but significantly, as a donor to both V(2) and V(3).



It is probable that oxidation of an intermediate trimeric vanadium(III) benzoate complex occurred during crystallization.

1.2.3. Oxidation State +3 (d^2)

Although vanadium complexes in oxidation state +3 tend to be air-sensitive, a reasonable number of compounds have been isolated and characterised. Most organometallic vanadium species in this oxidation

state are stabilised by the presence of one or two cyclopentadienyl ligands. As mentioned in the previous section, complexes VRCp_2 have been isolated, where $R = \text{Pr}^{\text{n}}$, Ph, C_6F_5 , $2\text{-MeC}_3\text{H}_4$, C_5H_5 , $\text{C}\equiv\text{CMes}$. Several methods ⁽³¹⁾ are available for the synthesis of these compounds - either from VClCp_2 or VCl_2Cp_2 with the appropriate lithium or Grignard reagent or from vanadocene with the appropriate alkyl halide. The latter method requires the use of excess vanadocene to prevent the formation of VXCp_2 ($X = \text{halide}$) and RR .

A variety of vanadocene derivatives of the form VXCp_2 can be synthesised where $X = \text{SR}$ ($R = \text{Me, Et, Bz, Ph, Bu}^{\text{t}}$), $\text{N}(\text{SiMe}_3)_2$, SnEt_3 , GeR_3 ($R = \text{Et, Ph, Pr}^{\text{i}}$). A thiogermyl derivative can be prepared from $\text{V}(\text{GeEt}_3)\text{Cp}_2$ and HSGeEt_3 or elemental sulphur ⁽³²⁾.

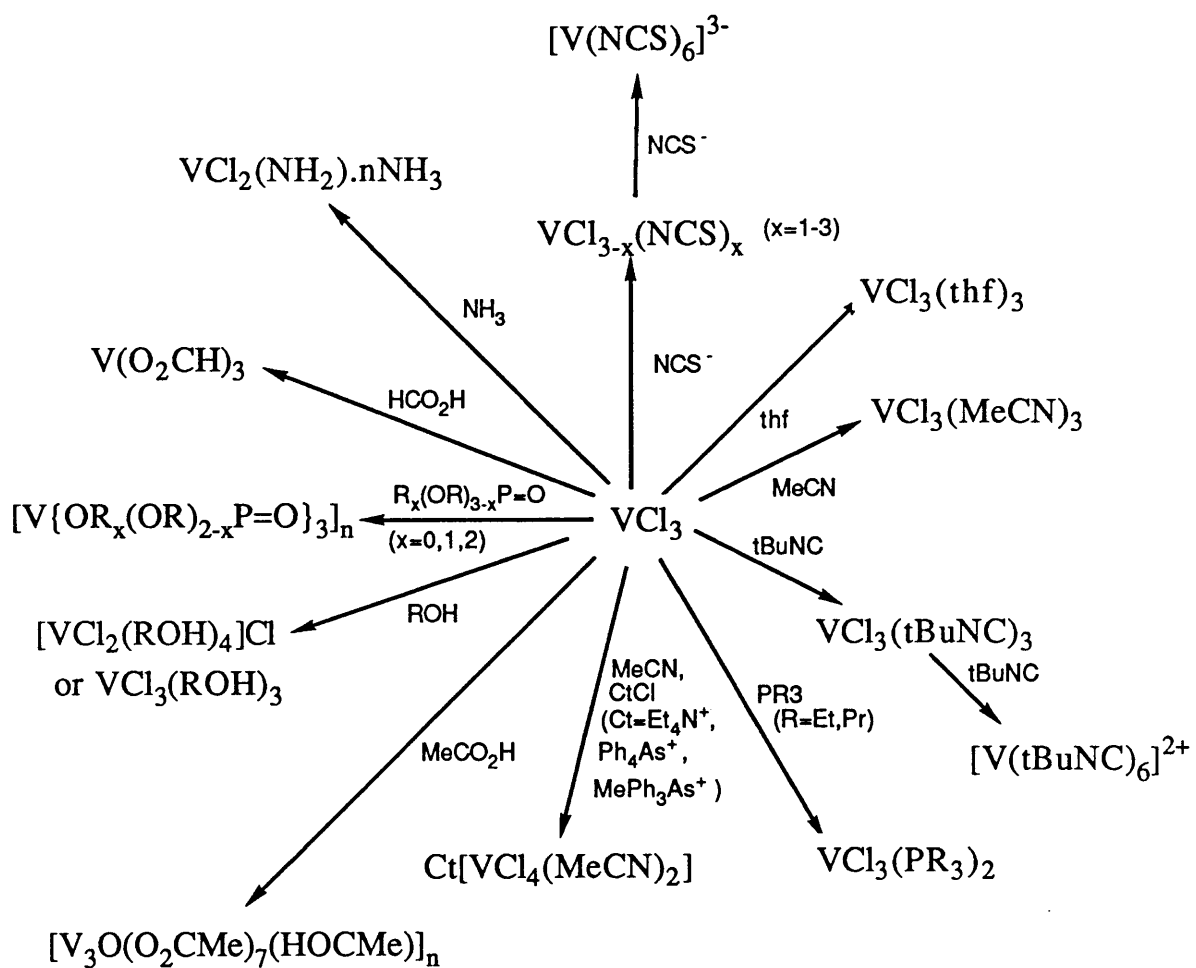
The cation $[\text{VCp}_2]^+$ has been reported ⁽³³⁾ but can only be isolated as a solvated species in the absence of a coordinating anion such as Cl^- or Br^- . This is also true for the permethylated species and demonstrates the coordinative unsaturation of metallocenes with a 14e configuration ⁽³⁴⁾.

Recently interest has been shown in the mono-cyclopentadienyl derivatives of vanadium because they are less sterically encumbered and offer more metal orbitals for transformations of coordinated ligands than the bis species. Of particular usefulness are the complexes of the form $\text{CpVX}_2(\text{PR}_3)_2$ ($X = \text{Cl, Br; R} = \text{Me, Et}$), which may be easily prepared from $\text{VX}_3(\text{PR}_3)_3$ and Cp_2Mg in tetrahydrofuran ⁽³⁵⁾. The chloride ligands in the trimethylphosphine complex can be replaced by alkyl and aryl groups to yield $\text{CpVR}_2(\text{PMe}_3)_2$ ($R = \text{Me, Ph}$) ⁽³⁶⁾.

A great many vanadium(III) coordination compounds are prepared from the vanadium(III) halides, VCl_3 and VBr_3 . Some of these reactions are shown in Scheme 1.2. The compound $\text{VCl}_3(\text{thf})_3$ is also a

SCHEME 1.2.

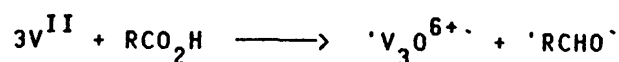
SOME REACTIONS OF VCl_3



useful starting material and provides a route to the phosphine complexes $\text{VCl}_3(\text{dmpe})_2(\text{thf})$ ⁽³⁵⁾ and $\text{VCl}_3(\text{PMePh}_2)_2$ ⁽³⁷⁾, which are inaccessible from VCl_3 . Vanadium(III) complexes containing a variety of sulphur ligands have been reported. $\text{VBr}_2 \cdot 6\text{H}_2\text{O}$ can be oxidised by diethylammonium dialkylthiocarbamates to give $[\text{V}(\text{S}_2\text{CNR}_2)_3]$ ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^n$ or Bu^i) ⁽³⁸⁾ and 'pure' dithiolate complexes of vanadium, $\text{Ct}[\text{V}_2(\text{SCH}_2\text{CH}_2\text{S})_4]$ ($\text{Ct} = \text{Et}_4\text{N}^+, \text{Ph}_4\text{P}^+$) ⁽³⁹⁾. The vanadium atoms are bridged by the four S atoms of the two dithiolate ions and the distance between the two vanadium atoms ($2.60 \pm 0.02 \text{ \AA}$) suggests metal-metal bonding, which is confirmed by the observed diamagnetism.

The remarkable seven coordinate vanadium(III) complex $\text{K}_4[\text{V}(\text{CN})_7]$ is known, and has a pentagonal bipyramidal structure ⁽⁴⁰⁾. The coordination number seven is unusual with monodentate ligands and the structure has been rationalised in terms of the 'nine-orbital' or '18-electron' rule ⁽⁴⁰⁾.

In addition to the carboxylate complexes shown in Scheme 1.2. it is possible to synthesise a series of mixed-valence oxo-centered clusters of the formula $\text{V}_3\text{O}(\mu\text{-O}_2\text{CR})_6 \cdot \text{L}_3$ ($\text{R} = \text{CF}_3, \text{Me}$ or CClH_2) from the reaction of either $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6][\text{Zn}_2\text{Cl}_6]$ or $\text{VCl}_3(\text{thf})_3$ with an appropriate carboxylic acid salt ⁽⁴¹⁾. All the compounds formed have formal oxidation states II,III,III or III,III,III even when vanadium(II) starting materials are employed. It is proposed that there is a strong thermodynamic tendency on the part of V(II) to abstract oxygen from the carboxyl function as shown below:



This provides the central oxygen atom in the V_3O -containing product

and also oxidises two-thirds of the V^{II} atoms to V^{III} .

Lastly, interesting binuclear vanadium(III) complexes containing a linear $[VOV]^{4+}$ bridging unit have been prepared. The presence of this unit is rare for V(III) and only two compounds have been structurally characterised - $V_2O(SCH_2CH_2NMe_2)_4$ and $(thf)_3Cl_2VOVCl_2(thf)_3$ (42).

1.2.4. Oxidation State +2 (d^3)

This is the least common oxidation state for vanadium. This is due to the ease with which the complexes are oxidised - there are many examples of applications of vanadium(II) as a reducing agent for a large number of both organic and inorganic species, usually acting as a one-electron reducing agent. Problems are also encountered in characterising vanadium(II) complexes because of contamination by higher oxidation state materials.

Simple octahedral anionic species, $[VX_6]^{4-}$ ($X = CN^-, NCS^-$) are known, as well as cationic compounds, $[VX_6]^{2+}$, with neutral donor molecules such as water, pyridine, acetonitrile, methanol, ammonia, methylamine and *t*-butylisocyanide. Bidentate neutral molecules also bind to the vanadium(II) centre. For example, complexes like $[VL_3]I_2$ ($L = bipy, phen$) can be isolated from solutions of VSO_4 by adding the appropriate ligand and iodine, and are useful starting materials for low-valent vanadium chemistry (43).

Neutral complexes can be prepared, containing a variety of nitrogen ligands, such as $VCl_2(py)_4$, $VCl_2(phen)_2$ etc.. Mani and co-workers have made a series of polypyrazolylborate complexes. The type of compound isolated is dependent on the nature of the ligand

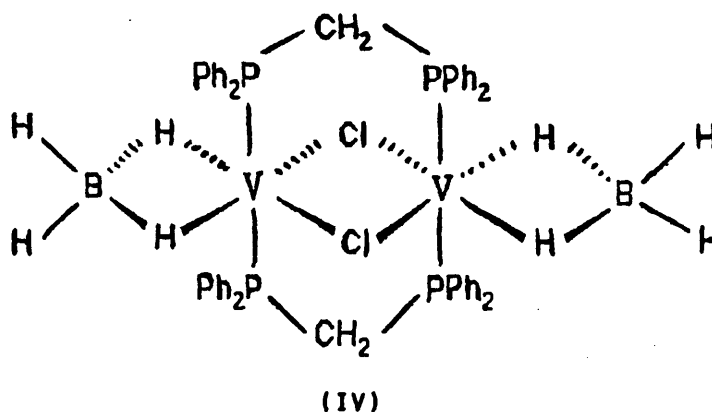
used i.e., the value of n in $H_n B(pz)_{4-n}^-$ ($n = 0, 1, 2$) - neutral species being obtained for $n = 0, 1$ and a monocation for $n = 2$ ⁽⁴⁴⁾.

The most interesting coordination compounds of vanadium(II) - and the ones most relevant to this thesis - are those which contain phosphines.

The dimeric complex $[VCl_2(PEt_3)_2]_2$ can be prepared from the zinc reduction of $VCl_3(PEt_3)_3$ or more conveniently from $[V_2Cl_3(thf)_6]_2^- [Zn_2Cl_6]$ and triethylphosphine. It has a low magnetic moment of 1.98 BM which is consistent with a polymeric structure. The reactivity of this complex towards small neutral molecules such as CO, H_2 , N_2 has been studied by high pressure spectroscopy ⁽⁴⁵⁾ and the results suggest the formation of trans- $V(CO)_2Cl_2(PEt_3)_2$ on prolonged exposure to high pressures of carbon monoxide. No reaction was observed with N_2 or H_2 .

$[V(\mu-Cl)_3(thf)_6]_2 [Zn_2Cl_6]$ can be used to make various other phosphine compounds - both with and without the presence of zinc atoms.

Reaction of the triple chloro-bridged dimer with sodium borohydride and dppm yields, together with other unidentified products, a complex with both bridging chlorine atoms and bridging diphosphinomethane ligands, $[V(\mu-Cl)(\mu-dppm)BH_4]_2$ ⁽⁴⁶⁾ (IV).



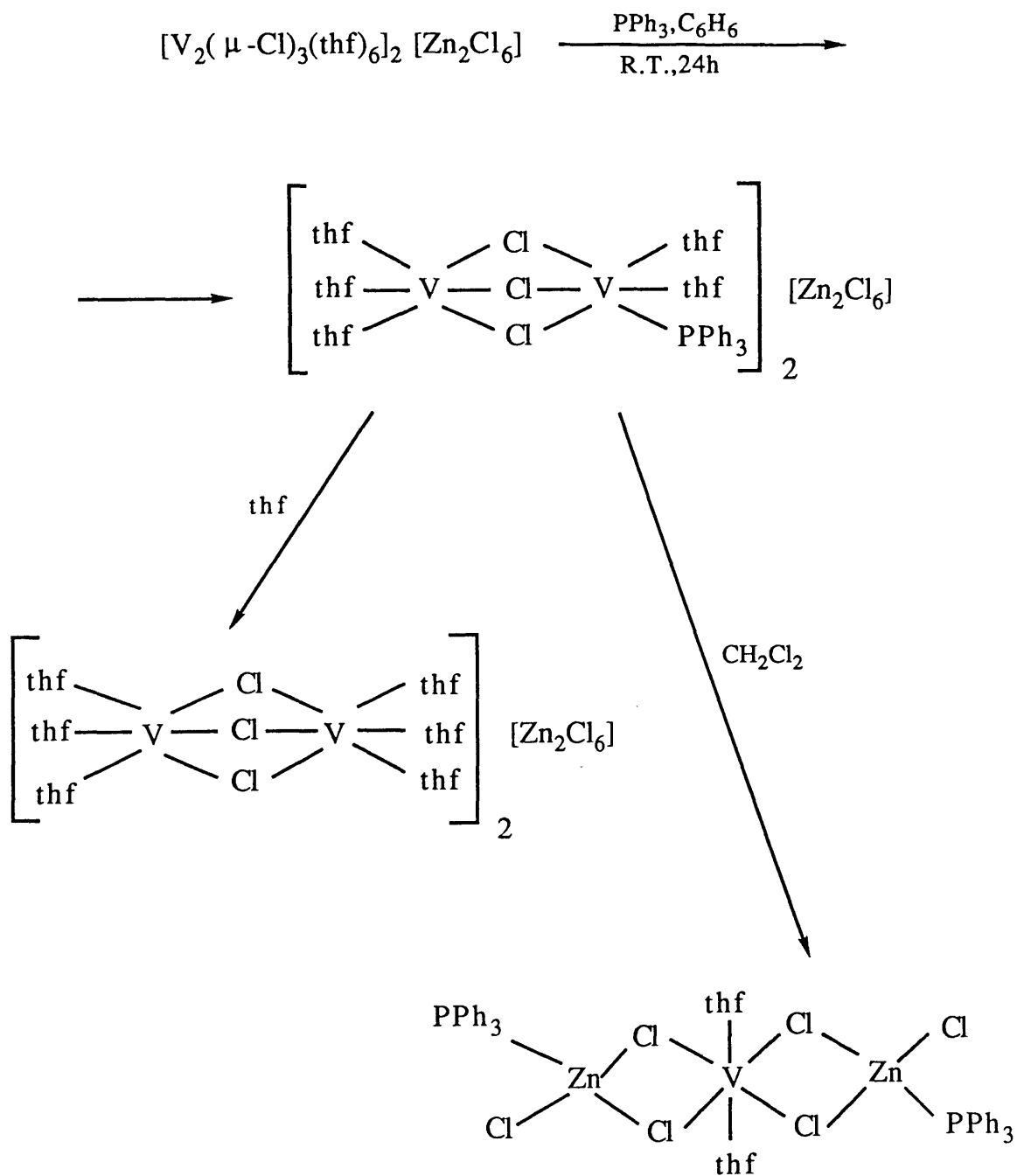
An analogous complex is formed when dmpm is used instead of dppm (47).

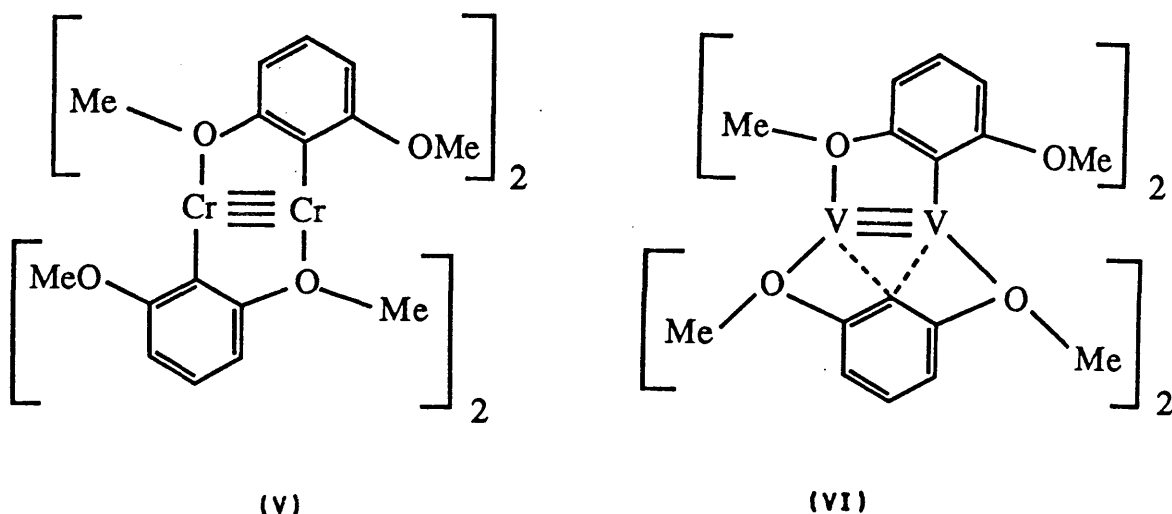
An unusual vanadium(II) complex containing both zinc and vanadium can be obtained from the treatment of $[V_2(\mu-Cl)_3(thf)_6]_2[Zn_2Cl_6]$ with PPh_3 and recrystallisation of the precipitate thus obtained from dichloromethane (48). The product is a bimetallic linear complex, $V[ZnCl_3(thf)(PPh_3)]_2 \cdot 2CH_2Cl_2$. The overall reaction pattern is shown in Scheme 1.3. There is no readily available explanation for this result.

The $[V_2(\mu-Cl)_3(thf)_6]^{2+}$ ion can be prepared using other counter-ions by the reduction of $VCl_3(thf)_3$ in tetrahydrofuran with $AlR_2(OR)$ ($R = Me, Et$) (49). These materials are much more soluble in organic solvents than the analogous zinc complex and could prove synthetically more useful for this reason. Vanadium(II) porphyrins can be synthesised by reduction of the corresponding dihalogenovanadium(IV) complexes. In the presence of phosphine, trans- $V(porph)(PR_3)_2$ ($PR_3 = PMe_2Ph$, porph = oep) (50) can be isolated and this species will react with oxygen to give a vanadyl compound.

The organometallic chemistry of vanadium in oxidation state +2 is dominated by cyclopentadienyl- and carbon monoxide-containing species. An exception to this is $[V_2(dmop)_4] \cdot thf$, prepared from $Li(dmop)$ ($dmop = 2,6$ -dimethoxyphenyl) and $VCl_3(thf)_3$ (51). This was originally thought to have an analogous structure to $Cr_2(dmop)_4$ (V) but in fact has the structure shown in (VI), with two bidentate and two tridentate dmop ligands.

SCHEME 1.3. REACTION OF $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$ WITH PPh_3

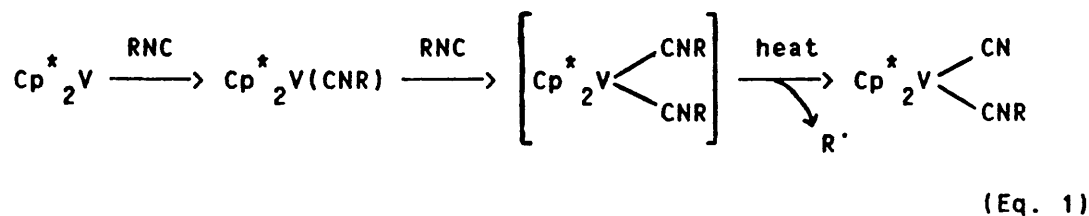




The highly unusual V(II) dianion, $\text{Li}_2[\text{V}(\text{dmop})_4]$, can be made from vanadocene and $\text{Li}(\text{dmop})$ at -30°C in tetrahydrofuran.

The complex central to the organic chemistry of vanadium is vanadocene, VCp_2 , which was the first isolable member of the series of metallocenes. It is an electronically and coordinatively unsaturated molecule with an interesting chemistry which has been reviewed (4).

Several ring-substituted derivatives of vanadocene are known. $(\text{Me}_5\text{C}_5)_2\text{V}$ shows a similar reactivity to vanadocene (34) although there are some differences due to the basic influence of the methyl groups. With isocyanides an unusual free-radical activation of the isocyanide ligand occurs as shown in Eq. 1 (52).

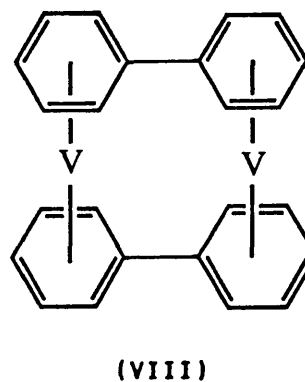
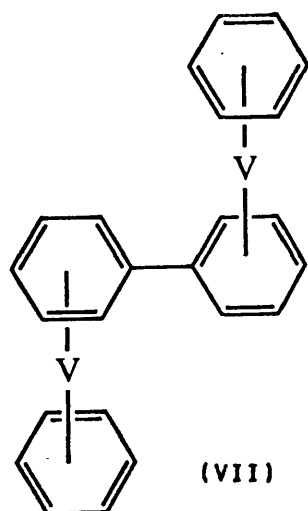


($\text{Cp}^* = \text{C}_5\text{Me}_5$, $\text{R} = \text{tBu}$, C_6H_{11}).

Bis(indenyl)vanadium(II) can be prepared from lithium indenide and $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$. Reaction of this complex with carbon

monoxide yields $(\eta^3\text{-Ind})(\eta^5\text{-Ind})\text{V}(\text{CO})_2$, which is the first structurally characterised example of the slipped η^3 -structure for first-row metals (53).

Dinuclear complexes related to vanadocene have been synthesised. The electron spin-spin interaction in these complexes can range from slight, as in $\mu\text{-}(\eta^6:\eta^6\text{-biphenyl})\text{bis}[(\eta^6\text{-benzene})\text{vanadium}]$ (54) (VII), to extensive, as in $\text{V}_2(\text{fulvalene})_2$ (55) (VIII) which is diamagnetic. Recently, a vanadium sandwich complex, $[\text{Cp}_2\text{V}]_2\text{C}_8\text{H}_8$, has been made which contains vanadium-vanadium metal bonds (56).



Finally, vanadium(II) organometallic complexes containing only one cyclopentadienyl ligand will be briefly mentioned. Reduction of $\text{CpVX}_2(\text{PR}_3)_2$ with zinc or aluminium in tetrahydrofuran yields a series of vanadium(II) species, $[\text{CpVX}(\text{PR}_3)]_2$ (57) ($\text{X} = \text{Cl}, \text{R} = \text{Me}, \text{Et}; \text{X} = \text{Br}, \text{R} = \text{Et}$). Addition of excess phosphine produces $\text{CpVX}(\text{PR}_3)_2$ and treating the dimers with bidentate phosphines gives $\text{CpVCl}(\text{P-P})$ [$\text{P-P} = \text{dmpe}, \text{dppe}$]. Methyl and phenyl derivatives of $\text{CpVCl}(\text{dmpe})$ can be prepared by reaction with MeLi and PhMgBr respectively. $\text{CpVCl}(\text{dmpe})$ can also readily be converted into $\text{CpV}(\text{BH}_4)(\text{dmpe})$, where the borohydride ligand is thought to be bidentate (36).

1.2.5. Oxidation States Below +2

Like vanadium(II), the chemistry of vanadium in these low oxidation states (-3 to +2) is mainly restricted to cyclopentadienyl and carbon monoxide derivatives.

Neutral $V(CO)_6$ is the only example of a stable, paramagnetic binary carbonyl and, together with its anion, $[V(CO)_6]^-$, is a useful starting material in vanadium carbonyl chemistry. $V(CO)_6$ readily disproportionates in the presence of N- and O-donors such as nitriles, aromatic amines, ethers, DMSO, ketones, etc. to form species of the general formula $[VL_n][V(CO)_6]_2$ ($n = 4$ or 6). In donor solvents e.g., Et_2O , a similar reaction occurs in the presence of phosphine but in non-donor solvents, e.g., CH_2Cl_2 , C_6H_6 , hexane, substitution of the carbonyl ligands takes place to give $V(CO)_{6-n}L_n$ ⁽⁴⁾. The degree of substitution is dependent on the reactant ratio and the temperature and full substitution has not been achieved. $[V(CO)_6]^-$ also undergoes substitution reactions but these are photochemically induced as $[V(CO)_6]^-$ is thermally inert to substitution. Some of the substitution products of $V(CO)_6$ and $[V(CO)_6]^-$ are summarised in Table 1.2. All these complexes are air-sensitive and the thermal stability of the neutral complexes increases with increasing n .

The complex $[V(CO)_5(Me_2SO)]^-$ provides an alternative route to pentacarbonylvanadates (-1) containing a wide range of ligands ⁽⁵⁸⁾. The method of ligand exchange, rather than that of photochemical substitution, has the advantages of being more specific and preventing the possibility of side reactions or decomposition.

An interesting derivative of $V(CO)_6$ is the highly reactive, thermally unstable species, $V(CO)_5(NO)$. This was first mentioned in

TABLE 1.2. SOME SUBSTITUTION PRODUCTS OF $V(CO)_6$ AND $[V(CO)_6]^-$

| | $V(CO)_{6-n}L_n$ | $[V(CO)_{6-n}L_n]^-$ | $[V(CO)_{6-n}L_n]^{2-}$ |
|---------|---|---|-------------------------|
| $n = 1$ | PPh_3 | $PPh_3, NH_3, MeCN,$ $py, P_2Cy_4, As_2Ph_4,$ $Sb_2Ph_4, dmso$ | CN |
| $n = 2$ | $PPh_3, PEt_3, PPr_3^{\eta}, PPhH_2$ $SbPh_3$ $L_2 : dppe,$ $PPh_2(2\text{-allylphenyl}),$ $PPh_2(2\text{-cispropenylphenyl}),$ | $L_2 : dmpe, diars,$ $Ph_2P(CH_2)_n PPh_2 (n = 1-4),$ $Fe(\eta^5-C_5H_4EPh_2)_2 (E = P, As),$ $PhP(CH_2CH_2PPh_2)_2,$ $cis-Ph_2PCH = CHPPh_2$ | |
| $n = 3$ | triphos | $P(CH_2CH_2PPh_2)_3,$ $Ph_2P(CH_2)_n PPh(CH_2)_n PPh_2(CH_2)_n PPh_2$ ($n = 2$) | |
| $n = 4$ | $L_2 : dppe$ | | |

the literature over 20 years ago but has only relatively recently been isolated and characterised (59). It undergoes facile reactions with Lewis bases at -30°C to 0°C to yield products $[\text{V}(\text{NO})(\text{CO})_{5-n}\text{L}_n]^z$ ($z = 0$; $n = 1$, $\text{L} = \text{PPh}_3, \text{PMe}_3, \text{NMe}_3$; $n = 2$, $\text{L}_2 = \text{dppe}$. $z = 1$; $n = 1$, $\text{L} = \text{Mn}(\text{CO})_5^-, \text{I}^-$; $n = 3$, $\text{L}_3 = \text{Cp}$).

Seven coordinate complexes $\text{VH}(\text{CO})_{6-n}\text{L}_n$ ($n = 1-4$), where L represents a variety of phosphines such as PPh_3 , dmpe , triphos , etc., can be prepared by treating the appropriate anion $[\text{V}(\text{CO})_{6-n}\text{L}_n]^-$ with water (60). The thermal stability of these species increases with increasing carbonyl substitution, and thus, $\text{VH}(\text{CO})_6$ has not been isolated but is implicated in the formation of $\text{V}(\text{CO})_6$ by the acidification of $[\text{V}(\text{CO})_6]^-$ (61). The only simple methyl analogue of these hydrides is $\text{VMe}(\text{CO})_4$ (diars), isolated from the reaction between $[\text{V}(\text{CO})_4(\text{diars})]^-$ and methyl iodide (60). A series of metal-metal bonded, seven-coordinate complexes of the general formula $\text{V}(\text{ML}_m^1)(\text{CO})_{6-n}\text{L}_n^2$ ($\text{ML}_m^1 = \text{SiH}_3, \text{SnPh}_3, \text{Tl}, \text{HgEt}, \text{Mn}(\text{CO})_5, \text{Au}(\text{PPh}_3)$) have been synthesised from the corresponding anion and metal halide. The hexacarbonyls are air-sensitive but carbonyl substitution with phosphines (L^2) lessens this sensitivity. The metal-metal bonds in these complexes are readily cleaved.

A rare example of an eight-coordinate carbonyl complex, $\text{VH}_3(\text{CO})_3$ (diars) can be prepared from $[\text{V}(\text{CO})_4(\text{diars})]^-$ and excess HX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (62).

$[\text{Na}(\text{diglyme})_2][\text{V}(\text{CO})_6]$ can be used to prepare $\text{V}(\text{CO})_4\text{Cp}$ by the addition of $\text{Hg}(\text{Cp})\text{Cl}$. This complex is the precursor to a wide range of organovanadium complexes. On a large scale it is normally synthesised by high pressure carbonylation of VCp_2 , generated in situ from NaNp and VCl_3 in tetrahydrofuran (63).

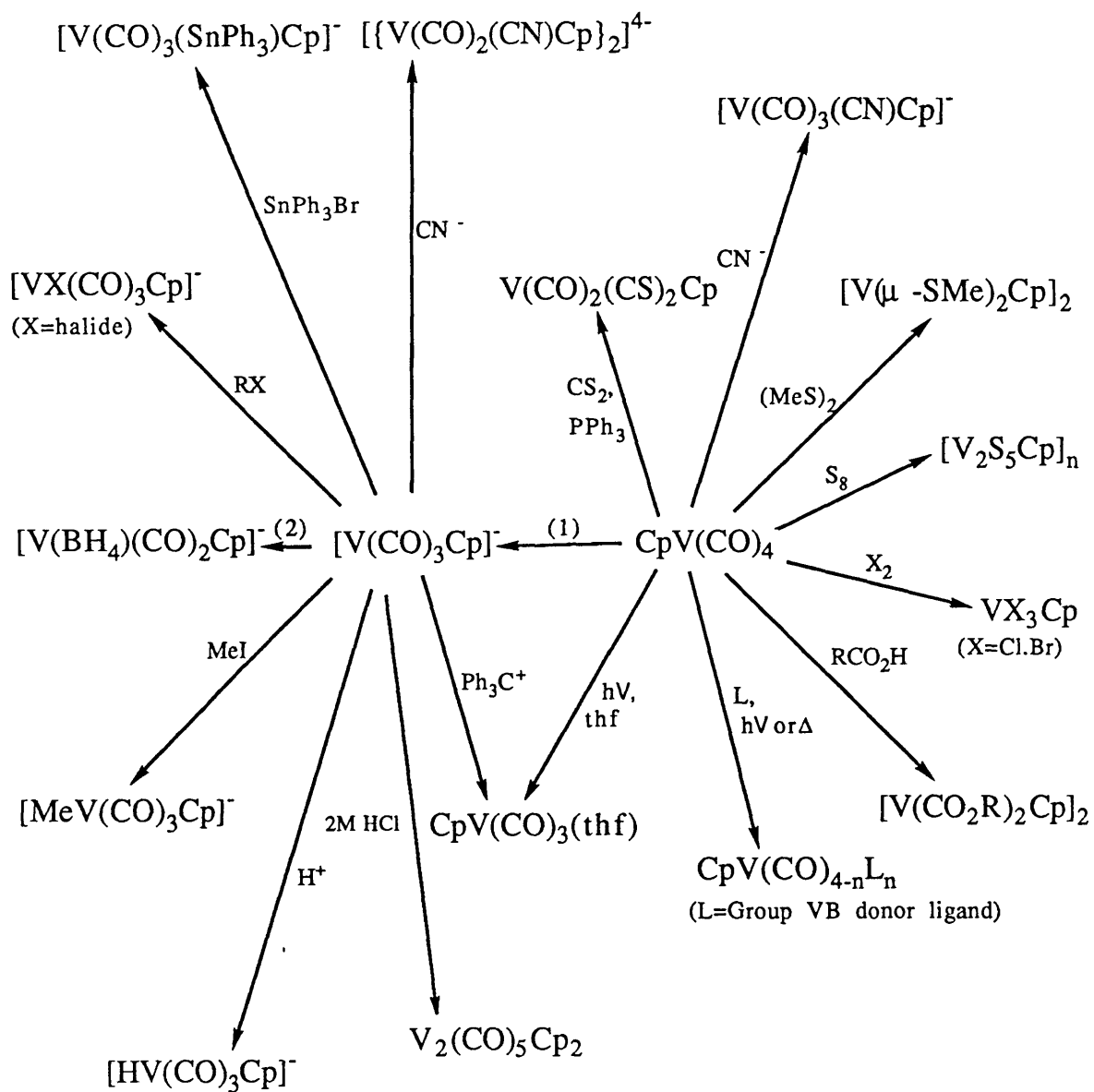
$V(CO)_4 Cp$ undergoes numerous transformations, normally involving the loss of one or more carbonyl ligands. Some of these reactions are summarised in Scheme 1.4., together with some reactions of the dianion, $[CpV(CO)_3]^{2-}$. Neutral derivatives of the $CpV(CO)_3$ unit can be prepared from $CpV(CO)_3(thf)$, and have the general formula $CpV(CO)_3L$ or $CpV(CO)_2(L-L)$ ($L = NCS^-$, NMe , CN^- , $C\equiv CPh^-$, $SnCl_3^-$, H^- , $CpVH(CO)_3^-$; $L-L = PhC\equiv CPh$, phen, bipy) ⁽⁶⁴⁾. Only the compounds with $L = NCS^-$, $TePh_2$, $CNCy$, $N-N$ can be isolated as solids.

Ring-substituted derivatives of $CpV(CO)_4$ can be obtained by a variety of methods. For example, $(\eta^5\text{-indenyl})V(CO)_4$ is isolated from the reaction of $[V(CO)_6]^-$ and $RHgCl$ ($R = \text{indenyl}$) ⁽⁶⁵⁾. Friedel-Crafts acetylation, using acetyl chloride or acetic anhydride affords the complex, $V(CO)_4(\eta^5\text{-C}_5\text{H}_4\text{(OMe)})$ ⁽⁶⁶⁾.

The ligands, bipy, phen and terpy, form a series of vanadium complexes with formal oxidation states from +2 to -3 ⁽⁴³⁾. The preparation and interconversions of the bipy complexes are shown in Scheme 1.5. In these low oxidation state compounds, it is open to question as to whether the electrons of the reduced species are located in the metal orbitals or in the π^* orbitals of the ligand, since reduced forms of bipy ($bipy^-$ and $bipy^{2-}$) are known. Electrochemical studies on $[V(bipy)_3]^z$ ($z = +2$ to -3) suggest that the electron added (or removed) for $z = +2, +1, 0$ was to (or from) the t_{2g} orbitals but that for $V(bipy)_3/V(bipy)_3^-$ and $V(bipy)_3^-/V(bipy)_3^{2-}$ the added electron would occupy orbitals with a predominant π^* character ⁽⁶⁷⁾.

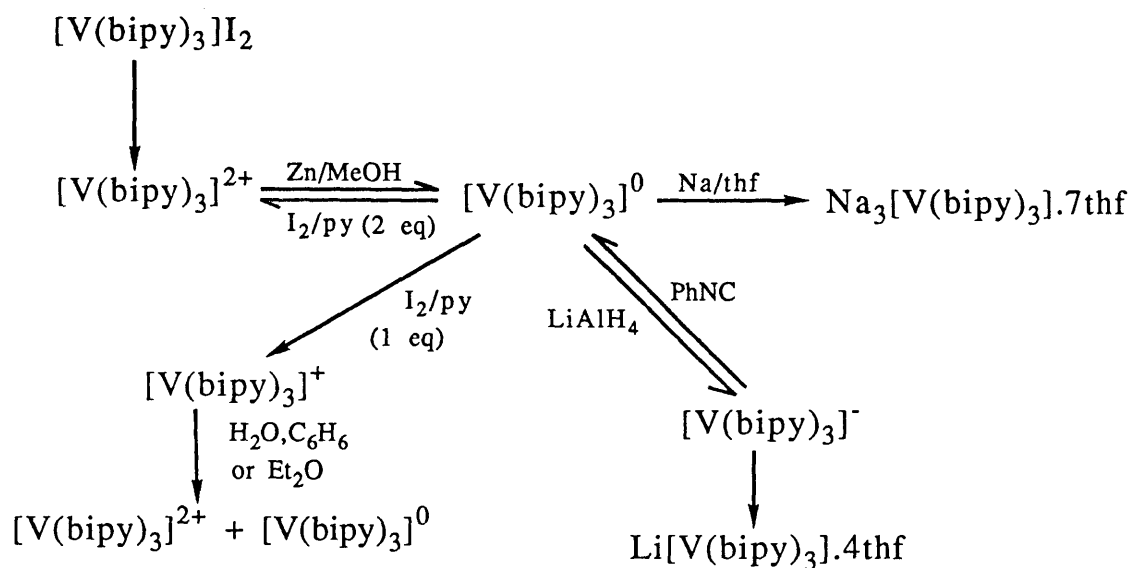
Reduction of VCl_3 with sodium amalgam in the presence of bipy yields $V(bipy)_3$. If the reduction is carried out in an atmosphere of carbon monoxide $V(CO)_4(bipy)$ is formed ⁽⁶⁸⁾. A nitrosyl derivative,

SCHEME 1.4. SOME REACTIONS OF $\text{CpV}(\text{CO})_4$ AND $[\text{V}(\text{CO})_3\text{Cp}]^{2-}$

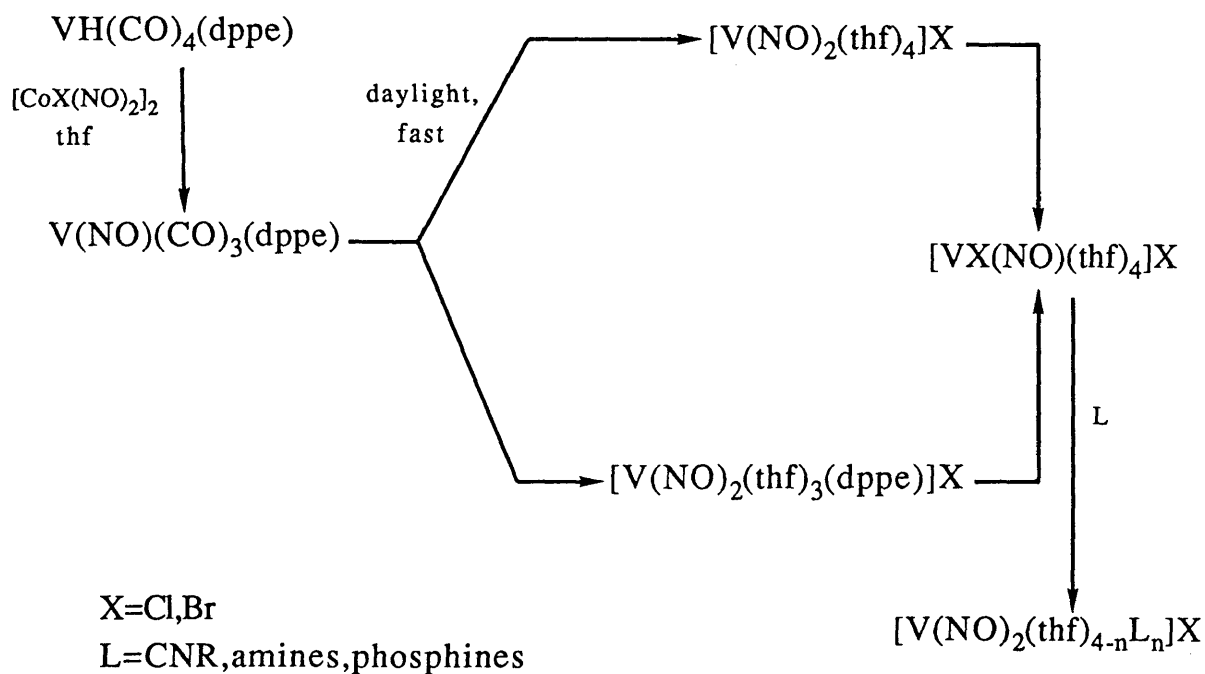


(1) $\text{NH}_3^{(1)}$, 1% Na/Hg, thf
 (2) BH_3

SCHEME 1.5. PREPARATION AND INTERCONVERSIONS OF LOW OXIDATION STATE BIPY COMPLEXES



SCHEME 1.6. PREPARATION OF DINITROSYL COMPLEXES (69)

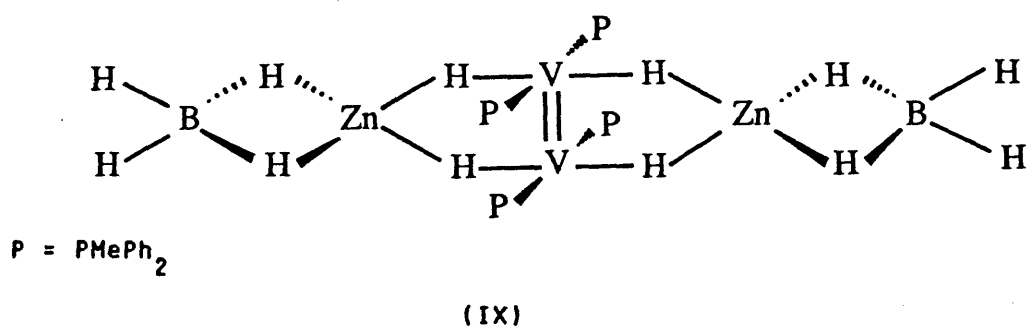


$V(NO)(bipy)_3$ was also isolated. Other nitrosyl complexes of vanadium have been prepared from $HV(CO)_4(dppe)$ using $[Co(NO)_2X]_2$ as the nitrosylating agent (see Scheme 1.6.). The interaction of dry NO and VCl_4 results in a polymeric species, $[V(NO)_3Cl_2]_n$, which loses NO in organic solvents to give mono- or di-nitrosyl complexes, depending on the solvent used. $[V(NO)_2L_2Cl]_n$ (L = MeCN) can be used to prepare $[V(NO)_2(t-BuNC)_4]$ (70).

The slow addition of sodium naphthalenide to a thf solution of VCl_3 and dmpe results in the formation of $V(dmpe)_3$, which can also be prepared in high yield by metal vapour synthesis (71).

$[Et_4N][V(PF_3)_6]$ was obtained from the UV irradiation of a diglyme solution of $[V(CO)_6]^-$ saturated with trifluorophosphine (72). The action of phosphoric acid on $[V(PF_3)_6]^-$ produces the seven-coordinate complex, $HV(PF_3)_6$.

An unusual dimeric vanadium(I) species can be isolated from the reaction of $[V(\mu-Cl)_3(thf)_6]_2[Zn_2Cl_6]$ with $PMePh_2$ followed by addition of $LiBH_4$ (73). The structure of this complex $V_2Zn_2H_4(BH_4)_2(PMePh_2)_4$ (IX) is shown below:



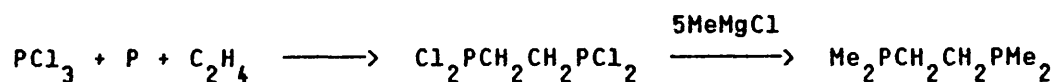
This compound contains a vanadium-vanadium double bond (V-V distance 2.400 Å).

Finally, vanadium tris(dithiolene) complexes can be prepared by

various methods, using VCl_3 , $\text{V}(\text{CO})_6$ or $[\text{V}(\text{CO})_6]^-$ as the starting material. These complexes have the general formula $[\text{V}(\text{S}_2\text{C}_R\text{R}_2)_3]^z$ ($z = 0$ to -3) or $[\text{V}(\text{S}_2\text{C}_6\text{H}_3\text{R})_3]^z$ ($z = -2, -3$), and the charge at the vanadium has been estimated as less than $+2$ (74).

1.3. 1,2-BIS(DIMETHYLPHOSPHINO)ETHANE (dmpe)

Dmpe was originally prepared by a method involving biologically active phosphorus-sulphur derivatives but is now synthesised from PCl_3 as shown in Eq. 2 (75).



(Eq. 2)

Dmpe has two characteristics which make it a particularly useful ligand in the preparation of first-row transition metal complexes.

Firstly, it is more basic *i.e.*, electron-releasing, than most tertiary phosphines, leading to compounds with electron-rich metal centres. This basicity, combined with its chelating ability, has allowed the isolation of electronically and sterically unsaturated compounds such as $\text{TiEtCl}_3(\text{dmpe})$ (76), which is formally a twelve electron species. An X-ray study showed that the β C-H bond of the ethyl group was activated towards the titanium centre.

Secondly, dmpe primarily acts as a chelating ligand although examples of bridging dmpe ligands are known (77), (78). This chelating ability is enhanced by a small cone angle ($\phi = 108^\circ$) and bite angle (82.5°). This enables it to stabilise compounds with a

high coordination number, as in the paramagnetic hydrides $MH_2X_2(dmpe)_2$ ($M = Nb, Ta$)⁽⁷⁹⁾. The chelating nature of dmpe has been used to stabilise and isolate otherwise labile molecules, where the use of monodentate phosphines has failed. This is illustrated by the isolation of $M(\eta-C_4H_6)_2(dmpe)_2$ ($M = Hf, Zr$)⁽⁸⁰⁾ when attempts to isolate the trimethylphosphine analogues were unsuccessful.

CHAPTER 2

SYNTHESIS AND REACTIONS OF TRANS- $\text{VCl}_2(\text{dmpe})_2$
AND RELATED COMPLEXES

2.1. INTRODUCTION

In contrast to the second and third row transition metals, phosphine complexes of the early first-row elements are relatively rare (81). Whereas for niobium and tantalum, the pentahalides, MCl_5 ($M = Ta, Nb$), provide useful starting materials for the synthesis of complexes MCl_2L_4 ($L = PMe_3, L_2 = dmpe$) (79) via the tetrahalide phosphine adducts, the preparation of vanadium analogues has been hampered by the lack of such suitable, i.e., easily prepared, starting materials.

One complex which has exhibited some potential in this direction is $[V_2(\mu-Cl)_3(thf)_6]_2[Zn_2Cl_6]$, which was initially thought to be the simple monomeric species, $VCl_2(thf)_2$ (82). The zinc reduction of this compound in the presence of triethylphosphine leads to the dimeric species $[VCl_2(PEt_3)_2]_2$ (45), and reaction with triphenylphosphine results in the substitution of one of the thf ligands with PPh_3 (48). It has also been used in the preparation of other dinuclear compounds with bridging chloride ions, bridging diphosphine and bidentate tetrahydroborates: $[V(\mu-Cl)(\mu-diphos)BH_4]_2$ (diphos = $dppm$ (46), $dmpm$ (47)).

In contrast to these slightly unusual reactions, $[V_2(\mu-Cl)_3(thf)_6]_2[Zn_2Cl_6]$ interacts with two equivalents of $dmpe$ in toluene at room temperature to give an intense purple solution, from which red-orange prisms of trans- $VCl_2(dmpe)_2$ can be isolated in good yield (83).

In light of recent work with the analogous chromium complex, trans- $CrCl_2(dmpe)_2$, which undergoes a variety of substitution and reduction reactions (83), (84), (85), it was thought that trans-

$\text{-VCl}_2(\text{dmpe})_2$ might provide a convenient gateway to low-valent vanadium phosphine chemistry. One particularly interesting reaction of trans- $\text{-CrCl}_2(\text{dmpe})_2$ was the formation of the air-stable complex $\text{Cr}(\text{N}_2)_2(\text{dmpe})_2$ ⁽⁸⁴⁾. The only evidence for a dinitrogen species for the Group 5 transition metals which has been reported is from the reduction of $\text{NbCl}_4(\text{dmpe})$ with magnesium⁽⁸⁶⁾, and it was hoped that trans- $\text{VCl}_2(\text{dmpe})_2$ might facilitate the preparation of a dinitrogen compound analogous to the chromium complex.

In addition, the ready reaction of $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$ with dmpe led to the study of similar reactions using other bidentate and monodentate phosphines.

2.2. RESULTS AND DISCUSSION

2.2.1. Reactions of $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$:

(a) with dmpe

The interaction of two equivalents of dmpe with $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$ in toluene led to the isolation of orange-red prisms of trans- $\text{VCl}_2(\text{dmpe})_2$ ⁽⁸³⁾. This compound is moderately air-stable in the solid state when dry but appears to be slightly hygroscopic, and has an increased sensitivity to aerial oxidation when in solution.

It is paramagnetic, as expected, and has an effective magnetic moment of 3.7 B.M. indicating the presence of three unpaired electrons. The e.s.r. spectrum (toluene, 77 K) exhibits two broad low-field features at ca. 140 and 240 mT, and several weaker features out to ca. 1000 mT: no hyperfine structure can be seen. However at room temperature, an isotropic spectrum can be obtained which yields the

values $A(^{51}\text{V}) = 0.0079 \text{ cm}^{-1}$ and $A(^{31}\text{P}) = 0.0025 \text{ cm}^{-1}$. The ^1H n.m.r. in d_6 -benzene shows two broad singlets at -25.9 p.p.m. (PMe_2) and -9.8 p.p.m. (PCH_2). The trans-dihalide geometry has been confirmed by an X-ray crystallographic study (83).

(b) with dppe

The reaction of $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$ with two equivalents of dppe in dichloromethane or refluxing toluene produced a yellow-green solution from which green crystals could be isolated. The infrared spectrum exhibited bands which indicated the presence of dppe. Elemental analysis suggested that the complex could be formulated as $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_2(\text{dppe})_2]_2[\text{Zn}_2\text{Cl}_6]$. Unfortunately further experimental data e.g., conductivity measurements, e.s.r. etc., could not be obtained due to the apparent instability of the complex in organic solvents, which led to the precipitation of free dppe.

The contrast in the nature of the products obtained from reaction of $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$ with dppe and dmpe - both bidentate, chelating phosphines - could be a consequence of the difference in the relative basicities of the two ligands. Dmpe, being the more electron-donating of the two, binds more strongly to the electron-poor metal centre and thus forms a stable monomeric species unlike dppe, which merely replaces some of the coordinated tetrahydrofuran molecules.

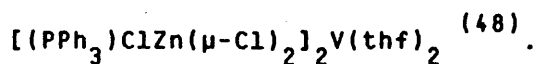
(c) with PMe_3

Stirring a toluene suspension of $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$ with an excess of trimethylphosphine produced a pink precipitate.

Extraction of the precipitate into dichloromethane followed by extended cooling of the solution led to the isolation of a purple crystalline solid. The infrared spectrum showed bands due to PMe_3 at 1435 and 1420 cm^{-1} . Conductivity measurements and elemental analysis suggested that replacement of all the tetrahydrofuran ligands by trimethylphosphine had occurred to yield $[\text{V}_2(\mu\text{-Cl})_3(\text{PMe}_3)_6]_2[\text{Zn}_2\text{Cl}_6]$.

This species is analogous to the known compound, $[\text{V}_2(\mu\text{-Cl})_3(\text{PMe}_3)_6][\text{AlEt}_2\text{Cl}_2]$, which was prepared from the reaction of $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6][\text{AlEt}_2\text{Cl}_2]$ with trimethylphosphine in tetrahydrofuran. The structure of the cation has been confirmed by X-ray crystallographic analysis (49).

No reaction was observed between $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$ and PPh_2Me or dppm [1,2-bis(diphenylphosphino)methane]. However when a solution of $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$ in tetrahydrofuran is stirred with two equivalents of dmpm [1,2-bis(dimethylphosphino)methane] an extremely air-sensitive, inhomogeneous green precipitate is obtained. Extraction of this solid into dichloromethane results in a purple solution. If the same reaction is performed in dichloromethane a purple solution forms immediately, from which small amounts of blue solid can be isolated by the addition of hexane. Infrared data and elemental analysis suggest that the product does contain dmpm , in addition to a large percentage of chlorine. At the present time the experimental data available does not allow speculation as to the identity of either the green or blue solids, but our preliminary work clearly indicates that this is a reaction of some complexity and well worth a more detailed investigation. Unusual products have previously been observed from the interaction of phosphine adducts of $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$ and dichloromethane e.g.,



The interaction of $[V_2(\mu-Cl)_3(thf)_6]_2[Zn_2Cl_6]$ with the bidentate N-donor ligands, tetramethylethylenediamine (tmeda) or 2,2'-bipyridyl, produces, in both cases, intense blue-green dichloromethane solutions. However these solutions quickly become purple, even at low temperature under an argon atmosphere, and no isolatable products were obtained.

2.2.2. Reactions of trans- $VCl_2(dmpe)_2$

The reactions of trans- $VCl_2(dmpe)_2$ can be divided into two general types. Firstly, the halide ligands can be substituted for some other charged or neutral ligand, yielding species in which the oxidation state of the metal is unchanged i.e., vanadium(II) (d^3). Secondly, the metal centre can be reduced with an excess of sodium amalgam in the presence of a neutral ligand. These reactions are summarised in Scheme 2.1.

(a) Substitution Reactions

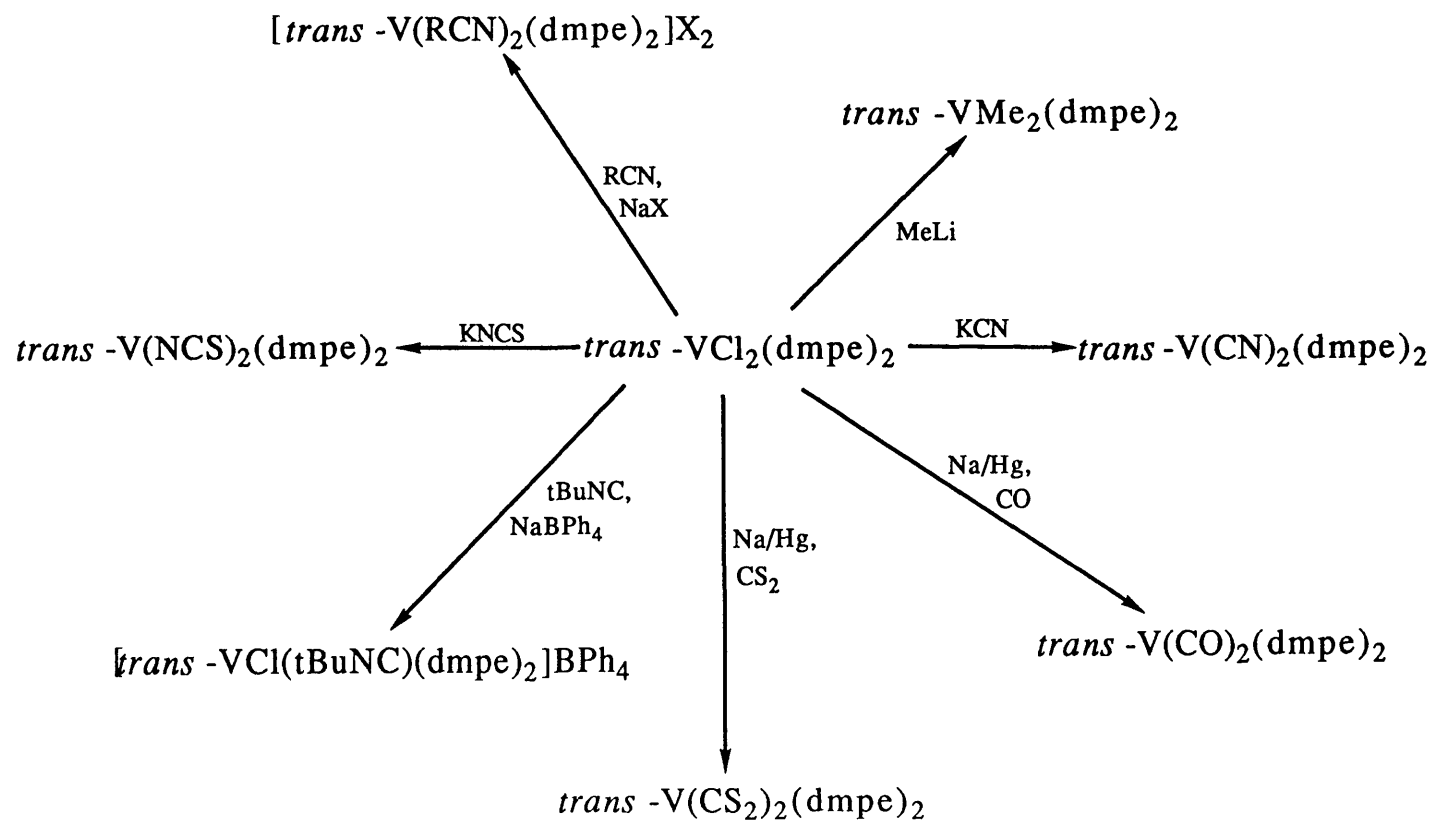
(i) MeLi

Treatment of trans- $VCl_2(dmpe)_2$ with two equivalents of methyl lithium in diethylether yielded the monomeric dark yellow complex trans- $VMe_2(dmpe)_2$ ⁽⁸³⁾. This was the first example of a vanadium(II) alkyl complex which does not contain a cyclopentadienyl ligand, although the benzyl compound $Li_2V(CH_2Ph)_4$ has been claimed ⁽⁸⁷⁾.

The dimethyl complex is paramagnetic with an effective magnetic moment of 3.7 B.M., which suggests a d^3 configuration with three unpaired electrons. The frozen e.s.r. spectrum in toluene is similar to its chloride analogue and the 1H n.m.r. (d_6 -benzene) exhibited two

SCHEME 2.1. REACTIONS OF TRANS-VCl₂(dmpe)₂

47



broad peaks at -13.5 p.p.m. (PMe_2) and 11.7 p.p.m. (PCH_2). No resonance was observed for the metal-bound methyl groups : presumably because they experience very large contact shifts due to their proximity to the paramagnetic vanadium centre.

The i.r. spectrum showed a low C-H stretching frequency at 2760 cm^{-1} which is probably the result of the electropositive nature of the metal centre i.e., electron-deficient which polarises the M-C bond and thus alters the C-H bond density. Unfortunately no crystallographic data can be obtained for trans- $\text{VMe}_2(\text{dmpe})_2$ (83).

(ii) $\text{RCN}(\text{R} = \text{Me, Et})$

When trans- $\text{VCl}_2(\text{dmpe})_2$ is stirred with two equivalents of NaBPh_4 in acetonitrile or propionitrile, dark red solutions are obtained from which the complexes $[\text{V}(\text{MeCN})_2(\text{dmpe})_2][\text{BPh}_4]_2$ and $[\text{V}(\text{EtCN})_2(\text{dmpe})_2][\text{BPh}_4]_2$ can be isolated respectively. The acetonitrile compound can also be isolated as the hexafluorophosphate salt by substituting NaPF_6 for NaBPh_4 . Both these complexes are moderately air-sensitive, red crystalline solids which are paramagnetic with effective magnetic moments of ca. 3.4 B.M.. The slightly low values (μ_{eff} for 3 unpaired electrons = 3.87 B.M.) are attributed to contamination of the products by residual sodium chloride.

Both complexes exhibit a weak band in their i.r. spectra at ca. 2250 cm^{-1} which is attributed to ν_{CN} of the nitrile ligands : the frequency of ν_{CN} being slightly lower for the propionitrile species. These values are lower than would be expected for coordinated nitriles, since coordination to a metal centre normally increases ν_{CN} , with respect to ν_{CN} for the free organonitrile, but this fact probably reflects the strongly electron-releasing nature of the dmpe ligands.

Conductivity measurements confirm that the compounds are 2 : 1 electrolytes. The molar conductivity of the propionitrile complex is less than that for the acetonitrile species - 183 and 249 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively. This is because the dielectric constant of propionitrile is less than that of acetonitrile and this causes a corresponding drop in the molar conductivity value (cf. expected range for 2 : 1 electrolyte : MeOH, 160-220 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$; EtOH, 70-90 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$).

The trans-arrangement for the nitrile ligands in $[\text{trans-V}(\text{MeCN})_2(\text{dmpe})_2][\text{BPh}_4]_2$ has been confirmed by an X-ray crystallographic study (see Fig. 2.1(a)). Selected bond lengths and angles are given in Table 2.1. The unit cell contains two independent cations both occupying centres of symmetry i.e., there is one unique V-N and two unique V-P distances for each cation. The V-N distances in each cation are identical and in molecule 1 (Fig. 2.1(a)), the two V-P distances are both 2.52 \AA while in molecule 2 (Fig. 2.1(b)), the average V-P distance is 2.50 \AA . However this difference may not be chemically significant since in molecule 2 the dmpe ligands are conformationally disordered, so the data discussed here will be that for molecule 1.

The V-N-C bond angle (172.76°) shows a deviation from the expected linearity which has been observed in other complexes containing coordinated acetonitrile ligands ⁽⁸⁸⁾. The V-N and C \equiv N bond lengths in the $[\text{trans-V}(\text{MeCN})_2(\text{dmpe})_2]^{2+}$ cation - 2.08 and 1.15 \AA respectively - are very similar to those in $[\text{V}(\text{MeCN})_6][\text{ZnCl}_4]$ (V-N_{av} = 2.11 \AA and C \equiv N_{av} = 1.14 \AA). It was suggested that the shortness of the V-N bond in the $[\text{V}(\text{MeCN})_6]^{2+}$ cation compared with other vanadium-acetonitrile complexes is due to substantial $d\pi \rightarrow \pi^*$

FIGURE 2.1(a) MOLECULAR STRUCTURE OF $[\text{TRANS-V}(\text{MeCN})_2(\text{dmpe})_2][\text{BPh}_4]_2$

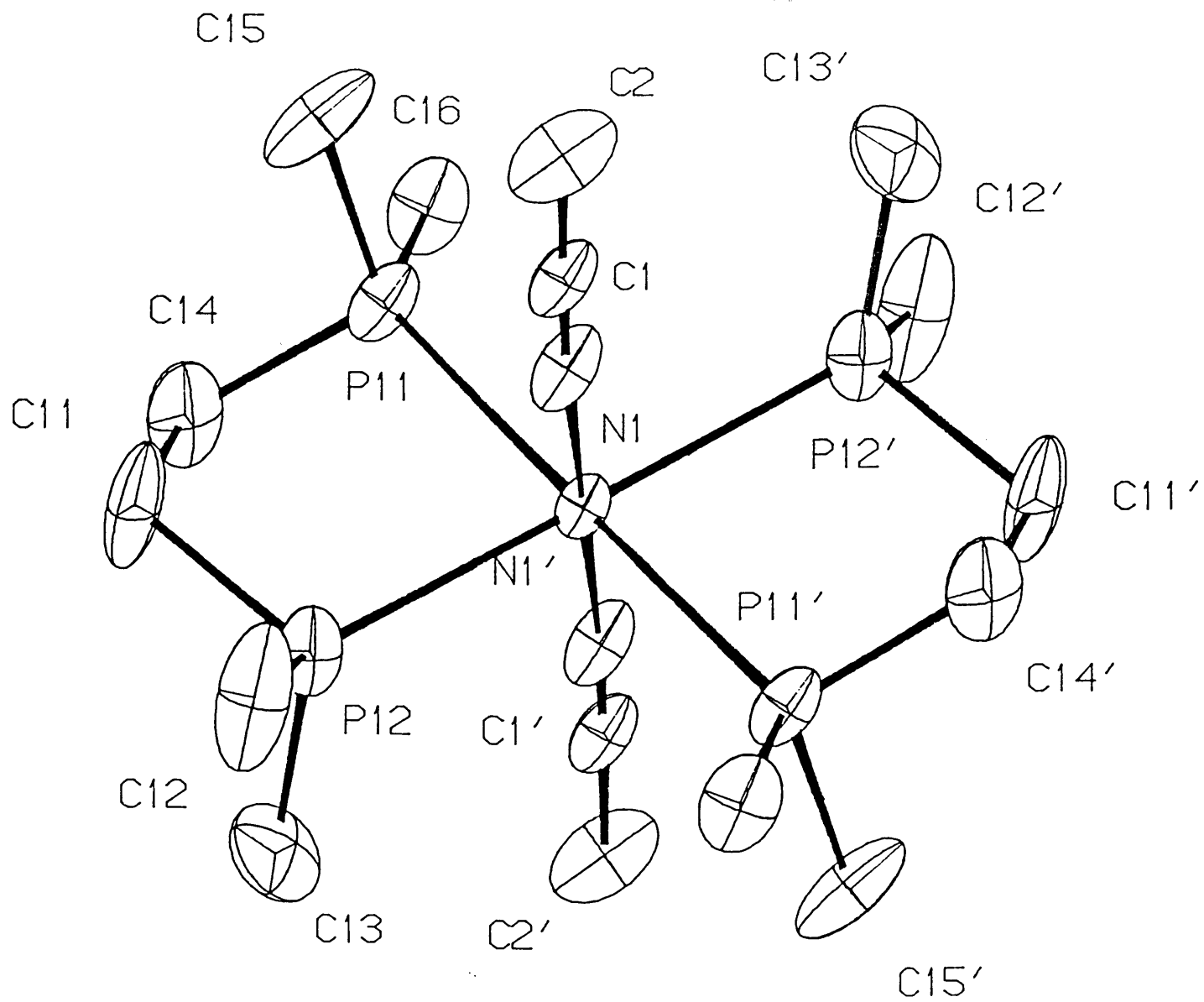


FIGURE 2.1(b)

MOLECULAR STRUCTURE OF $[\text{TRANS-V}(\text{MeCN})_2(\text{dmpe})_2][\text{BPh}_4]_2$

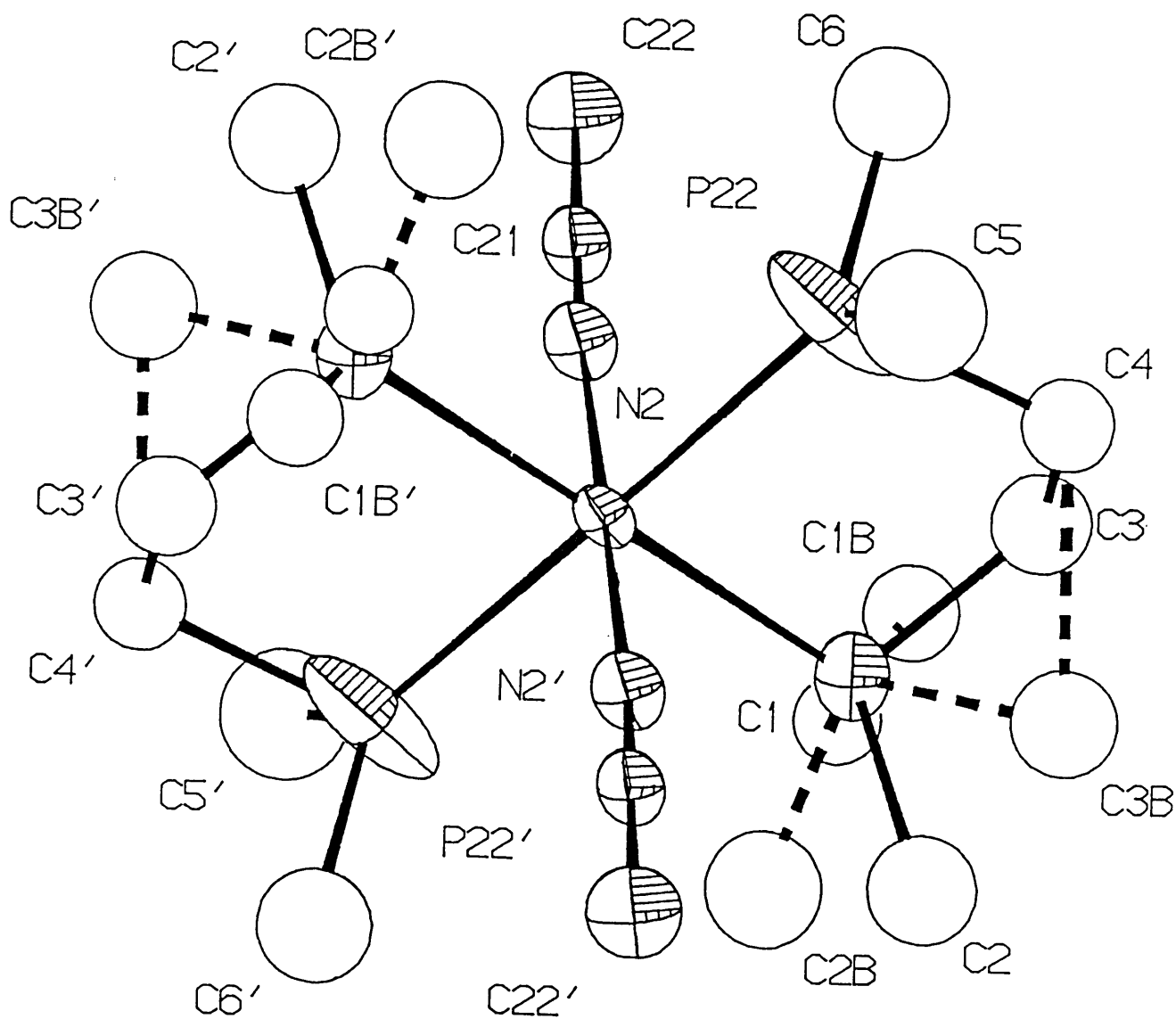
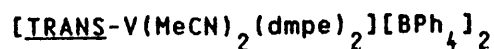


TABLE 2.1. SELECTED BOND LENGTHS AND ANGLES FOR



Selected bond lengths (Å) for [V(MeCN)₂(dmpe)₂][BPh₄]₂

| | | | |
|-------------|-------|-------------|-------|
| P(11)-V(1) | 2.522 | P(21)-V(2) | 2.505 |
| N(1)-V(1) | 2.077 | N(2)-V(2) | 2.077 |
| P(12)-V(1) | 2.523 | P(22)-V(2) | 2.495 |
| | | | |
| N(1)-C(1) | 1.145 | N(2)-C(21) | 1.138 |
| C(1)-C(2) | 1.491 | N(21)-C(22) | 1.469 |
| | | | |
| P(11)-C(14) | 1.848 | P(21)-C(3) | 1.800 |
| C(14)-C(11) | 1.560 | P(21)-C(3B) | 1.800 |
| P(12)-C(11) | 1.891 | C(3)-C(4) | 1.531 |
| | | P(22)-C(4) | 2.047 |

Selected bond angles (°) for [V(MeCN)₂(dmpe)₂][BPh₄]₂

| | | | |
|------------------|--------|------------------|--------|
| P(11)-V(1)-P(12) | 79.76 | P(21)-V(2)-P(22) | 87.54 |
| V(1)-N(1)-C(1) | 172.76 | V(2)-N(2)-C(21) | 176.33 |
| N(1)-C(1)-C(2) | 177.55 | N(2)-C(21)-C(22) | 179.23 |
| | | | |
| N(1)-V(1)-P(11) | 90.19 | N(2)-V(2)-P(21) | 89.84 |
| N(1)-V(1)-P(12) | 91.74 | N(2)-V(2)-P(22) | 89.09 |
| V(1)-P(11)-C(14) | 107.60 | V(2)-P(21)-C(3) | 104.48 |
| V(1)-P(12)-C(11) | 107.80 | V(2)-P(21)-C(3B) | 121.91 |
| | | V(2)-P(22)-C(4) | 101.46 |

(ligand) interaction ⁽⁸⁹⁾, and it would seem that the degree of back-bonding is of the same magnitude in [trans-V(MeCN)₂(dmpe)₂]²⁺. This is surprising in light of the electron-donating properties of the dmpe ligand which would be expected to increase the extent of the d π \rightarrow π^* back-bonding. It has previously been noted that the presence of half-filled d-orbitals, as in a d³ configuration, tends to inhibit back-bonding in transition metal complexes ⁽⁹⁰⁾. However comparison of the $\nu_{\text{CN(symmetric)}}$ stretching frequencies of [trans-V(MeCN)₂(dmpe)₂]²⁺ and [V(MeCN)₆]²⁺ - 2250 and 2280 cm⁻¹ respectively - suggests that the degree of back-bonding is greater in the phosphine-acetonitrile complex.

Complexes analogous to the vanadium-nitrile described here have been prepared for chromium either by the protonation of trans-Cr(N₂)₂(dmpe)₂ in acetonitrile or propionitrile ⁽⁸⁵⁾ or by the reaction of trans-CrCl₂(dmpe)₂ with NaBPh₄ in the appropriate solvent ⁽⁹¹⁾. The X-ray structure of these complexes have been determined and in [trans-Cr(MeCN)₂(dmpe)₂][CF₃SO₃]₂, the M-N and M-P bond lengths are shorter than those in the corresponding vanadium complex by ca. 0.14 Å. A decrease of ca. 0.09 Å would be expected from the difference in the ionic radii of V²⁺ and Cr²⁺ (low-spin) : the additional decrease is due to the possibility of Cr-P and Cr-N π -bonding. A similar trend has been observed for trans-MCl₂(dmpe)₂ ⁽⁸³⁾.

For chromium, it is possible to synthesise the partially substituted compounds, [trans-CrCl(RCN)(dmpe)₂][BPh₄] (R = Me, Et), by the interaction of one, rather than two equivalents of NaBPh₄ with trans-CrCl₂(dmpe)₂ ⁽⁹¹⁾. Attempts to obtain similar species by the same method using trans-VCl₂(dmpe)₂ were unsuccessful and merely led to the isolation of reduced yields of the disubstituted products.

(iii) $t\text{-BuNC}$

Interaction of a methanolic solution of $\text{trans-VCl}_2(\text{dmpe})_2$ with two equivalents of sodium hexafluorophosphate, in the presence of an excess of tert-butyl isocyanide, produces a purple solution and a small quantity of pale orange precipitate. Refluxing the reaction mixture decreases the amount of precipitate. Recrystallisation of the methanol-soluble residue from tetrahydrofuran led to the isolation of purple-red crystals which analysed for $[\text{VCl}(t\text{-BuNC})(\text{dmpe})_2][\text{PF}_6]$. Conductivity measurements in acetonitrile confirmed that the product was a 1 : 1 electrolyte ($\Lambda_M = 114 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$). The infrared spectrum shows a strong single band at 2130 cm^{-1} for $\nu_{\text{C}\equiv\text{N}}$.

The e.s.r. spectrum of this complex (thf, 77 K) comprised two broad low-field features at ca. 120 and 280 mT and two weaker features at ca. 520 and 800 mT and is consistent with an $S = \frac{3}{2}$ system, i.e., three unpaired electrons. This spectrum, together with the e.s.r. spectra of related vanadium(II) complexes, will be discussed in more detail in Chapter 4.

It is noteworthy that the main product in this reaction is the partially substituted complex $[\text{trans-VCl}(t\text{-BuNC})(\text{dmpe})_2]$ whereas, when the incoming neutral ligand is an organonitrile, only the disubstituted species are formed. The disubstituted tert-butyl isocyanide compound is the minor product i.e., the orange precipitate is more easily prepared from $[\text{trans-V}(\text{MeCN})_2(\text{dmpe})_2][\text{PF}_6]_2$ as is discussed in Chapter 4.

The monosubstituted product is formed in preference to $[\text{trans-V}(t\text{-BuNC})_2(\text{dmpe})_2]^{2+}$ because the trans effect of the chloride ligand has been shown to be greater than that of tert-butyl isocyanide, thus the ligand trans to V-Cl is selectively exchanged ⁽⁹²⁾. This is in accord with the relative CO labilizing abilities of chloride ion and

phenyl isocyanide in $M(CO)_5A$ complexes (93).

Reaction of trans- $VCl_2(dmpe)_2$ with $NaBPh_4$ in tetrahydrofuran in the presence of pyridine led to the isolation of two products - an orange and a purple solid - which both exhibited peaks in the infrared at ca. 1610 cm^{-1} , suggesting the presence of coordinated pyridine. Analysis confirmed that pyridine had been incorporated into the complexes but problems with purification have impeded further identification of the products.

(iv) KCN or KNCS

Treatment of trans- $VCl_2(dmpe)_2$ with two equivalents of potassium cyanide or potassium thiocyanate leads to the replacement of both chloride ligands, thus forming the complexes trans- $V(CN)_2(dmpe)_2$ and trans- $V(NCS)_2(dmpe)_2$ respectively. Both compounds are moderately air-stable solids - the cyano complex being orange and the thiocyanato species dark red.

Both these compounds are paramagnetic with effective magnetic moments of 3.7 B.M., thus suggesting the presence of three unpaired electrons i.e., vanadium(II). However the e.s.r. spectra of the two complexes are different although they are both consistent with vanadium in oxidation state +2. These differences will be discussed in Chapter 4, together with the e.s.r. spectra of related complexes. The e.s.r. spectrum (MeCN, 77 K) of trans- $V(CN)_2(dmpe)_2$ shows a strong feature at ca. 315 mT with weaker features at ca. 160 and 810 mT whilst that of trans- $V(NCS)_2(dmpe)_2$ exhibits four resonances at ca. 120, 320, 570 and 815 mT.

A strong band at 2055 cm^{-1} is seen in the infrared spectrum of the dicyano complex, attributable to ν_{CN} . A similar band is observed

in the infrared spectrum of trans-V(NCS)₂(dmpe)₂ at 2060 cm⁻¹ (ν_{CN}), which suggests that the thiocyanate ligands are coordinated to the metal centre through the N-atom of the thiocyanate group.

The interaction of trans-VCl₂(dmpe)₂ with LiNMe₂, LiNPh₂ or LiPPh₂ led to the formation of orange-red solutions. However the only crystalline product which could be isolated from the reaction mixture in all cases was unreacted trans-VCl₂(dmpe)₂.

Attempts to prepare an aluminohydride from trans-VCl₂(dmpe)₂, analogous to [(dmpe)₂CrH(AlH₄)]₂ isolated from the reaction of trans-CrCl₂(dmpe)₂ and LiAlH₄, were unsuccessful. No reaction occurred between trans-VCl₂(dmpe)₂ and either LiAlH₄ or NaAlH₄, even in the presence of TDA-1 (a solubilising agent). Vanadium aluminohydrides stabilised by η⁵-cyclopentadienyl ligands have been reported - [Cp₂VAH₄]₂.OEt₂ and [Cp₂V]₂AlH₂Cl.OEt₂⁽⁹⁴⁾ - but they are not well characterised.

Reaction of trans-VCl₂(dmpe)₂ with lithium borohydride in tetrahydrofuran resulted in a red solution. Removal of the solvent produced a pyrophoric grey-white solid, which redissolved in tetrahydrofuran to give a red solution. However the only product which could be isolated was unreacted trans-VCl₂(dmpe)₂.

Vanadium-borohydride species are relatively rare : the reaction of [V₂(μ-Cl)₃(thf)₆]₂[Zn₂Cl₆] with dmpm or dppm and LiBH₄ produces the complexes [V(μ-Cl)(μ-P-P)(BH₄)₂](P-P = dmpm, dppm) in very low yields⁽⁴⁷⁾. These compounds decompose spontaneously in solution, producing a grey amorphous solid. In the presence of the monodentate phosphine, PMePh₂, the reaction of [V₂(μ-Cl)₃(thf)₆]₂[Zn₂Cl₆] with LiBH₄ produced the unusual complex [V(PMePh₂)₂(μ-H)₂Zn(η²-BH₄)]₂⁽⁷³⁾.

(b) Reduction Reactions

(i) CO

Treatment of trans-VCl₂(dmpe)₂ with an excess of sodium amalgam in tetrahydrofuran in the presence of carbon monoxide resulted in the formation of an orange solution. Orange prisms of trans-V(CO)₂(dmpe)₂ can be obtained on recrystallisation from hexane at -20°C. This extremely air-sensitive solid is paramagnetic with an effective magnetic moment of 1.5 B.M., which suggests a low-spin d⁵ configuration with one unpaired electron. The e.s.r. spectrum observed in toluene at 77 K is consistent with an $S = \frac{1}{2}$ system exhibiting a complex pattern (see Fig. 2.2). It is best interpreted as the overlapping of three sets of eight lines (⁵¹V, $I = \frac{7}{2}$, 100%), corresponding to the interaction of the one unpaired electron on the vanadium atom with the nuclear spin of $I = \frac{7}{2}$ in the three axial directions (x, y and z). Although the infrared spectrum in hexane shows only a single band at 1763 cm⁻¹, as is expected for a trans stereochemistry, the solid state spectrum (Nujol mull) exhibits two bands, which are presumably due to solid state splitting.

The trans-geometry of the carbonyl ligands is confirmed by an X-ray crystallographic analysis (see Fig. 2.3). Selected bond lengths and angles are given in Table 2.2. The V-C distances are ca. 0.1 Å longer than the Cr-C distances in cis-Cr(CO)₂(dmpe)₂ and the V-P bonds are also ca. 0.1 Å longer than the two mutually trans Cr-P bonds in that complex ⁽⁸⁴⁾, and the Cr-P bonds in the analogous Cr⁰ complex, cis-Cr(N₂)₂(dmpe)₂ ⁽⁸⁴⁾. These differences are probably a reflection of the greater metal radius for vanadium rather than a difference in the degree of back-bonding to the phosphine or carbonyl ligands. However, the V-C distances are only 0.05 Å greater than the Cr-N

FIGURE 2.2. E.S.R. SPECTRUM OF TRANS-V(CO)₂(dmpe)₂
IN TOLUENE AT 77 K

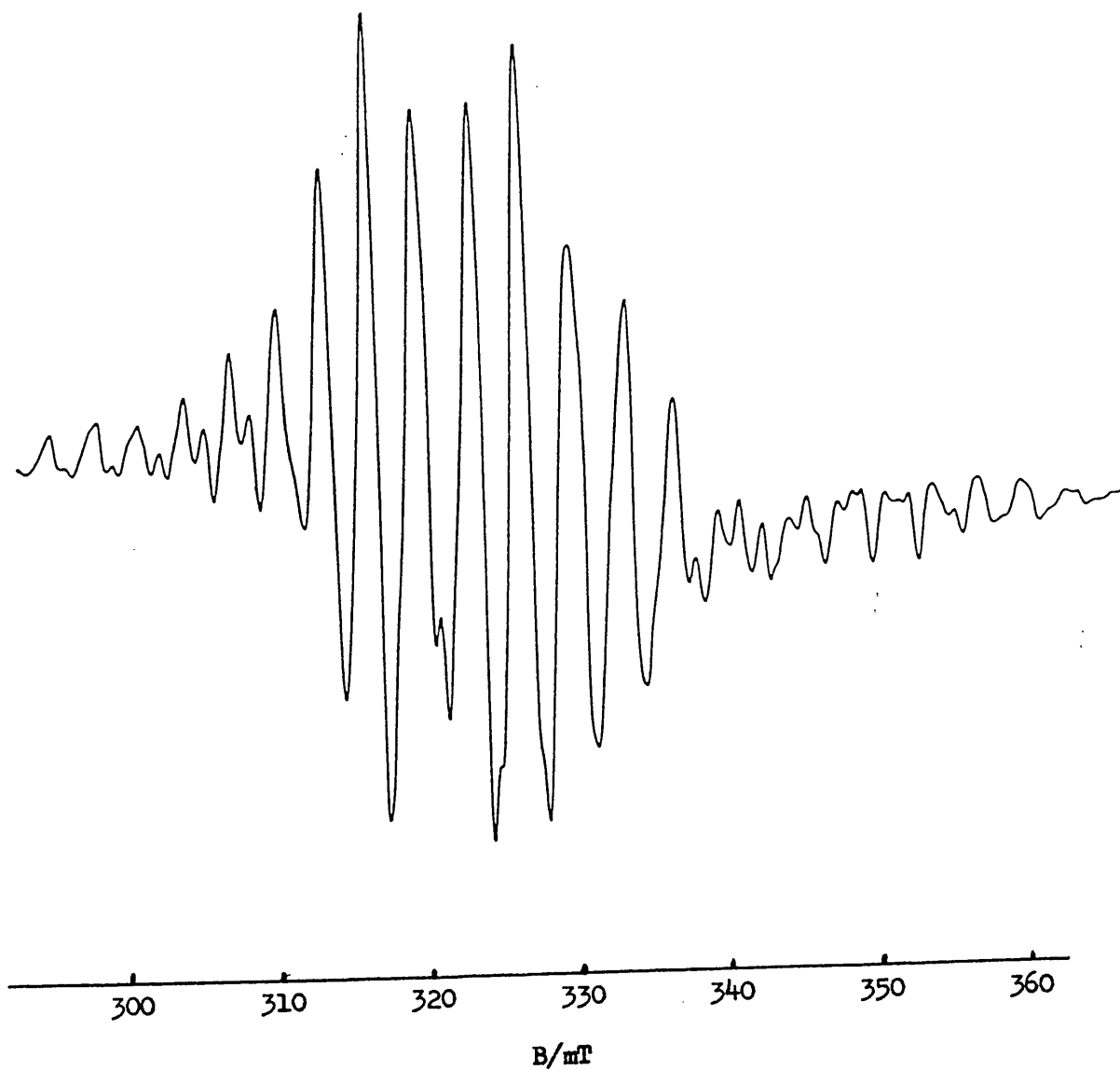


FIGURE 2.3. MOLECULAR STRUCTURE OF TRANS-V(CO)₂(dmpc)₂

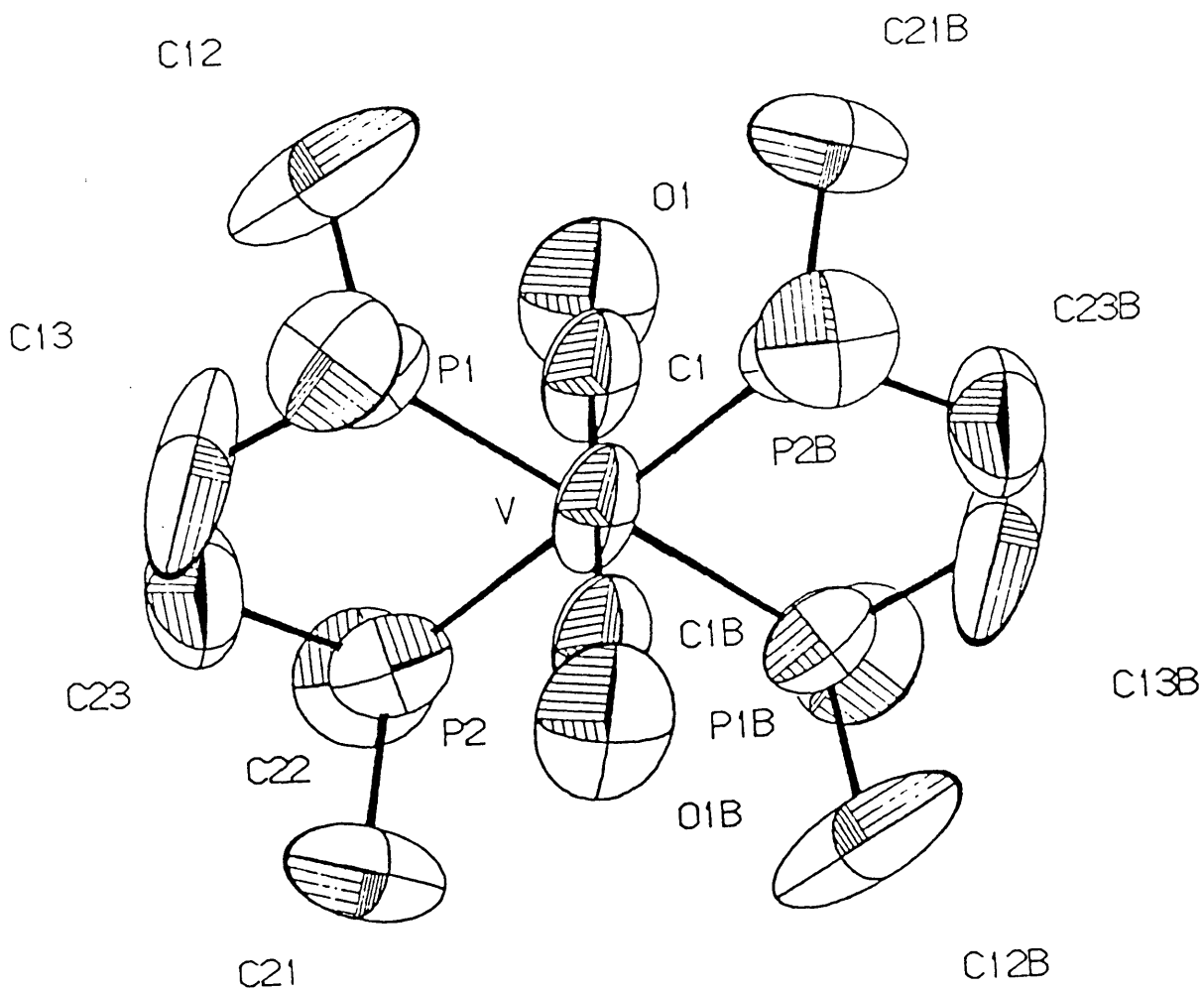
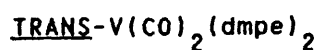


TABLE 2.2. SELECTED BOND LENGTHS AND ANGLES FOR



Selected bond lengths (Å) for trans-V(CO)₂(dmpe)₂

| | |
|------------|----------|
| P(1)-V(1) | 2.381(3) |
| P(2)-V(1) | 2.384(4) |
| O(1)-V(1) | 3.074 |
| C(1)-V(1) | 1.923(1) |
| C(11)-V(1) | 3.688 |
| C(12)-V(1) | 3.684 |
| C(13)-V(1) | 3.504 |
| C(21)-V(1) | 3.708 |
| C(22)-V(1) | 3.672 |
| C(23)-V(1) | 3.536 |

Selected bond angles (°) for trans-V(CO)₂(dmpe)₂

| | |
|------------------|----------|
| P(2)-V(1)-P(1) | 78.7(1) |
| C(1)-V(1)-P(1) | 98.6(4) |
| C(1)-V(1)-P(2) | 90.2(4) |
| C(11)-P(1)-V(1) | 121.5(5) |
| C(12)-P(1)-V(1) | 121.5(6) |
| C(12)-P(1)-C(11) | 100.0(8) |
| C(13)-P(1)-V(1) | 112.1(5) |
| C(13)-P(1)-C(11) | 98.1(9) |
| C(12)-P(1)-C(12) | 99.2(1) |
| C(12)-P(1)-V(1) | 121.5(5) |
| C(22)-P(2)-V(1) | 119.7(5) |
| C(22)-P(2)-C(21) | 101.4(7) |
| C(23)-P(2)-V(1) | 111.6(6) |

distances, which is an indication of the greater π -acceptor capability of the carbonyl ligand.

The vanadium dicarbonyl complex is strictly octahedral with an M-C-O angle of 179.8° . Interestingly, the volume per molecule of this vanadium compound is ca. 20 \AA^3 less than that of the dinitrogen complex. Although the thermal ellipsoids for the atoms of the dmpe ligand indicate considerable thermal motion or disorder in the vanadium compound, it would seem that the crystal packing in this monoclinic structure is better than that for the dinitrogen chromium structure, which is triclinic.

The formation of the trans-isomer for the vanadium dicarbonyl compared with the cis-isomer found for the analogous chromium compound can be rationalised by MO calculations ⁽⁹⁵⁾ which suggest that, in 18-electron species such as the chromium dicarbonyl, the cis isomer is more stable but for $V(CO)_2(dmpe)_2$, which is a 17-electron complex, the trans isomer is thermodynamically preferred.

In an attempt to prepare a species analogous to trans- $V(CO)_2(dmpe)_2$ but containing trimethylphosphine ligands instead of dmpe, $[V_2(\mu-Cl)_3(thf)_6]_2[Zn_2Cl_6]$ was treated with an excess of sodium amalgam in the presence of PMe_3 and under an atmosphere of carbon monoxide. Extraction of the reaction mixture into toluene and subsequent concentration of the solution yielded small quantities of bright yellow solid which were no longer soluble in toluene.

The elemental analysis of this extremely air-sensitive yellow solid indicates a C : H : O : P ratio of ca. 5 : 9 : 2 : 1, suggesting a PMe_3 : CO ratio of 1 : 2.

The e.s.r. spectrum in thf at 77 K (see Fig. 2.4.) shows a complex pattern similar to that of trans- $V(CO)_2(dmpe)_2$, which implies

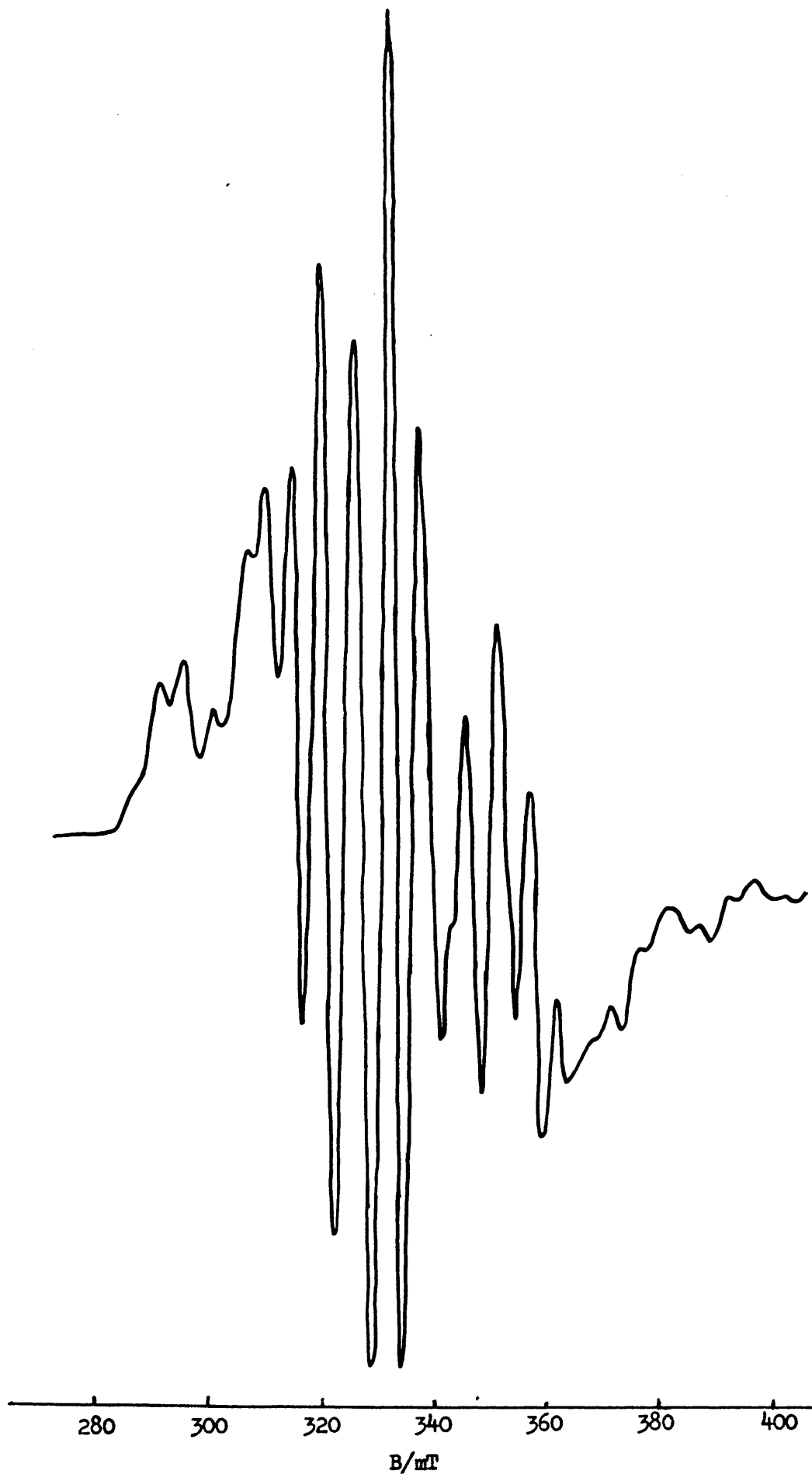


FIGURE 2.4. E.S.R. SPECTRUM OF $\text{Na}[\text{VCl}(\text{CO})_4(\text{PMe}_3)_2]$ IN THF AT 77 K

that it is due to a zerovalent vanadium species. Hyperfine structure due to ^{31}P ($I = \frac{1}{2}$) is evident and the observed peak intensity ratio of 1 : 2 : 1 indicates that there are two phosphine ligands per vanadium nucleus. The $A(^{31}\text{P})$ value is large along the z-axis ($A_{\parallel} = 0.014 \text{ cm}^{-1}$) and small along the x and y axes ($A_{\perp} = 0.005 \text{ cm}^{-1}$), thus suggesting that the phosphine ligands lie closer to the z-axis than to the x and y axes.

The infrared spectrum of the complex exhibits a single strong band at 1824 cm^{-1} in the carbonyl stretching region, suggesting the presence of trans terminal carbonyl ligands.

This data is consistent with the formulation trans- $\text{V}(\text{CO})_4(\text{PMe}_3)_2$ for the product. However the solid is conducting in methanol and the percentage values in the elemental analysis are too low to be consistent with an empirical formula of $\text{C}_{10}\text{H}_{18}\text{O}_4\text{P}_2\text{V}$.

Considering the experimental data available at the present time, one possible formulation for the product is $\text{Na}[\text{VCl}(\text{CO})_4(\text{PMe}_3)_2]$. We are currently awaiting the results of a halide analysis. Neutral seven-coordinate species of the type $[\text{VX}(\text{CO})_4(\text{L-L})]$ ($\text{L-L} = \text{dppe}$, diars, $\text{X} = \text{I, H}$) are known ⁽⁴⁾ but to our knowledge the possibilities for reducing such species have not been studied.

(ii) CS_2

Treatment of trans- $\text{VCl}_2(\text{dmpe})_2$ with an excess of sodium amalgam in tetrahydrofuran, in the presence of carbon disulphide, led to the formation of a red solution. Extended cooling of this solution produced a small amount of orange powder.

The infrared spectrum of this solid exhibited a strong, sharp band at 1103 cm^{-1} , which was assigned as a C=S stretching frequency.

The position of this band suggests that it is due to the out-of-ring $\nu(\text{C}=\text{S})$ vibration of a π -coordinated CS_2 group. A strong stretch at 581 cm^{-1} could be due to the in-ring $\nu(\text{C}-\text{S})$ vibration although it is slightly lower than the quoted literature range for such vibrations ($653\text{-}632 \text{ cm}^{-1}$) (96).

The mass spectrum of the complex shows a parent ion at 503 a.m.u. which suggests, together with the spectroscopic data, that the compound should be formulated as trans- $\text{V}(\text{CS}_2)_2(\text{dmpe})_2$. Vanadium species containing $\pi\text{-CS}_2$ ligands are not unknown: vanadocene reacts with CS_2 to give maroon crystals of $\text{Cp}_2\text{V}(\eta^2\text{-CS}_2)$ (97), which exhibit ν_{CS} at 1141 cm^{-1} .

Attempts to make a dinitrogen vanadium complex analogous to $\text{Cr}(\text{N}_2)_2(\text{dmpe})_2$ were unsuccessful, resulting in the formation of $\text{V}(\text{dmpe})_3$ or no reaction. However this is not that surprising since the only zerovalent vanadium dinitrogen species known to date is $\text{V}(\text{N}_2)_6$ which has been prepared in frozen matrices. Comparison with $\text{V}(\text{CO})_6$ suggested that dinitrogen is acting as a weak ligand compared with CO i.e., a poorer σ -donor and a poorer π -acceptor (98).

Other reduction reactions in the presence of hydrogen, ethylene and tert-butyl isocyanide were also unsuccessful.

(c) Miscellaneous Reactions

(i) NO

Bubbling dry NO gas through a toluene solution of trans- $\text{VCl}_2(\text{dmpe})_2$ produced a pale yellow precipitate, which showed a strong stretch at 1565 cm^{-1} in its infrared spectrum, attributable to ν_{NO} . Elemental analysis and mass spectroscopic data indicated the presence of coordinated dmpe oxide ligands and a possible formulation of the

product as $V(NO)Cl_2[(Me_2P=O)_2CH_2]_2$. This oxidation of phosphine ligands by NO has been observed in the attempted preparation of other transition metal-phosphine-NO complexes (81). A similar precipitate was obtained from the interaction of trans- $CrCl_2(dmpe)_2$ with NO gas in hexane (99).

An attempt to prepare $V(NO)Cl_2(dmpe)_2$ by addition of excess dmpe to $V(NO)Cl_2(thf)_4$ (70) was unsuccessful.

2.3. CONCLUSIONS

The reactions of $[V_2(\mu-Cl)_3(thf)_6]_2[Zn_2Cl_6]$ with phosphines have been shown to be complex, and dependent on both the electronic and steric nature of the phosphine used. Dmpe appears to be the only tertiary phosphine capable of forming an easily isolatable monomeric vanadium(II) complex when $[V_2(\mu-Cl)_3(thf)_6]_2[Zn_2Cl_6]$ is used as a starting material. This is probably a reflection on its chelating ability, which is enhanced by its small cone and bite angles, and also on the highly basic nature of the dmpe ligand which enables it to form strong bonds to electron-poor metal centres such as vanadium(II).

It is evident that trans- $VCl_2(dmpe)_2$ is not as reactive as the analogous trans- $CrCl_2(dmpe)_2$, i.e., it does not readily undergo substitution of the chloride ligands. This can be attributed to the kinetic inertness of vanadium(II) because of its d^3 configuration, thus making substitution reactions relatively slow [cf., Cr^{3+}] (100).

However trans- $VCl_2(dmpe)_2$ easily forms complexes of the type trans- $VX_2(dmpe)_2$ when $X = CN^-$, NCS^- , and the chlorides are readily removed by $NaBPh_4$ or $NaPF_6$ in the presence of a coordinating solvent such as acetonitrile. This could be due to the nature of the solvent

used for the reactions; in all the examples given above the solvent used was reasonably polar and thus able to stabilize an ionic five-coordinate transition state. Other substitution reactions attempted were mainly carried out in non-polar solvents, such as diethylether, because the nature of the reagents employed, e.g., LiAlH_4 , NaBH_4 , etc., required the use of an unreactive solvent.

CHAPTER 3

REACTIONS OF TRANS-V(CO)₂(dmpe)₂

3.1. INTRODUCTION

As mentioned in the previous chapter, one vanadium dicarbonyl complex with bidentate chelating phosphine ligands, trans- $\text{V}(\text{CO})_2(\text{dppe})_2$, was known prior to this work ⁽¹⁰¹⁾. However the instability of this complex in solution, with respect to loss of dppe, has meant that its reaction chemistry has not been studied. The dmpe analogue, trans- $\text{V}(\text{CO})_2(\text{dmpe})_2$, is more stable due to the more basic nature of the dmpe ligand, and in this chapter some of its reactions with various acids and oxidising agents are described. Much work has been done on the protonation and oxidation of first-row metal carbonyls of the general type $\text{M}(\text{CO})_2(\text{diphos})_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) ⁽¹⁰²⁾ and the synthesis of trans- $\text{V}(\text{CO})_2(\text{dmpe})_2$ now allows similar reactions to be carried out for vanadium.

3.2. RESULTS AND DISCUSSION

3.2.1. Reactions of trans- $\text{V}(\text{CO})_2(\text{dmpe})_2$ with coordinating acids

Reaction of trans- $\text{V}(\text{CO})_2(\text{dmpe})_2$ with acids of the general formula HX ($\text{X} = \text{Cl}, \text{MeCO}_2, \text{EtCO}_2, \text{CF}_3\text{CO}_2, \text{NH}_2\text{SO}_3, \text{PhHPO}_2$) in diethylether, tetrahydrofuran or toluene gives products which analyse for $[\text{V}(\text{CO})_2(\text{dmpe})_2\text{X}]$. These complexes can be recrystallised from hexane or diethylether to give red needles. This suggests that they are neutral seven coordinate species rather than complexes of the form $[\text{V}(\text{CO})_2(\text{dmpe})_2][\text{X}]$. Their neutrality is confirmed by their lack of conductance. The carbonyl region of the i.r. spectra of these complexes are all very similar exhibiting two strong bands around 1810 and 1750 cm^{-1} - both in Nujol mull and hexane solution. This suggests

a cis configuration for the two carbonyl ligands.

The acetato complex, cis-V(CO)₂(dmpe)₂(MeCO₂), exhibits two bands at 1604 and 1323 cm⁻¹ which are attributed to ν_{CO_2} (asymmetric) and ν_{CO_2} (symmetric) respectively. The large value of $\Delta\nu$ ($\Delta\nu = \nu_{\text{CO}_2}(\text{asym}) - \nu_{\text{CO}}(\text{sym})$) (281 cm⁻¹) is consistent with inequivalent C-O bonds and indicates that the acetato ligand is unidentate (103). The ν_{CO_2} (symmetric) cannot be seen for the propionato and trifluoroacetato complexes but the X-ray crystal structure of the propionato compound [see Fig. 3.1.], which will be discussed in more detail in Section 3.2.5., confirms the $\eta^1\text{-O}_2\text{CR}$ coordination. The spectroscopic data for the PhHPO₂⁻ and NH₂SO₃⁻ complexes suggests that they are structurally analogous to the carboxylate compounds. Full details of the i.r. data for these compounds are shown in Table 3.2. The ³¹P-{¹H} n.m.r. of the complexes in d⁶-benzene all show an octet, indicating the presence of equivalent phosphorus atoms coupled to the central vanadium nucleus [⁵¹V, I = $\frac{7}{2}$]. An additional resonance is seen in the spectrum of V(CO)₂(dmpe)₂(PhHPO₂) which is attributed to the phosphorus atom in the O₂PHPh group. The values for the chemical shifts and coupling constants ($J_{\text{P-V}}$) are shown in Table 3.4., together with the ¹H n.m.r. chemical shifts.

3.2.2. Reactions of cis-V(CO)₂(dmpe)₂Cl

Reaction of cis-V(CO)₂(dmpe)₂Cl with MeLi in diethylether yields trans-V(CO)₂(dmpe)₂ and no evidence for the formation of a methyl complex can be seen. Presumably the vanadium(I) species is simply reduced by the alkylating agent. However treatment of the vanadium dicarbonyl chloride with an excess of NaN₃ or KCN in methanol does

FIGURE 3.1. MOLECULAR STRUCTURE OF

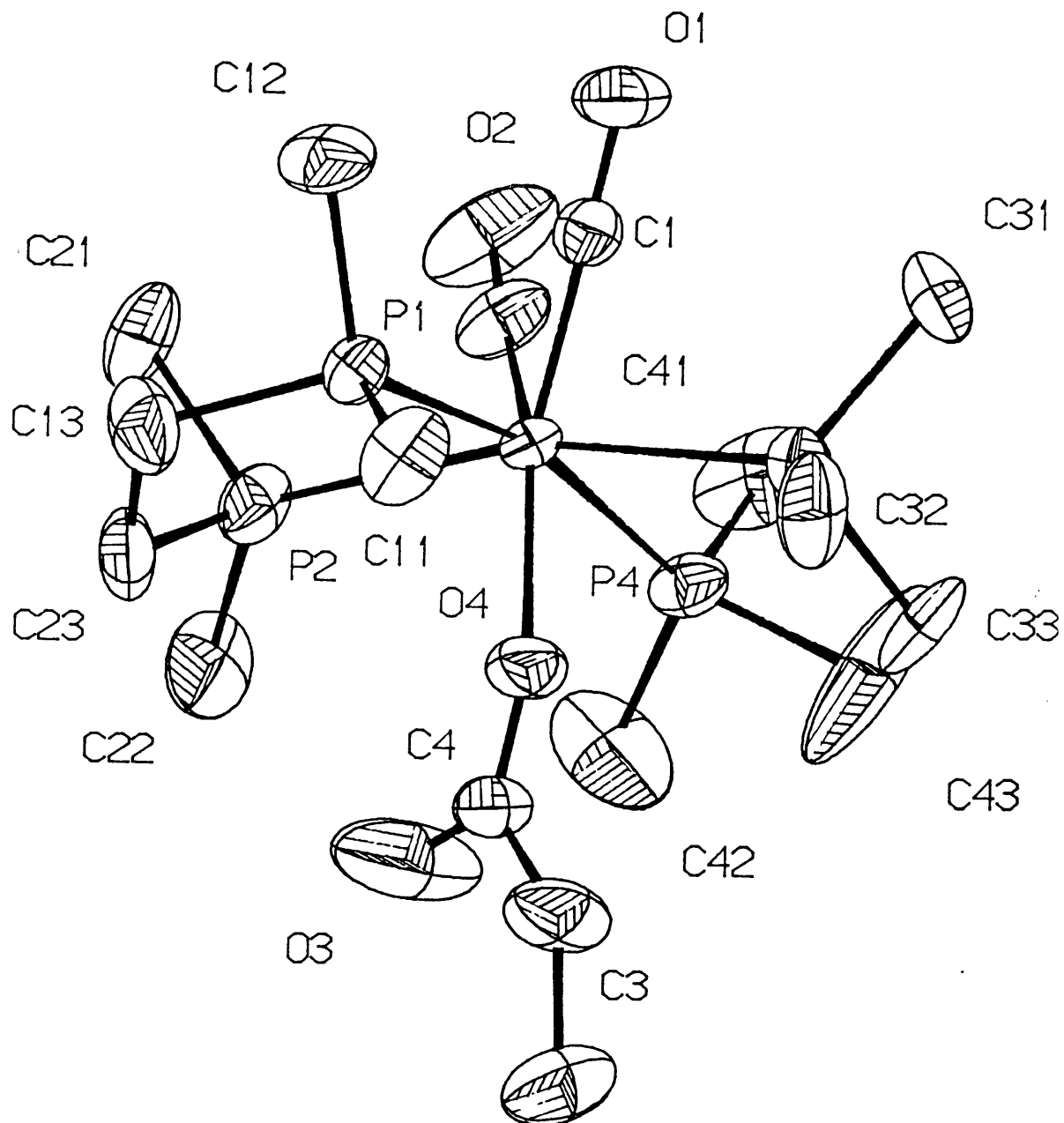
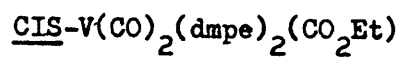
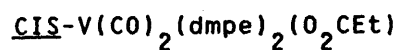


TABLE 3.1. SELECTED BOND LENGTHS AND ANGLES FOR



Selected bond lengths (Å) for V(CO)₂(dmpe)₂(O₂CET)

| | | | |
|-------------|-----------|-------------|-----------|
| P(1)-V(1) | 2.507(6) | P(2)-V(1) | 2.479(5) |
| P(3)-V(1) | 2.481(5) | P(4)-V(1) | 2.478(5) |
| O(4)-V(1) | 2.141(9) | C(1)-V(1) | 1.858(14) |
| C(2)-V(1) | 1.854(13) | C(1)-O(1) | 1.201(14) |
| C(2)-O(2) | 1.189(14) | C(3)-O(3) | 1.245(16) |
| C(3)-O(4) | 1.191(14) | C(3)-C(4) | 1.518(20) |
| C(4)-C(5) | 1.451(21) | C(13)-P(1) | 1.828(15) |
| C(23)-P(2) | 1.820(17) | C(23)-C(13) | 1.503(20) |
| P(3)-C(33) | 1.888(14) | P(4)-C(43) | 1.749(21) |
| C(33)-C(43) | 1.429(24) | | |

Selected bond angles (°) for V(CO)₂(dmpe)₂(O₂CET)

| | | | |
|----------------|-----------|----------------|-----------|
| P(1)-V(1)-P(2) | 74.3(2) | P(3)-V(1)-P(1) | 103.8(2) |
| P(3)-V(1)-P(2) | 163.0(1) | P(4)-V(1)-P(1) | 165.6(1) |
| P(4)-V(1)-P(2) | 102.0(2) | P(4)-V(1)-P(3) | 75.6(2) |
| O(4)-V(1)-P(1) | 81.1(3) | O(4)-V(1)-P(2) | 86.7(3) |
| O(4)-V(1)-P(3) | 76.4(3) | O(4)-V(1)-P(4) | 84.8(3) |
| C(1)-V(1)-P(1) | 78.4(4) | C(1)-V(1)-P(2) | 118.9(5) |
| C(1)-V(1)-P(3) | 76.3(5) | C(1)-V(1)-P(4) | 114.9(4) |
| C(1)-V(1)-O(4) | 140.6(4) | C(2)-V(1)-P(1) | 115.2(5) |
| C(2)-V(1)-P(2) | 76.4(6) | C(2)-V(1)-P(3) | 118.5(6) |
| C(2)-V(1)-P(4) | 76.5(4) | C(2)-V(1)-O(4) | 151.3(4) |
| C(2)-V(1)-C(1) | 67.9(7) | O(1)-C(1)-V(1) | 175.9(12) |
| O(2)-C(2)-V(1) | 174.8(13) | C(3)-O(4)-V(1) | 147.7(8) |
| O(4)-C(3)-O(3) | 120.5(13) | C(4)-C(3)-O(4) | 120.3(14) |

lead to replacement of the chloride ligand thus forming the complexes $\text{cis-V(CO)}_2(\text{dmpe})_2(\text{N}_3)$ and $\text{cis-V(CO)}_2(\text{dmpe})_2\text{CN}$ respectively. The azido species can also be made from the interaction of $\text{trans-V(CO)}_2(\text{dmpe})_2$ with Me_3SiN_3 in benzene.

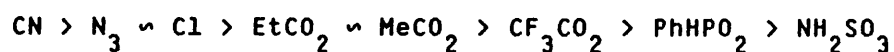
Both these compounds are structurally analogous to the previously mentioned seven coordinate vanadium(I) species, as evidenced by their spectroscopic properties [see Tables 3.3., 3.4.].

The i.r. spectrum (Nujol mull) of the azido complex shows, in addition to the two carbonyl stretches, a strong band at 2060 cm^{-1} , which is attributed to the antisymmetric stretch (ν_3) of the N_3^- ligand. The position of this band would suggest that the azido group is linear ⁽¹⁰⁴⁾. There is no evidence for the symmetric azide stretch (ν_1) which is as expected for symmetrical azide coordination, where ν_1 is only Raman-active ⁽¹⁰⁴⁾. However it may simply be obscured by other absorptions in this region ($\sim 1300\text{ cm}^{-1}$).

The i.r. spectrum (Nujol mull) of the cyano complex exhibits the expected bands in the carbonyl region and also a strong band at 2070 cm^{-1} , attributable to $\nu_{(\text{C}\equiv\text{N})}$ of the cyano ligand. The value for $\nu_{(\text{C}\equiv\text{N})}$ for the free cyanide ion is 2080 cm^{-1} and coordination to a metal centre normally shifts $\nu(\text{C}\equiv\text{N})$ to higher frequencies ⁽¹⁰⁵⁾. However the strongly electron-releasing nature of dmpe encourages π back-bonding into the antibonding $2p\ \pi^*$ orbital of the cyano ligand, thus decreasing the frequency of $\nu(\text{C}\equiv\text{N})$. Additionally a high coordination number tends to decrease $\nu(\text{C}\equiv\text{N})$ as it lowers the positive charge on the metal centre and thus weakens the σ -bonding. σ -Donation tends to raise $\nu(\text{C}\equiv\text{N})$ since electrons are removed from the $5\ \sigma$ orbital, which is weakly antibonding ⁽¹⁰⁵⁾.

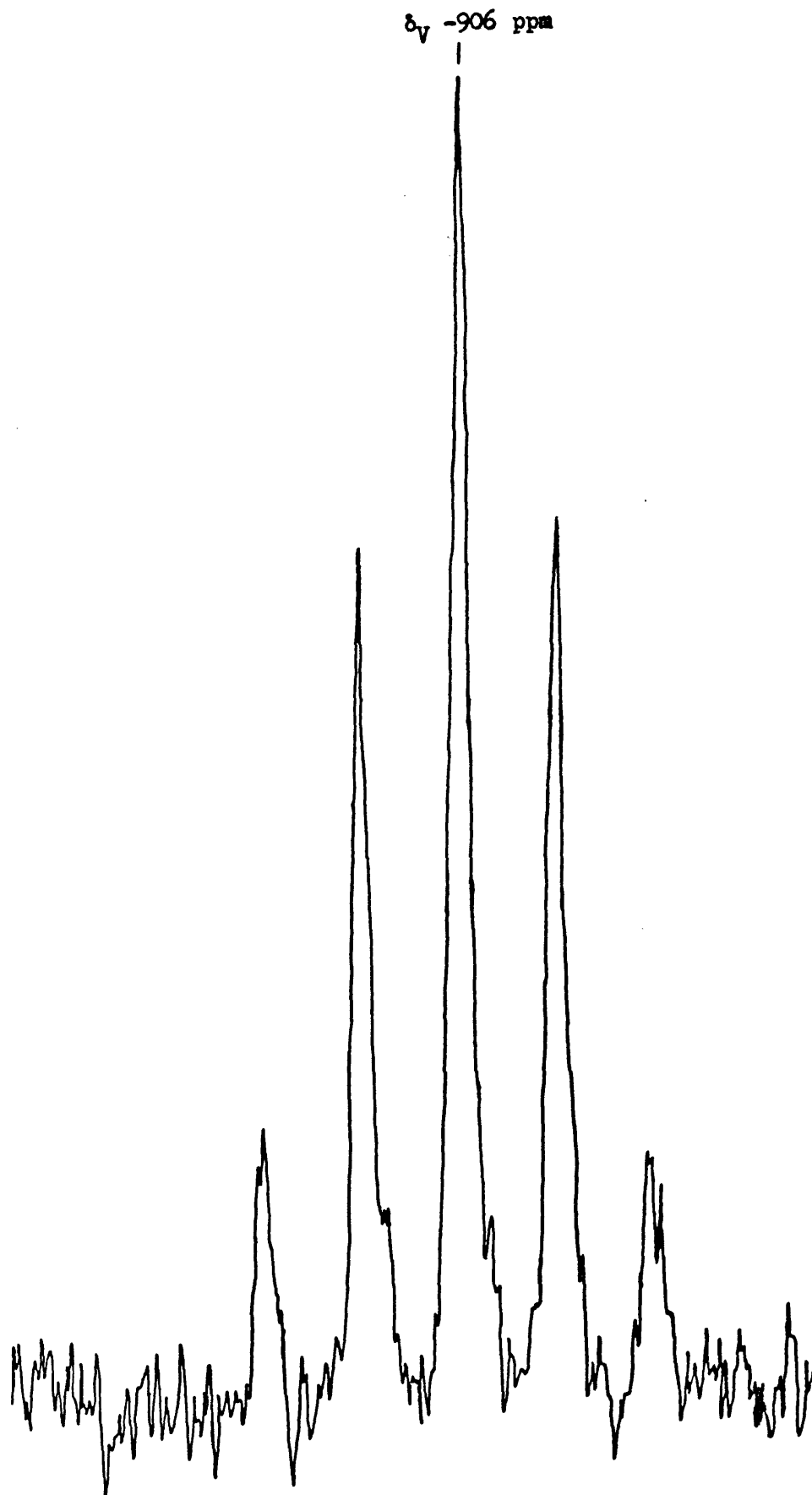
3.2.3. ^{51}V n.m.r. spectra of cis- $\text{V}(\text{CO})_2(\text{dmpe})_2\text{X}$

The ^{51}V n.m.r. of these complexes all show a quintet (see Fig. 3.2.) due to the splitting of the vanadium nucleus by four equivalent phosphorus atoms. The chemical shifts lie between (-906) to (-1248) ppm, which is within the expected range for vanadium(I) compounds [(-870) to (-1540) ppm] ⁽¹⁰⁶⁾. The complexes cis- $\text{V}(\text{CO})_2(\text{dmpe})_2\text{X}$ lie towards the high frequency end of this range because of the low electronegativity of the methyl groups on the dmpe ligands. Rehder and his co-workers have shown that there is a clear tendency for an increase in ^{51}V deshielding as the bulk of the phosphine increases and the electronegativities of the R groups decrease ⁽¹⁰⁷⁾. The small $^1\text{J}(\text{V-P})$ values (~ 160 Hz) for these complexes are in accord with those expected for alkylphosphine-vanadium compounds ⁽¹⁰⁸⁾. The values for the chemical shifts and $^1\text{J}(\text{V-P})$ are shown in Table 3.4. The nature of the substituent X exerts a strong influence on the chemical shift values for cis- $\text{V}(\text{CO})_2(\text{dmpe})_2\text{X}$. The ^{51}V shielding increases in the order:



This demonstrates that the shielding of the vanadium nucleus decreases as the electronegativity of the ligand atom bound to the metal increases, i.e., $\text{C} < \text{N} < \text{Cl} < \text{O}$. Closely related trends have been observed for the series of vanadium(I) complexes, $\text{CpV}(\text{NO})_2\text{L}$ ⁽¹⁰⁹⁾, and also $[\text{V}(\text{CO})_5\text{L}]^-$ ⁽⁵⁸⁾.

FIGURE 3.2. $^{51}\text{V}-\{^1\text{H}\}$ N.M.R. SPECTRUM OF
CIS-V(CO)₂(dmpe)₂(NH₂SO₃) IN C₆D₆ AT 298 K



3.2.4. Reactions of trans-V(CO)₂(dmpe)₂ with non-coordinating acids

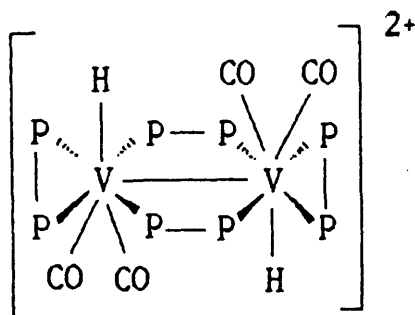
Interaction of trans-V(CO)₂(dmpe)₂ with one equivalent of tetrafluoroboric acid in methanol at -78°C gives a red solution; on warming to room temperature an orange solution is obtained, from which orange crystals can be isolated. Reaction of trans-V(CO)₂(dmpe)₂ with HCP(SO₂CF₃)₂ in toluene yields a similar orange precipitate. Elemental analysis of the BF₄⁻ and PhC(SO₂CF₃)₂⁻ salts (see Table 3.4.) indicates that the cation has stoichiometry [HV(CO)₂(dmpe)₂]. Conductivity measurements suggest that the complexes are 1 : 1 electrolytes. The i.r. spectra (Nujol mull) both show two strong bands in the terminal carbonyl region at 1865 and 1827 cm⁻¹ which are attributed to cis carbonyl ligands. A weak, sharp band is also seen at 1952 cm⁻¹ which is assigned to ν(M-H). In CH₂Cl₂ solution two bands are observed in the terminal hydride stretching region at 1960 and 1942 cm⁻¹; the number of ν_{CO} bands does not alter. The presence of V-H linkages is confirmed by essentially quantitative formation (g.l.c.) of CHCl₃ on refluxing the compound with carbon tetrachloride.

However magnetic susceptibility and e.s.r. measurements show that the cation is diamagnetic thus eliminating the possibility that the ion is analogous to [MH(CO)₂(dmpe)₂]⁺ (M = Cr⁽⁸⁵⁾, Mo, W⁽¹¹⁰⁾). The ³¹P-{¹H} and ⁵¹V-{¹H} n.m.r. spectra do not provide any useful structural information, showing broad resonances at +55.8 p.p.m. and (-1311) p.p.m. respectively. This broadening of the resonances can be ascribed to quadrupolar relaxation caused by the presence of the vanadium nucleus, and thus cooling the n.m.r. sample merely broadens the signals. This quadrupolar relaxation probably also accounts for

the fact that no resonance for the hydride proton can be seen in the ^1H n.m.r..

The diamagnetism of the cation suggests that dimerisation of a paramagnetic vanadium(II) species, $[\text{VH}(\text{CO})_2(\text{dmpe})_2]^+$, has occurred, presumably with the formation of a V-V bond. The driving force for this dimerisation must be the attainment of eighteen electrons per metal centre. In the absence of conclusive structural data it is only possible to speculate on the structure on the basis of the spectroscopic data. The i.r. spectra show no evidence for bridging carbonyl or hydrido groups and since there are two V-H stretches in the solution spectra, it may be that isomers or some lack of symmetry exists in solution. The $^{19}\text{F}-\{^1\text{H}\}$ n.m.r. spectrum of the BF_4^- salt indicates that the only fluorine-containing species present in the compound is uncoordinated BF_4^- .

Considering all the collected experimental data, (Table 3.5.) a reasonable possibility for the structure of the complex is shown below:



Vanadium-vanadium bonds have been discussed ⁽¹¹¹⁾ and there is a precedent for bridging dmpe in the compounds $\text{Rh}^{\text{I}}(\text{CH}_2\text{SiMe}_3)_2(\text{dmpe})_3$ ⁽⁷⁷⁾ and $\text{Fe}_2(\text{dmpe})_5$ ⁽⁷⁸⁾, which have single dmpe bridges.

3.2.5. Oxidation of trans-V(CO)₂(dmpe)₂ by silver salts

Oxidation of trans-V(CO)₂(dmpe)₂ by AgSO₃CF₃ in acetonitrile at -30°C yields the cation [V(CO)₂(dmpe)₂(MeCN)][SO₃CF₃]. Orange crystals of this complex can be obtained by exchanging the counter-ion for tetraphenylborate. The i.r. spectrum (Nujol mull) of [V(CO)₂(dmpe)₂(MeCN)][BPh₄] shows two strong carbonyl bands at 1836 and 1779 cm⁻¹ [cf. 1820 and 1760 cm⁻¹ for the neutral dicarbonyl complex]. The slight increase in frequency is attributed to the positive charge on the metal centre. The i.r. spectrum in acetonitrile also shows two bands at the same frequencies [cf. trans-V(CO)₂(dmpe)₂ ν(C≡O) 1733 cm⁻¹ in acetonitrile] which suggests a cis, rather than trans, configuration for the carbonyl groups. The i.r. spectrum (Nujol mull) also contains a weak band at 2250 cm⁻¹ which is attributed to the ν_{CN}(symmetric) of coordinated acetonitrile. Coordination to a metal centre normally increases ν_{CN} for organonitriles (112). The slightly low value observed here can probably be attributed to the electron-releasing nature of dmpe, which increases the electron density on the metal centre, thus leading to back-bonding into the nitrile π* orbitals (113). An X-ray crystallographic study confirms the presence of acetonitrile as a ligand [see Fig. 3.3.].

The structure of this cation and V(CO)₂(dmpe)(O₂CET) illustrated previously (see Fig. 3.1.) are essentially analogous, and may be described as 'pseudo octahedral', with 'equatorial' bis dmpe groups and one axial site occupied by the acetonitrile or unidentate propionate ligands and the other being 'split' and accommodating the two carbonyls. The near equality of C-V-N and C-V-O angles between the axial sites preclude the possibility of using a capped octahedral

FIGURE 3.3. MOLECULAR STRUCTURE OF THE CATION

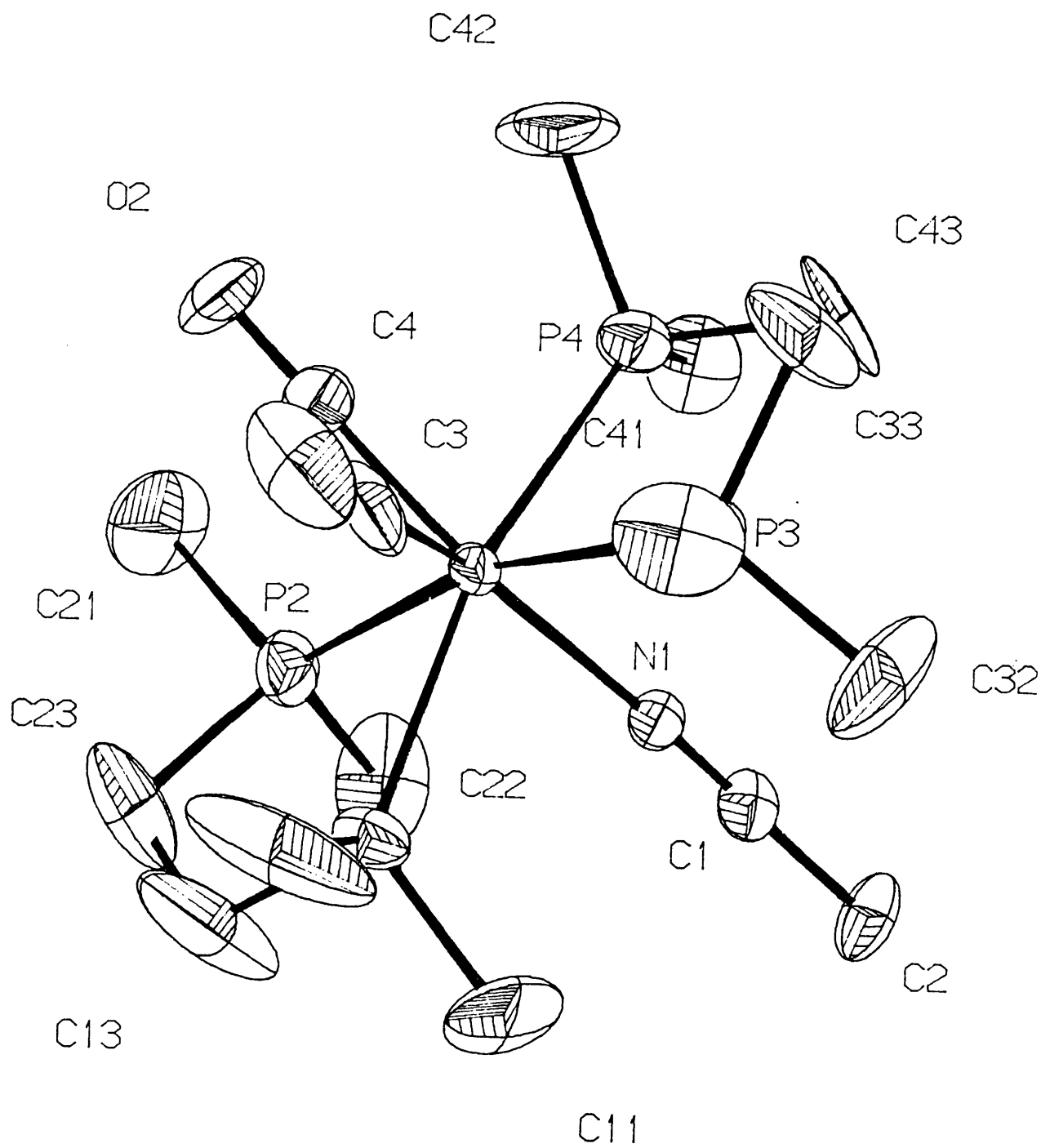
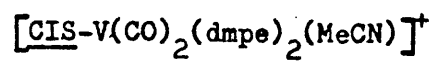


TABLE 3.2. SELECTED BOND LENGTHS AND ANGLES FOR



Selected bond lengths (Å) for [V(CO)₂(dmpe)₂(MeCN)](BPh₄)

| | | | |
|-------------|-----------|-------------|-----------|
| P(1)-V(1) | 2.479(5) | P(2)-V(1) | 2.475(5) |
| P(3)-V(1) | 2.477(6) | P(4)-V(1) | 2.459(6) |
| N(1)-V(1) | 2.166(10) | C(3)-V(1) | 1.851(15) |
| C(4)-V(1) | 1.831(15) | C(3)-O(1) | 1.172(13) |
| C(4)-O(2) | 1.196(14) | C(1)-N(1) | 1.123(12) |
| C(2)-C(1) | 1.477(17) | P(1)-C(13) | 1.775(19) |
| P(2)-C(23) | 1.771(16) | P(3)-C(33) | 1.756(17) |
| P(4)-C(43) | 1.849(14) | C(13)-C(23) | 1.478(21) |
| C(33)-C(43) | 1.518(19) | | |

Selected bond angles (°) for [V(CO)₂(dmpe)₂(MeCN)](BPh₄)

| | | | |
|----------------|-----------|----------------|-----------|
| P(1)-V(1)-P(2) | 75.1(2) | P(3)-V(1)-P(1) | 98.6(2) |
| P(3)-V(1)-P(2) | 164.6(1) | P(4)-V(1)-P(1) | 166.3(1) |
| P(4)-V(1)-P(2) | 106.5(2) | P(4)-V(1)-P(3) | 76.3(2) |
| N(1)-V(1)-P(1) | 84.1(3) | N(1)-V(1)-P(2) | 83.4(3) |
| N(1)-V(1)-P(3) | 82.0(3) | N(1)-V(1)-P(4) | 82.5(3) |
| C(3)-V(1)-P(1) | 78.0(5) | C(3)-V(1)-P(2) | 115.7(5) |
| C(3)-V(1)-P(3) | 75.8(5) | C(3)-V(1)-P(4) | 112.4(5) |
| C(3)-V(1)-N(1) | 148.9(6) | C(4)-V(1)-P(1) | 117.3(5) |
| C(4)-V(1)-P(2) | 74.1(5) | C(4)-V(1)-P(3) | 120.9(5) |
| C(4)-V(1)-P(4) | 75.7(5) | C(4)-V(1)-N(1) | 142.4(6) |
| O(1)-C(3)-V(1) | 175.6(15) | O(2)-C(4)-V(1) | 176.6(12) |
| C(1)-N(1)-V(1) | 176.3(9) | C(2)-C(1)-N(1) | 177.6(12) |
| C(3)-V(1)-C(4) | 68.7(8) | | |

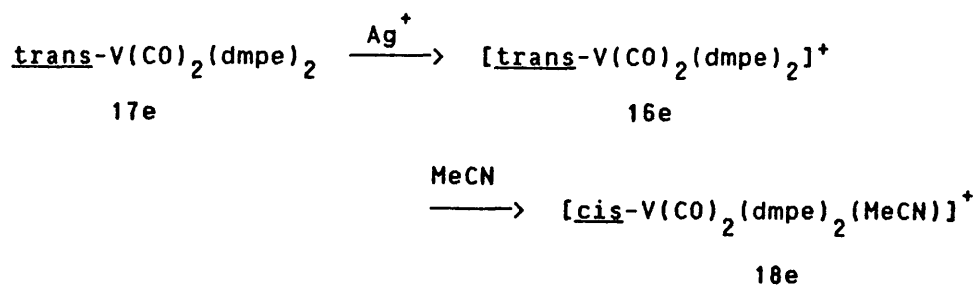
description. One particular feature of this bonding of the two carbonyls is the very narrow C-V-C angle in both structures (ca. 68°) and the resulting very close non-bonded approach of the two carbon atoms (ca. 2.1 \AA).

The V-C and V-P distances are very similar in both complexes. The former are ca. 0.05 \AA shorter than in trans- $\text{V}(\text{CO})_2(\text{dmpe})_2$ (see Chapter 2) but the V-P distances are ca. 0.1 \AA longer. This difference probably reflects the greater π -acceptor ability of the carbonyls in a non-trans arrangement and bonded to an 18e metal centre. The V-N and V-O distances are very similar at 2.15 \AA .

The ^1H n.m.r. spectrum of the vanadium(I) cation in CD_2Cl_2 at 298 K shows resonances at δ 7.3 (8 H), 7.0 (8 H), and 6.9 (4 H) p.p.m. for the phenyl protons of the BPh_4^- anion. The methyl and methylene region of the spectrum is complex, containing resonances due to the acetonitrile and dmpe protons, and stretches from δ 1.3 to 2.0 p.p.m..

Conductivity studies in acetonitrile show that the salt is a 1 : 1 electrolyte ⁽¹¹⁴⁾. The low value for the molar conductivity ($\Lambda_M = 61 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) is due to the size of the tetraphenylborate counter-ion.

Presumably trans- $\text{V}(\text{CO})_2(\text{dmpe})_2$ is initially oxidised to [trans- $\text{V}(\text{CO})_2(\text{dmpe})_2$]⁺, a reactive sixteen electron species, which is then stabilised by coordination of an acetonitrile molecule, thus forming a stable seven coordinate eighteen electron complex as shown below:



Similar behaviour has been observed in the oxidation of $(\text{Me}_5\text{Cp})_2\text{V}$ in acetonitrile solution, where the only product isolated was $[(\text{Me}_5\text{Cp})_2\text{V}(\text{MeCN})]^+$ (34).

Repeated attempts were made to isolate this sixteen electron species by oxidation of the neutral vanadium dicarbonyl in non-coordinating solvents such as dichloromethane, diethylether and toluene. Oxidations in non-coordinating solvents under an atmosphere of carbon monoxide were also tried in an attempt to isolate a CO adduct of $[\text{trans-V}(\text{CO})_2(\text{dmpe})_2]^+$ since, in the $(\text{Me}_5\text{Cp})_2\text{V}$ system mentioned earlier, it was possible to isolate the species $[(\text{Me}_5\text{Cp})_2\text{V}(\text{CO})_2]^+$. In addition, one of the two cationic seven-coordinate carbonyl complexes known prior to this work was the diarsine species, $[\text{V}(\text{CO})_3(\text{diars})_2]\text{-}[\text{BPh}_4]$, which can be prepared from the reaction of $\text{V}(\text{CO})_6$ and diars (60).

However the only product characterised from these reactions was the dimeric vanadium hydride, $[\text{V}_2\text{H}_2(\text{CO})_4(\text{dmpe})_4]^{2+}$. This may be due to the presence of water in the extremely hygroscopic oxidising agents (AgBF_4 and AgSO_3CF_3) or hydride abstraction from the solvent (110). Spectroscopic evidence (^{51}V n.m.r. and i.r.) for the formation of cis- $\text{V}(\text{CO})_2(\text{dmpe})_2\text{Cl}$ was also observed when dichloromethane was used as the solvent.

Presumably cis- $[\text{V}(\text{CO})_2(\text{dmpe})_2(\text{MeCN})]^+$ is formed, rather than the vanadium hydride complex when the reaction solvent is acetonitrile, because of the large excess of acetonitrile present. It should also be noted that $[\text{V}_2\text{H}_2(\text{CO})_4(\text{dmpe})_2]^{2+}$ can be converted to $[\text{V}(\text{CO})_2(\text{dmpe})_2(\text{MeCN})]^+$ merely by allowing an acetonitrile solution of the hydride to stand for several days.

3.2.6. Attempted reduction of trans-V(CO)₂(dmpe)₂

When trans-V(CO)₂(dmpe)₂ is stirred with cobaltocene (CoCp₂) or sodium amalgam in tetrahydrofuran for several days no evidence is seen in the solution i.r. spectrum for further reduction of the neutral dicarbonyl species to [V(CO)₂(dmpe)₂]⁻.

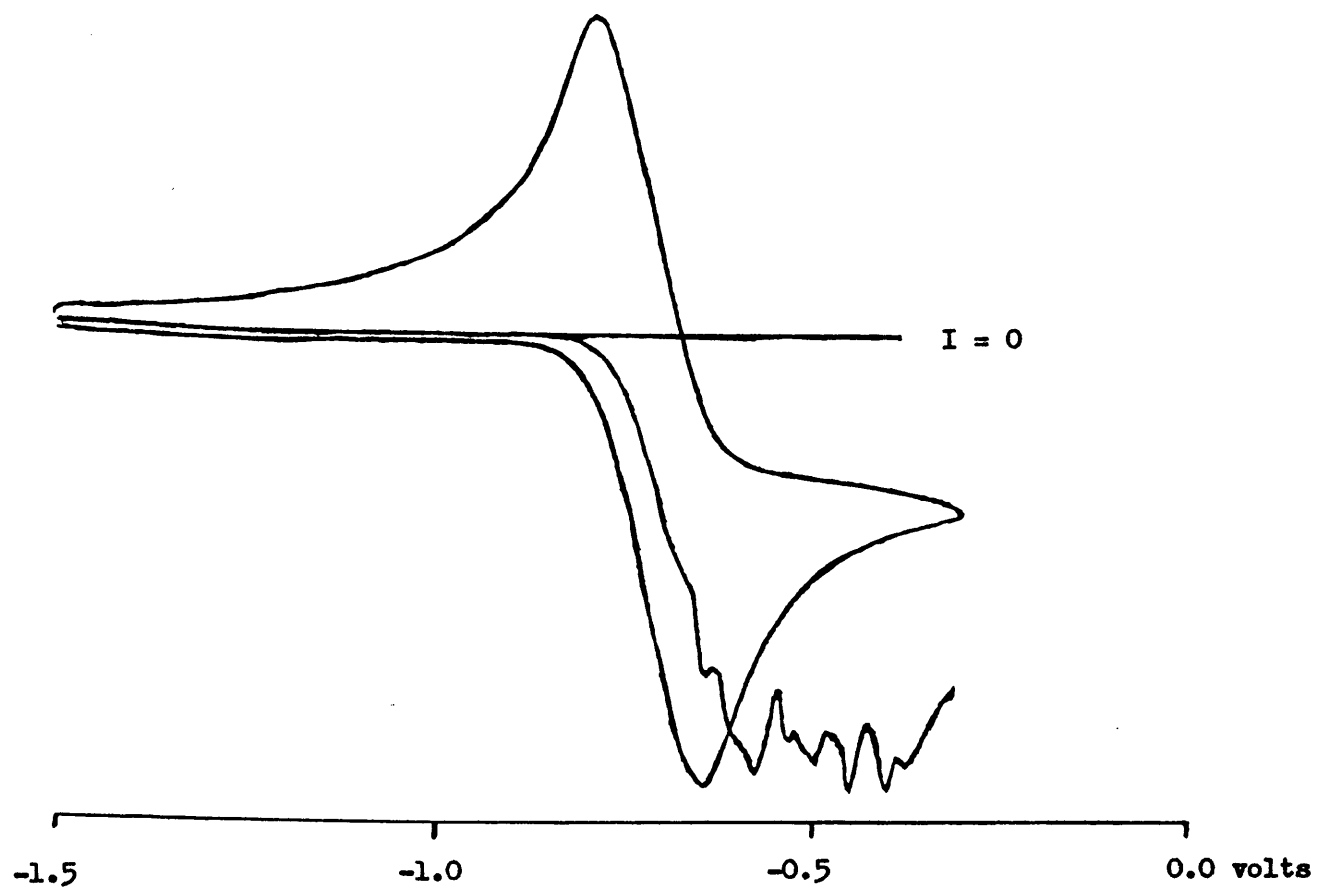
This is unsurprising in the light of electrochemical studies on trans-V(CO)₂(dmpe)₂ in dichloromethane, which show that the dicarbonyl undergoes a reversible one-electron oxidation at ca. -0.7 V (see Fig. 3.4.). There is no sign of any reduction before the solvent front at ca. -2.0 V.

The easy oxidation of trans-V(CO)₂(dmpe)₂ and the absence of a reduced species can be ascribed to the basic nature of the dmpe ligand, which increases the electron density at the metal centre. However the anion [V(CO)₄(dmpe)]⁻ is known, and these observations are in accordance with the general trend for increasing ease of oxidation of complexes of the type [V(CO)_{6-n}L_n] (L = phosphine) with increasing carbonyl substitution (4).

This behaviour of trans-V(CO)₂(dmpe)₂ is in direct contrast to that of the analogous tantalum system where reduction of Ta(CO)₂(dmpe)₂Cl, prepared from NaNp and TaCl₂(dmpe)₂ in the presence of carbon monoxide, is easily achieved, yielding Na[Ta(CO)₂(dmpe)₂]: no evidence for the paramagnetic neutral species has been observed (115). There is no ready explanation for this as tantalum is generally regarded as more difficult to reduce than vanadium and normally the lower oxidation states are less frequently encountered. It should be mentioned that no zerovalent carbonyl derivatives are known for tantalum although it is possible to synthesise the fully

FIGURE 3.4.

STIRRED AND UNSTIRRED VOLTAMMETRY OF $t\text{-V(CO)}_2(\text{dmpe})_2$ IN $0.2 \text{ M } t\text{-Bu}_4\text{N}^+\text{PF}_6^-$, CH_2Cl_2



substituted species $Ta(LL)_3$ (LL = dmpe, bipy, o-phen) ⁽¹¹⁶⁾.

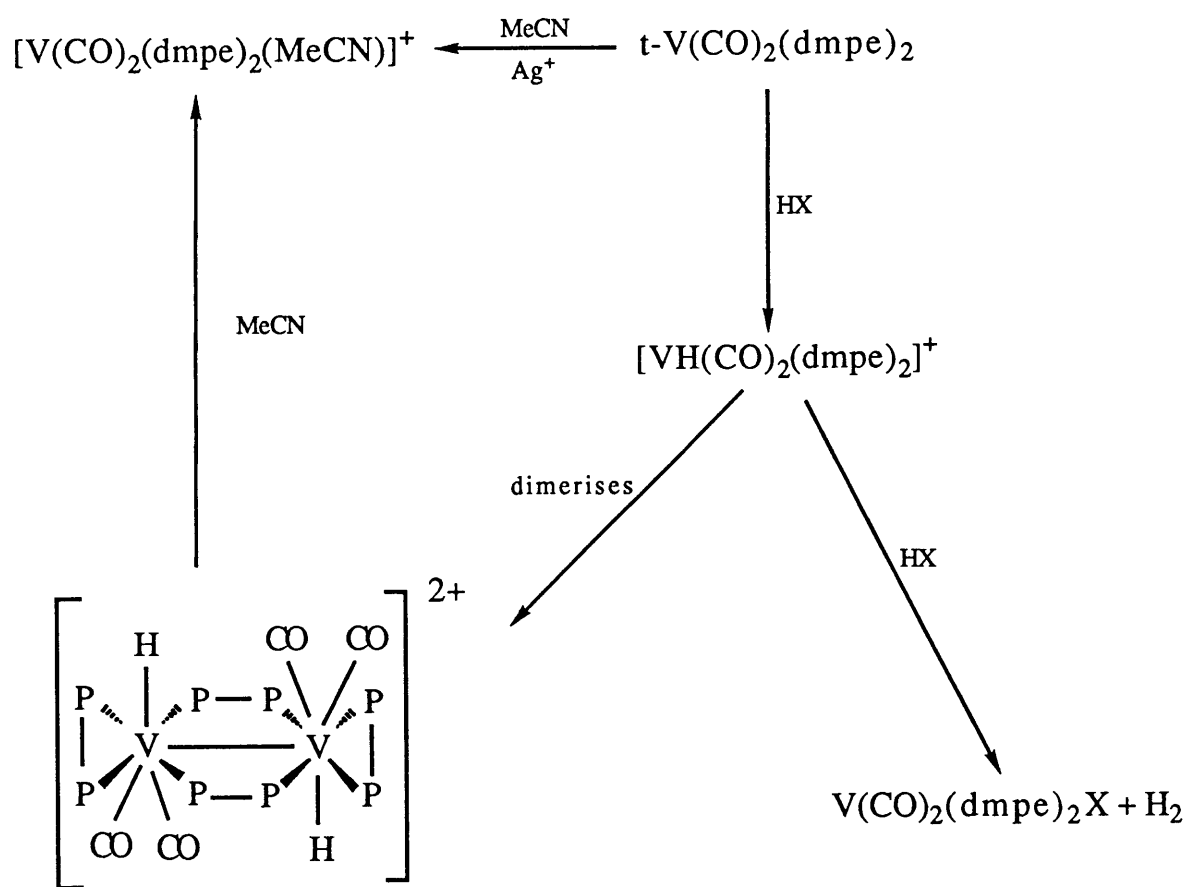
3.3. CONCLUSIONS

The chemistry of trans- $V(CO)_2(dmpe)_2$ appears to be dominated by the ease with which it undergoes one-electron oxidation to vanadium(I) and the resulting formation of eighteen electron complexes in the presence of coordinating ligands. This, and the corresponding absence of a reduced vanadium(-1) eighteen electron species is probably due to the electron-donating ability of the dmpe ligand which results in an electron-rich metal centre.

The reactions of trans- $V(CO)_2(dmpe)_2$ are summarised in Scheme 3.1.. There appear to be close parallels between the neutral vanadium dicarbonyl complex and the anionic species $[Ta(CO)_2(dmpe)_2]^-$ in that they both react with coordinating acids such as HCl or CF_3CO_2H to give neutral seven coordinate compounds $[M(CO)_2(dmpe)_2X]$. For the tantalum system it has been demonstrated that these reactions proceed through the hydride $TaH(CO)_2(dmpe)_2$ ⁽¹¹⁷⁾. Therefore it is proposed that trans- $V(CO)_2(dmpe)_2$ reacts in a similar manner with the initial formation of a cationic seven coordinate hydride species, which then reacts with a further equivalent of acid to yield $[V(CO)_2(dmpe)_2X]$ and hydrogen. In the absence of acid, this unstable intermediate dimerises to give the diamagnetic dimeric complex $[{HV(CO)_2(dmpe)_2}]_2^{2+}$.

It has been shown that protonation of trans- $V(CO)_2(dmpe)_2$ and cis- $Cr(CO)_2(dmpe)_2$ yield quite different products - binuclear $[V_2H_2(CO)_4(dmpe)_4]^{2+}$ and mononuclear $[CrH(CO)_2(dmpe)_2]^+$ ⁽⁸⁵⁾ respectively. The reason for this is clearly the one electron difference in

SCHEME 3.1. REACTIONS OF TRANS- $V(CO)_2(dmpe)_2$



the d^n population of the two zerovalent metal centres. The driving force for the formation of the product in both cases is the attainment of an eighteen electron configuration. This behaviour is again seen in the oxidation of the neutral dicarbonyl complexes, where the V^+ metal centre can achieve the desired number of electrons by coordinating an acetonitrile ligand whereas for chromium, solvent coordination does not occur as this would create an unfavourable 19e complex - a 17 electron metal centre being preferred because of the basicity of the dmpe ligand.

TABLE 3.3. I.R.^a SPECTRA FOR CIS-V(CO)₂(DMPE)₂X COMPLEXES

| X | $\nu(\text{CO})/\text{cm}^{-1}$ | Other Bands/ cm^{-1} |
|---------------------------------|---|---|
| Cl | 1811s, 1748s 1838s, 1777s ^b | |
| MeCO ₂ | 1809s, 1741s | 1624 [v(CO ₂)(asym)] 1323 [v(CO ₂)(sym)] |
| EtCO ₂ | 1808s, 1750s | 1602 [v(CO ₂)(asym)] |
| CF ₃ CO ₂ | 1816s, 1752s 1828s, 1767s ^c | 1696 [v(CO ₂)(asym)] 1698 ^c |
| PhPO ₂ H | 1808s, 1743s | 2268m [v(P-H)] 1200s [v(P=O)] |
| NH ₂ SO ₃ | 1816s, 1750s | 3370w [v(NH ₂)(asym)] 3260w [v(NH ₂)(sym)] 1570w [δ(NH ₂)] 1182 [v(S=O)] |
| N ₃ | 1800s, 1745s | 2060 [v(N≡N)] |
| CN | 1815s, 1765s | 2070 [v(C≡N)] |

a In Nujol mulls unless otherwise stated

b In hexane

c In toluene

TABLE 3.4. ^1H , ^{31}P AND ^{51}V N.M.R. DATA FOR $\text{CIS-V}(\text{CO})_2(\text{dmpe})_2\text{X}$
COMPLEXES

| X | $\delta(^{31}\text{P})^a$ ppm | J(P-V) Hz | $\delta(^{51}\text{V})^a$ ppm | J(V-P) Hz | $\delta(^1\text{H})^a$ ppm |
|--------------------------|----------------------------------|----------------|----------------------------------|----------------|--|
| Cl | 53.7 | 153 | -1134 | 157 | 1.32s (dmpe) |
| CF_3CO_2 | 54.0 | 153 | -1009 | 158 | 1.26s (dmpe) |
| MeCO_2 | 52.9 | 161 | -1074 | 159 | 1.69s (CH_3) 1.32s (dmpe) |
| EtCO_2 | 56.7 | 158 | -1083 | 161 | 1.88q (CH_2) 1.13s (dmpe) 1.08t (CH_3) |
| PhHPO_2 | 53.9 ^b | 157 | -975 | 160 | 1.34s (dmpe) |
| NH_2SO_3 | 52.6 | 164 | -906 | 161 | 1.22m, 0.88m (dmpe) 4.29s (NH_2) |
| N_3 | 53.6 | 153 | -1161 | 161 | 1.25s (dmpe) |
| CN | 57.4 ^c | <u>ca.</u> 117 | -1248 ^c | <u>ca.</u> 135 | 1.28s (dmpe) |

a in d^6 -benzene

b Additional singlet at 17.2 p.p.m. attributed to the P atom in the O_2PPh

c Broad signal due to increased quadrupolar relaxation

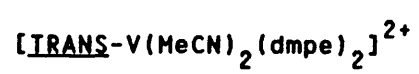
TABLE 3.5. ANALYTICAL AND SPECTROSCOPIC DATA FOR SALTS
OF THE $[\text{V}_2\text{H}_2(\text{CO})_4(\text{dmpe})_4]^{2+}$ ION

| | BF_4^- | | | $\text{PhC}(\text{SO}_2\text{CF}_3)_2^-$ | | |
|--------------------------------------|-------------------------------|--|-------------------|--|-------------------------|-------------------|
| Analysis ^a | C, 34.4 (34.2) | H, 6.4 (7.0) | P, 23.7 (23.5) | C, 36.0 (36.2) | H, 4.6 (5.0) | P, 14.7 (16.2) |
| | O, 9.0 (9.1) | F, 14.6 ^b (14.4) | | F, 15.2 (14.9) | | |
| IR ^c (cm^{-1}) | $\nu(\text{C}\equiv\text{O})$ | 1865, 1827 | | $\nu(\text{C}\equiv\text{O})$ | 1860, 1828 | |
| | $\nu(\text{C}\equiv\text{O})$ | 1875, 1850 ^d | | $\nu(\text{C}\equiv\text{O})$ | 1875, 1850 ^d | |
| | $\nu(\text{M-H})$ | 1952 | | $\nu(\text{M-H})$ | 1949 | |
| | $\nu(\text{M-H})$ | 1960, 1942 ^d | | $\nu(\text{M-H})$ | 1960, 1945 ^d | |
| NMR ^e : | ³¹ P | 55.8br | | | | |
| | ⁵¹ V | -1311br | | | | |
| | ¹⁹ F | -152s | | | | |
| | ¹ H | 1.63s [48 H], 2.06 ^f [16 H] | | | | |

- a Found (required)
b For methanol solvate (1 : 1)
c In Nujol mulls unless otherwise stated
d In CH_2Cl_2
e In CD_2Cl_2 at 298 K, δ values in p.p.m.
f Virtually coupled triplet

CHAPTER 4

REACTIONS OF THE CATION



4.1. INTRODUCTION

Recent studies on the chromium dication, [trans-Cr(MeCN)₂-(dmpe)₂]²⁺ have yielded some interesting results. The interaction of the tetraphenylborate salt of this cation with hydrogen resulted in the formation of the unique complex [Cr⁰(H.MeCN)₂(dmpe)₂][BPh₄]₂. The protons in this species are thought to be situated on the C≡N triple bonds of the acetonitrile ligands, the position of greatest electron density⁽⁹¹⁾. [trans-Cr(MeCN)₂(dmpe)₂]²⁺ was also attacked rapidly by methanol to yield the ethylidene amido complex, [trans-Cr(N=CHMe)₂-(dmpe)₂][BPh₄]₂⁽⁹¹⁾. In the light of these results, it was felt that undertaking similar studies on [trans-V(MeCN)₂(dmpe)₂][BPh₄]₂ could be worthwhile.

Additionally, substitution of the acetonitrile ligands in [trans-V(MeCN)₂(dmpe)₂]²⁺ was attempted as we felt that they might be easier to displace than the halide ligands in trans-VCl₂(dmpe)₂, especially if a solvent other than acetonitrile was used for the substitution reactions.

4.2. RESULTS AND DISCUSSION

4.2.1. Protonation Reactions of [trans-V(MeCN)₂(dmpe)₂]²⁺

The interaction of [trans-V(MeCN)₂(dmpe)₂][BPh₄]₂ with the fluorosulphonic acid, HCPH(SO₂CF₃)₂, in acetonitrile results in the isolation of two products - a few green plate-like crystals and a white solid. The infrared spectrum of the green crystals exhibited two bands at 2310 and 2280 cm⁻¹ which were assigned to ν_{CN}(asymmetric)

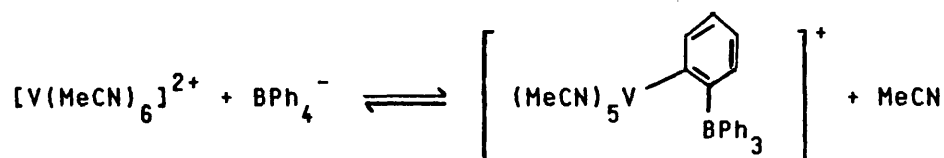
and ν_{CN} (symmetric) of coordinated acetonitrile respectively. The increase in the frequencies of these vibrations compared to free acetonitrile (2290 and 2245 cm^{-1}) is as expected (105). Elemental analysis revealed that the compound contained an inordinately large percentage of nitrogen. However insufficient quantities of these green crystals could be reliably isolated by this method of synthesis to definitively characterise them. Therefore, speculating that the product might contain the cation $[\text{V}(\text{MeCN})_6]^{3+}$ (considering the amount of nitrogen present), it was decided to attempt to synthesise this species using a more rational approach and then compare the properties of the two compounds.

Addition of three equivalents of NaBPh_4 to an acetonitrile solution of $\text{VCl}_3(\text{MeCN})_3$ produces a green solution and a white precipitate. Concentration of this green solution results in the precipitation of copious quantities of green mica-like crystals. The infrared spectrum is identical to that of the product from the acidification of $(\text{trans-V}(\text{MeCN})_2(\text{dmpe})_2)[\text{BPh}_4]_2$, i.e., ν_{CN} 2310 and 2280 cm^{-1} . This, together with the appearance of the complex, suggests that the two products are the same compound.

Elemental analysis of the green crystals leads to their formulation as $[\text{V}(\text{MeCN})_6][\text{BPh}_4]_2$. The +2 oxidation state of the metal is confirmed by magnetic susceptibility measurements which give $\mu_{\text{eff}} = 4.0$ B.M., thus indicating the presence of three unpaired electrons. The e.s.r. spectrum in acetonitrile at 77 K shows a strong feature at ca. 330 mT and can be interpreted as the result of the overlapping of eight equally spaced lines with $A(^{51}\text{V}) = 0.0073$ cm^{-1} . The real spectrum, together with a simulation based on the above interpretation, is shown in Fig. 4.1.. An eight-line pattern is observed because of

the presence of the vanadium nucleus (^{51}V , $I = 7/2$).

Conductivity measurements in acetonitrile indicate that the complex is a 2 : 1 electrolyte ($\Lambda_M = 158 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$). This value is slightly low [literature range for 2 : 1 electrolyte 220-300 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in MeCN ⁽¹¹⁴⁾] but this can probably be attributed to the size of the tetraphenylborate counter-ion. It is also possible that in solution an equilibrium of the type shown in Eq. (1) is set up, which would explain the lowered value for the molar conductivity.



Eq. (1)

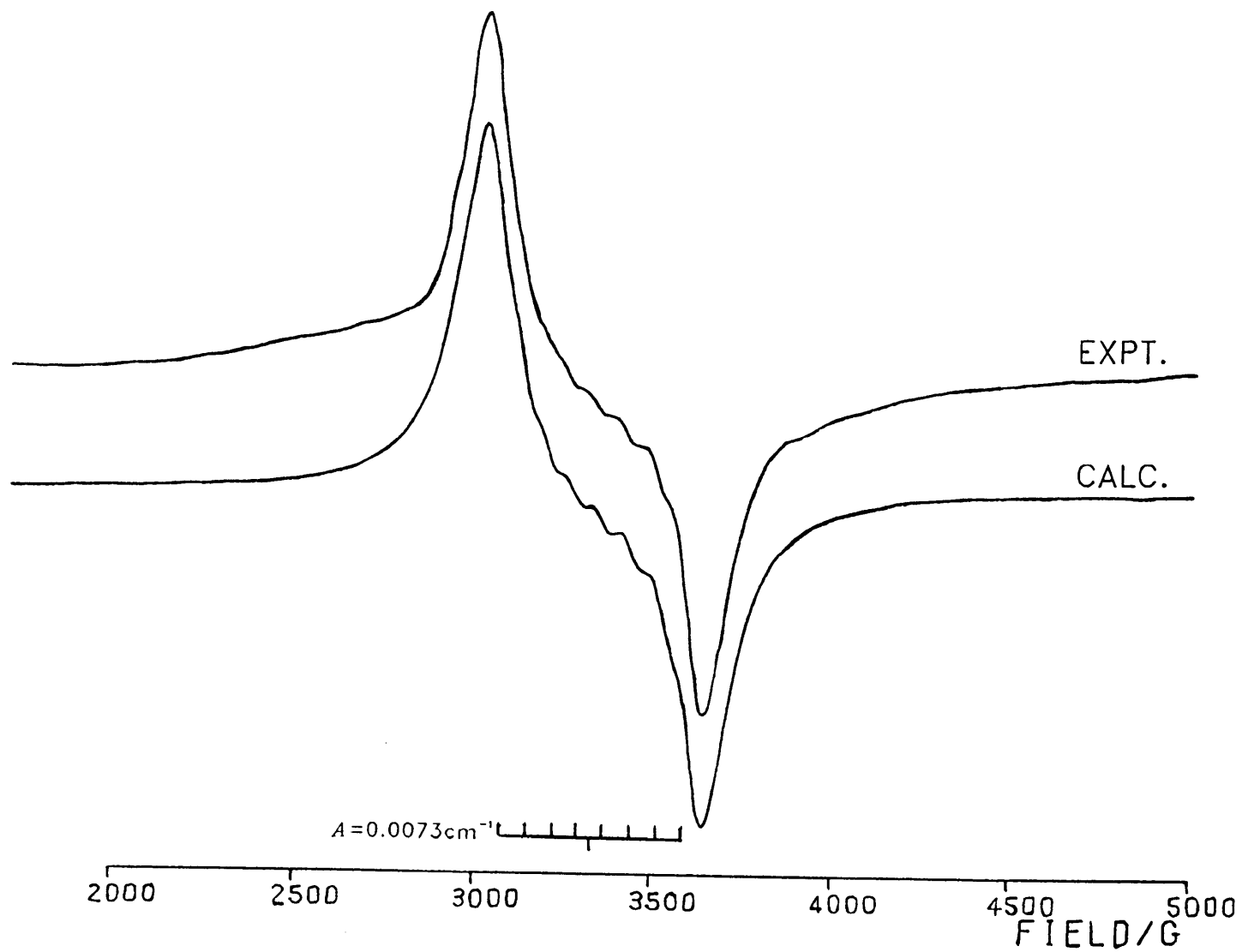
This might account for the fact that attempts to make the hexafluorophosphate salt of the dication, by substitution of NaPF_6 for NaBPh_4 , were unsuccessful, with no reaction occurring.

It is presumed that the reducing agent in the reduction of $\text{VCl}_3(\text{MeCN})_3$ to $[\text{V}(\text{MeCN})_6]^{2+}$ is the solvent, acetonitrile. The ability of acetonitrile to act as a reducing agent has been observed previously in the reaction of organonitriles with VCl_4 , leading to the isolation of the complexes $\text{VCl}_3(\text{RCN})_3$ ($\text{R} = \text{Me}, \text{Et}$) ⁽¹¹⁸⁾.

The X-ray structure of the $[\text{V}(\text{MeCN})_6]^{2+}$ dication has been determined ⁽⁸⁹⁾, isolated as the ZnCl_4^- salt from the reduction of VCl_3 by ZnEt_2 in acetonitrile.

The isolation of small quantities of $[\text{V}(\text{MeCN})_6][\text{BPh}_4]_2$ from the acidification of $[\text{trans-V}(\text{MeCN})_2(\text{dmpe})_2]^{2+}$ is presumably the result of protonation of the dmpe ligands, which then dissociate to give a

FIGURE 4.1. E.S.R. SPECTRA (EXPERIMENTAL AND SIMULATED) OF $[V(MeCN)_6][BPh_4]_2$



(dmpe)⁺ or (dmpe)²⁺ salt, followed by occupation of the vacant coordination sites around the vanadium(II) nucleus by solvent molecules.

[trans-V(MeCN)₂(dmpe)₂][BPh₄]₂ does not react with hydrogen, even at high temperature (> 100°C) or pressure (50 atm).

The addition of an excess of dmpe to an acetonitrile solution of [V(MeCN)₆][BPh₄]₂ results in the formation of [trans-V(MeCN)₂(dmpe)₂]-[BPh₄]₂: no evidence for the species [V(dmpe)₃]²⁺ is observed. However with other phosphines, e.g., PMe₃, dmpm, dppm, no substitution of the acetonitrile ligands occurs, with unreacted [V(MeCN)₆][BPh₄]₂ being isolated from the reaction mixtures. These results are probably due to the basicity and chelating ability of the dmpe ligand.

The addition of two equivalents of bipy to [V(MeCN)₆][BPh₄]₂ resulted in a reduced yield of the known complex [V(bipy)₃]²⁺; no evidence of any partially substituted products could be seen.

Unlike [trans-Cr(MeCN)₂(dmpe)₂]²⁺ which is rapidly attacked by methanol at room temperature, [trans-V(MeCN)₂(dmpe)₂]²⁺ shows no sign of reaction with methanol, even under refluxing conditions. A possible explanation for this lack of reactivity of [trans-V(MeCN)₂(dmpe)₂]²⁺, compared to its chromium analogue, is the greater nucleophilicity of the Cr(II) centre, since the initial step in the reaction is presumed to be oxidative addition of methanol⁽⁹¹⁾. In the chromium complex, there is a greater degree of π-back bonding to the dmpe ligand, thus decreasing the electron density at the chromium core and increasing the possibility for nucleophilic attack.

4.2.2. Substitution Reactions

(i) ^tBuNC

The interaction of [trans-V(MeCN)₂(dmpe)₂][PF₆]₂ with tert-butyl

isocyanide in refluxing methanol results in the precipitation of an orange solid, which can be recrystallised from acetonitrile at -20°C to yield large prisms of $[\text{trans-V}(\text{t-BuNC})_2(\text{dmpe})_2][\text{PF}_6]_2$.

The infrared spectrum of this moderately air-sensitive solid exhibits a strong band at 2150 cm^{-1} , attributable to ν_{CN} . Conductivity measurements in acetonitrile confirm that the complex is a 2 : 1 electrolyte ⁽¹¹⁴⁾ [$\Lambda_{\text{M}} = 270\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$].

The trans configuration for the isocyanide ligands has been confirmed by an X-ray crystallographic analysis (see Fig. 4.2.). Selected bond lengths and angles are given in Table 4.1. The structure contains one cation which is centrosymmetric. Comparison of this structure with that of $[\text{trans-V}(\text{MeCN})_2(\text{dmpe})_2]^{2+}$ shows that, within the limits of experimental error, the V-P distances in both complexes are the same [2.50 and 2.52 Å respectively] and that the V-C bond length in the isocyanide complex is approximately the same as the V-N distance in the acetonitrile compound [V-C = 2.10 Å and V-N = 2.08 Å]. This similarity in V-C and V-N bond lengths has also been observed when comparing these distances in $[\text{VL}_6]^{2+}$ [L = t-BuNC ⁽¹¹⁹⁾, MeCN ⁽⁸⁹⁾] where $V-C_{\text{av}} = 2.10\ \text{Å}$ and $V-N_{\text{av}} = 2.11\ \text{Å}$ respectively. Again, as in the comparison of $[\text{trans-V}(\text{MeCN})_2(\text{dmpe})_2]^{2+}$ and $[\text{V}(\text{MeCN})_6]^{2+}$, the V-C and C-N bond lengths in $[\text{trans-V}(\text{t-BuNC})_2(\text{dmpe})_2]^{2+}$ are almost identical to the corresponding average bond distances in $[\text{V}(\text{t-BuNC})_6]^{2+}$, thus indicating that the electron-releasing nature of the dmpe ligands is having little effect on the degree of $d\pi \rightarrow \pi^*$ (ligand) bonding. However, as in the acetonitrile case, there is a drop in the ν_{CN} stretching frequency of ca. 40 cm^{-1} [$[\text{V}(\text{t-BuNC})_6]^{2+}$, $\nu_{\text{CN}} = 2190\text{ cm}^{-1}$] when the four isocyanide ligands are replaced by the two dmpe ligands.

FIGURE 4.2. MOLECULAR STRUCTURE OF THE CATION

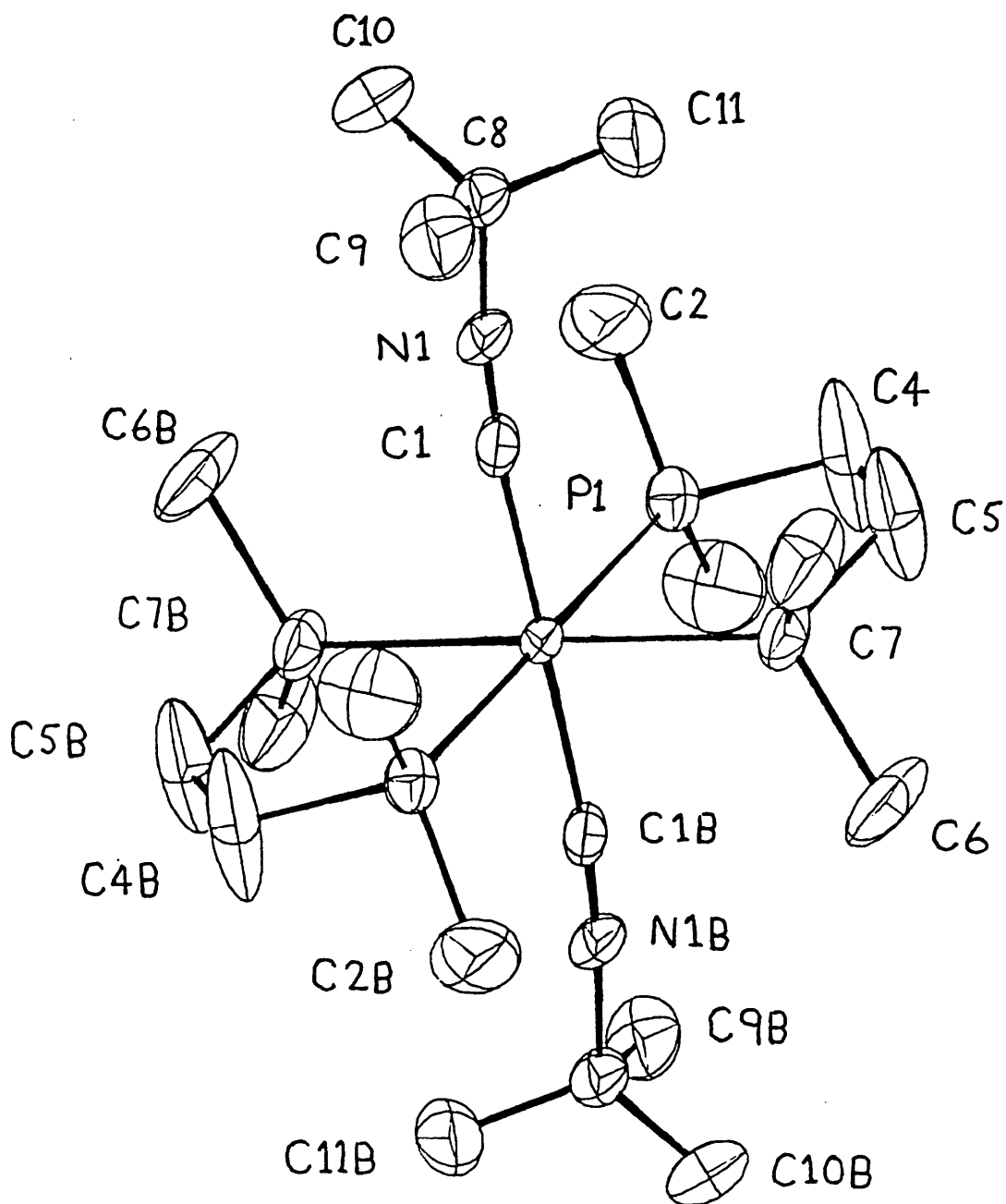
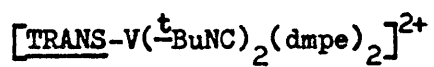
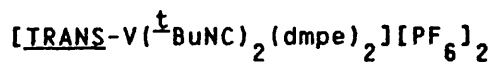


TABLE 4.1. SELECTED BOND LENGTHS AND ANGLES FOR



Selected bond lengths (Å) for [trans-V(^tBuNC)₂(dmpe)₂][PF₆]₂

| | | | |
|-----------|-------|-----------|-------|
| P(1)-V(1) | 2.495 | P(2)-V(1) | 2.502 |
| P(1)-C(4) | 1.825 | P(2)-C(5) | 1.811 |
| C(4)-C(5) | 1.337 | V(1)-C(1) | 2.099 |
| C(1)-N(1) | 1.154 | N(1)-C(8) | 1.490 |
| C(8)-C(9) | 1.561 | P(1)-C(2) | 1.812 |

Selected bond angles (°) for [trans-V(^tBuNC)₂(dmpe)₂][PF₆]₂

| | | | |
|----------------|--------|----------------|--------|
| P(1)-V(1)-P(2) | 80.78 | V(1)-P(1)-C(4) | 107.22 |
| V(1)-P(2)-C(5) | 107.83 | V(1)-C(1)-N(1) | 174.67 |
| C(1)-N(1)-C(8) | 174.91 | C(1)-V(1)-P(1) | 88.97 |
| C(1)-V(1)-P(2) | 87.73 | | |

The e.s.r. spectrum of [trans-V(^tBuNC)₂(dmpe)₂][PF₆]₂ shows a strong feature at ca. 330 mT, together with two weaker features at ca. 160 and 50 mT (see Fig. 4.3(a)). It is very similar to the spectrum of trans-V(CN)₂(dmpe)₂ (see Fig. 4.3(b)). From a study of the D v. B plots for S = 3/2 systems, it is apparent that the zero-field splitting parameter (D) is small in both cases. From the width of the line at g = 2.00 it is possible to put an upper limit on D of 0.01 cm⁻¹. The features at 160 mT in both spectra could be due to the forbidden transition ΔM_s = 2 while that at 50 mT in Fig. 4.3(a) might be due to the ΔM_s = 3 transition.

The e.s.r. spectra of trans-V(NCS)₂(dmpe)₂ and [trans-VCl(^tBuNC)(dmpe)] are also similar [Fig. 4.3(c) and (d) respectively] and can be interpreted using the same plots. It can be seen that D and λ (a symmetry parameter that can vary from zero for axial symmetry to one-third for maximum possible rhombic symmetry) are larger than in the spectra described above. The value for λ probably lies between 0.07 and 0.1 (i.e., near-axial symmetry) and D = 0.3-0.5 cm⁻¹. Exact values for λ and D cannot be obtained without a full simulation of the spectra. The e.s.r. spectrum of [trans-V(MeCN)₂(dmpe)₂]²⁺ (Fig. 4.3(e)) has a distinctive feature at ca. 7 mT which indicates that the value of D must lie between 0.14 and 0.16 cm⁻¹. However, without a full simulation of the spectrum, it is not possible to speculate as to the value of λ because of the width of the spectrum and the complexity of the theoretical spectra.

In all the complexes described here, the chelating nature of dmpe results in the phosphines being pulled into an oblong, rather than a square, geometry which leads to a reduction of the ligand field along a line bisecting the open angles in the plane, so that this line

FIGURE 4.3. E.S.R. SPECTRA OF $[\text{TRANS-VXX}'(\text{dmpe})_2]^{z+}$ ($z = 0, 1, 2$)

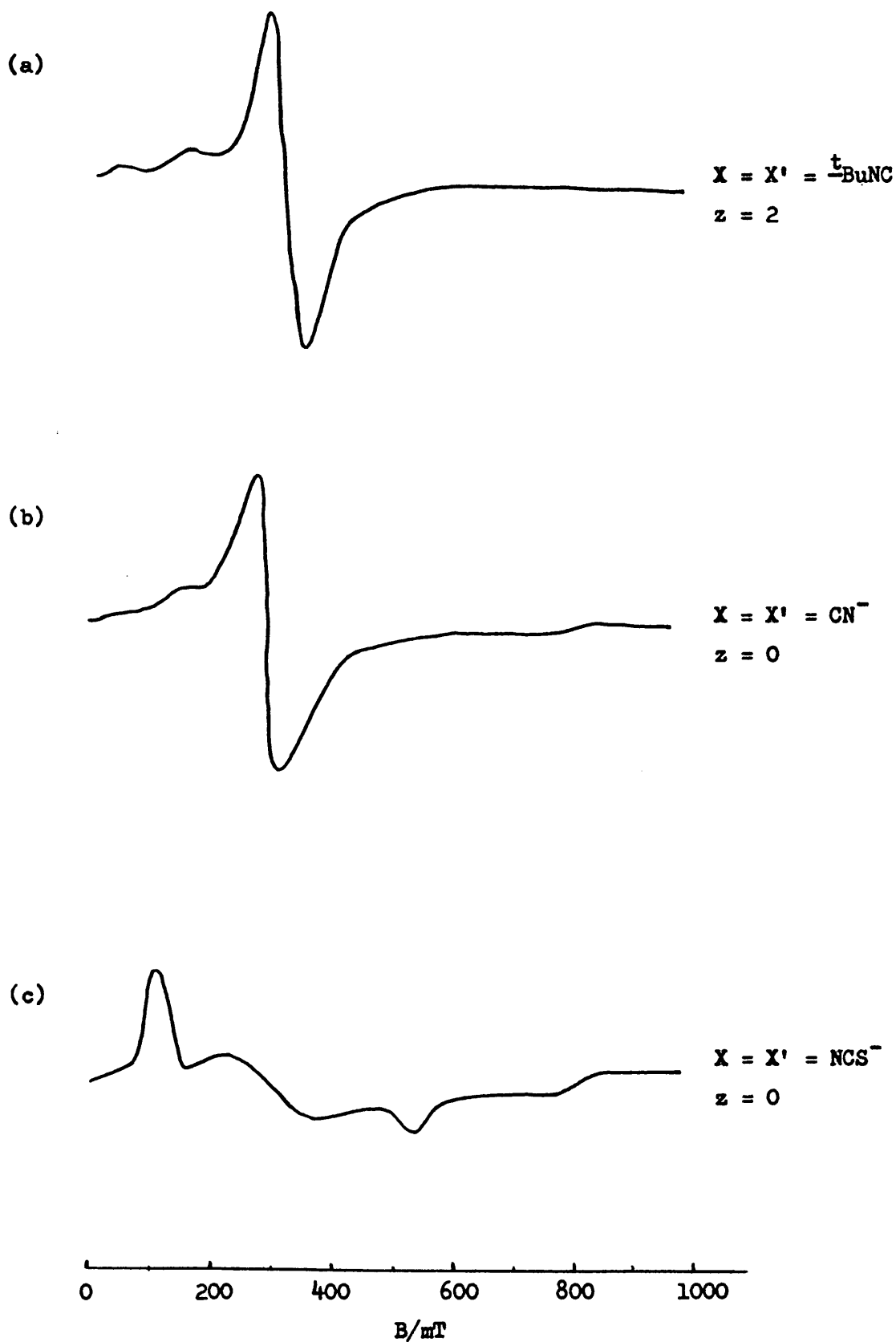
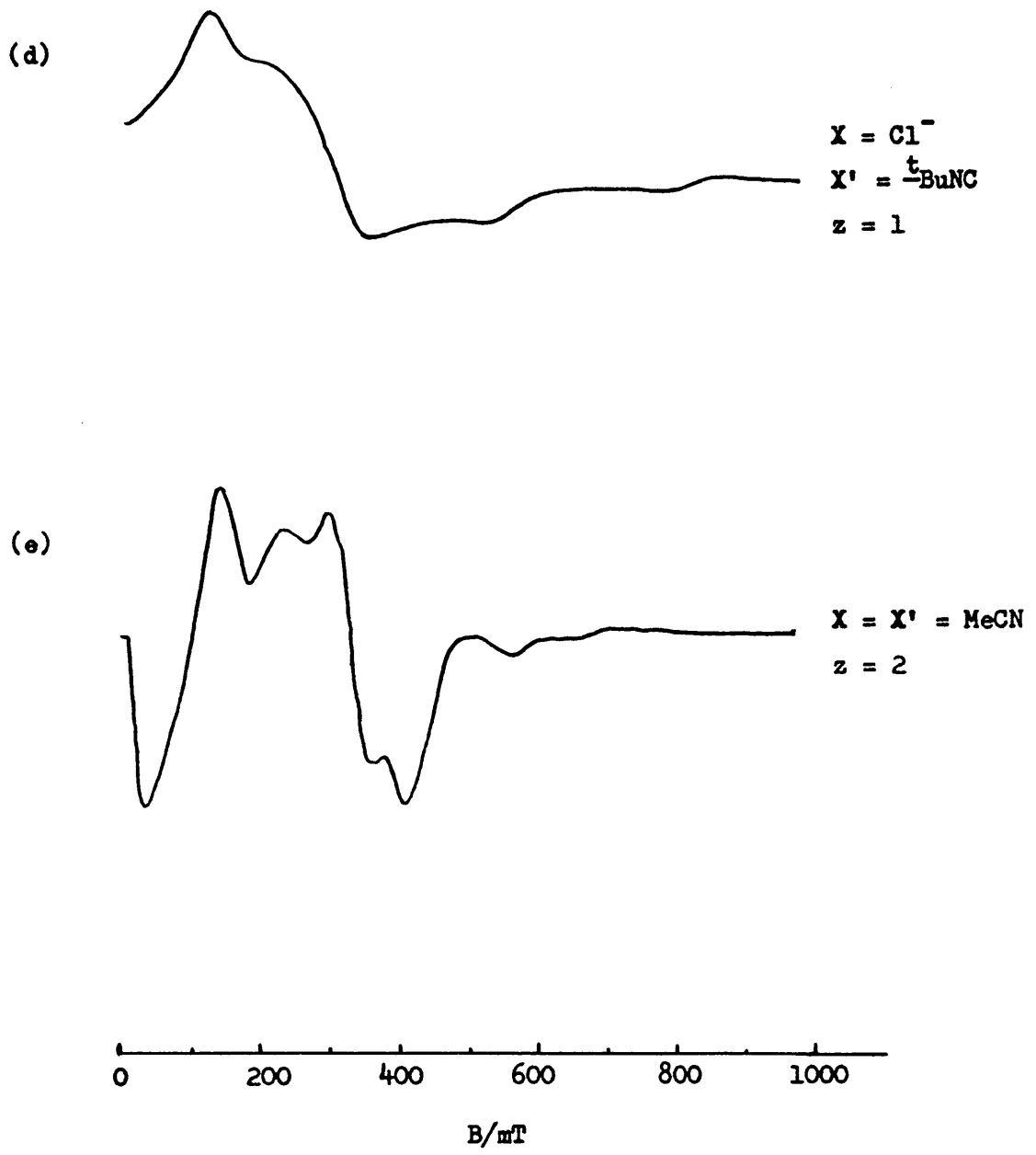
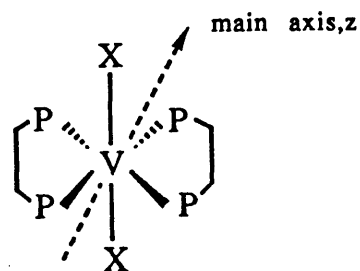


FIGURE 4.3. (continued)

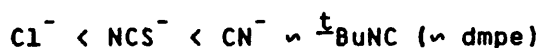


becomes the main spin-spin interaction axis (i.e., the z-axis for the D-tensor) ⁽¹²⁰⁾ as illustrated below:



The spin-Hamiltonian parameter, E, is governed by the distortion of the ligand field in that plane, which contains one X ligand and one dmpe ligand. Thus, from the experimental E values ($E = \lambda.D$), it should be possible to make a qualitative assessment of the ligand field strength of X relative to dmpe ⁽¹²⁰⁾.

From the rough estimates for λ and D obtained from the spectra, which give approximate values for E, it is possible to range the X ligands in order of ligand field strength relative to dmpe as shown below:



There is an inverse relationship between the ligand field strength and E. It is not possible to assign a position to MeCN due to the uncertainty as to the value of λ . The above order is in good agreement with the spectrochemical series of ligands ⁽¹²¹⁾. The position of dmpe i.e., of comparable ligand field strength to $\text{}^t\text{BuNC}$ and CN^- , is in accord with its strong σ -donor and weak π -acceptor properties in these complexes.

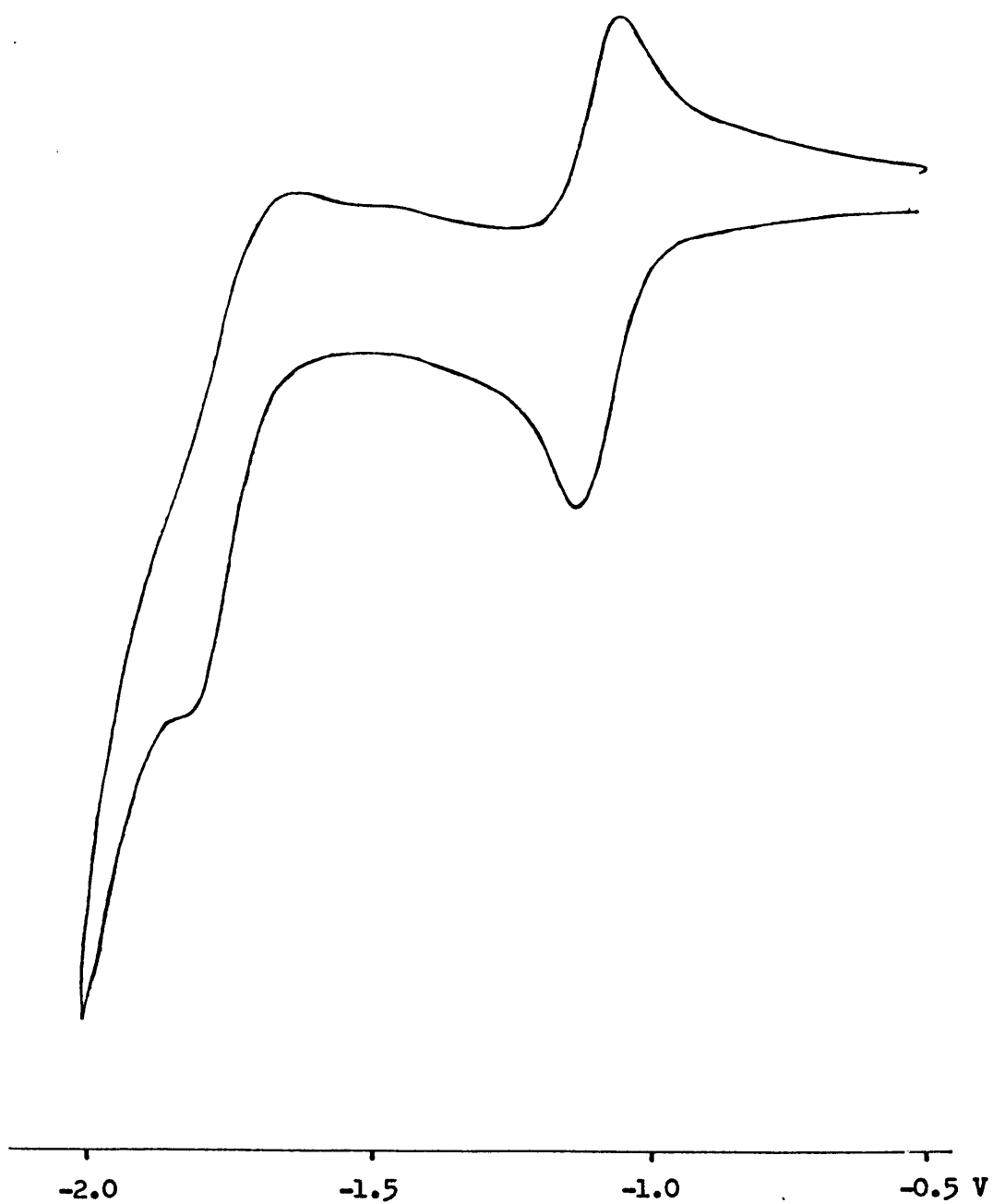
Electrochemical studies on $[\text{trans-V}(\text{}^t\text{BuNC})_2(\text{dmpe})_2][\text{PF}_6]_2$ in

acetonitrile show that the dication undergoes a reversible, 1e reduction at ca. -1.0 V (see Fig. 4.4.). The reversible nature of this reduction suggests that the sixteen electron vanadium(I) species, [trans-V(tBuNC)₂(dmpe)₂]⁺ is being formed in solution. This is in contrast to the oxidation of trans-V(CO)₂(dmpe)₂ in acetonitrile, where the only product isolated was the seven coordinate, eighteen electron vanadium(I) complex, [cis-V(CO)₂(dmpe)₂(MeCN)]⁺. This difference in the products formed can be attributed to the greater steric requirements of the bulky tert butyl isocyanide ligands compared to CO. The size of the isocyanide ligands prevents adoption of the cis-geometry, which would leave a vacant coordination site for a solvent molecule.

An attempt to synthesise the vanadium(I) isocyanide complex chemically, using zinc dust as a reducing agent, was unsuccessful.

In addition to the 1e reversible reduction observed, there is another reduction process on the edge of the solvent front at ca. -1.7 V. This wave, due to the process V^I/V^0 , does not appear to be reversible and attempts to make the zerovalent vanadium isocyanide compound were unsuccessful. It is not surprising that, for the complexes $[VL_2(dmpe)_2]^{z+}$, when $L = \text{t-BuNC}$ the species with $z = 2$ is easily isolated but when $L = CO$, the only stable complex has $z = 0$. This is a result of the greater σ -donor ability of tert-butyl isocyanide compared to CO, which allows for stabilisation of higher oxidation states. Carbon monoxide, being a better π -acceptor, enables the zerovalent vanadium dicarbonyl species to be isolated.

FIGURE 4.4. CYCLIC VOLTAMMAGRAM OF
 $[\text{TRANS-V}(\text{t-BuNC})_2(\text{dmpe})_2]^{2+}$ IN $0.2 \text{ M } \text{t-Bu}_4\text{N}^+\text{PF}_6^-$, MeCN



EXPERIMENTAL SECTION

EXPERIMENTAL : CHAPTER 1

All manipulations were carried out under oxygen-free nitrogen or argon or in vacuo, employing general Schlenk techniques. Microanalyses were performed by Pascher (Bonn) and Imperial College Laboratories. Melting points were determined under argon in sealed capillaries. Solvents were dried over sodium (except dichloromethane, acetonitrile and propionitrile which were dried over CaH_2 , and methanol which was dried over magnesium) and distilled from sodium benzophenone under nitrogen immediately before use. The petroleum used had boiling point $40\text{-}60^\circ\text{C}$. The trifluoromethanesulphonic acid was used as a stock solution in diethylether as were the hydrochloric, acetic, trifluoroacetic, propanoic and tetrafluoroboric acids.

Instruments Used

N.m.r. : Bruker WM-250 and JEOL FX90Q. δ values in p.p.m. relative to Me_4Si (^1H), 85% H_3PO_4 external (^{31}P) and VOCl_3 external (^{51}V) and run in d^6 -benzene, d^2 -dichloromethane or d^3 -acetonitrile.

I.r. : Perkin-Elmer 683; spectra in Nujol mulls unless otherwise stated.

E.s.r. : Varian E-12 (X-band); spectra in frozen solutions at 77 K.

Mass Spectrometry : VG Micromass 7070 and MS-9.

Conductivities : Data Scientific PTI-18, data in $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ and determined in acetonitrile unless otherwise stated.

Magnetic Susceptibilities : Were determined in solution using a modification of the Evans' method and in the solid state at ambient temperatures on an Evans' balance ^{*a}. Data in B.M. (B.M. = $0.927 \times 10^{-23} \text{ A m}^2$).

Electrochemistry : Was performed in acetonitrile or dichloromethane with 0.2 M solution of $(\text{t-Bu})_4\text{NPF}_6$ as inert electrolyte. Princeton Applied Research (EG and G). Model 174A Polarographic Analyzer.

X-ray Crystallography : Crystals were sealed under argon in thin-walled glass capillaries. All crystallographic measurements were made using a CAD4 diffractometer operating in the ω - 2θ scan mode with graphite-monochromated Mo-K α radiation ($\mu = 0.71069 \text{ \AA}$) in a manner previously described in detail ^{*b}.

*a D.F. Evans, J. Chem. Soc., 1959, 2003.

*b M.B. Hursthouse, R.A. Jones, K.M.A. Malik and G. Wilkinson, J. Am. Chem. Soc., 1979, 101, 4128.

EXPERIMENTAL : CHAPTER 2

2.1. Bis[tri- μ -chlorohexakis(tetrahydrofuran)vanadium(II)][hexachlorodizincate]

VCl_3 (10.0 g, 63.5 mmol) was placed in a Soxhlet thimble and was extracted with tetrahydrofuran (150 cm^3), containing zinc dust (2.1 g, 32.1 mmol) for ca. 72 h. After allowing the reaction mixture to cool to room temperature, the resulting green precipitate was collected, washed with tetrahydrofuran until a colourless filtrate was obtained, and then dried in vacuo.

Yield: 20.0 g, 75%.

2.2. trans-dichlorobis[1,2-bis(dimethylphosphino)ethane]vanadium(II)

To a suspension of $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$ (3.37 g, 2.08 mmol) in toluene (75 ml) was added dmpe (2.5 cm^3 , 16.67 mmol). The solution rapidly became red-purple in colour, and was stirred at room temperature for 24 h. Subsequent filtration, concentration and cooling to -20°C gave red-orange prisms of the complex.

Yield: 3.05 g (57%), m.p. 340°C [Found: C, 34.4; H, 7.65;

P, 28.2; Cl, 16.6. $\text{C}_{12}\text{H}_{32}\text{Cl}_2\text{P}_4\text{V}$ requires: C, 34.2; H, 7.65;

P, 29.4; Cl, 16.8%].

I.r.: 1420s, 1298s, 1280s, 1260w, 1132m, 1126m, 1083m, 990m, 950vs, 925s, 888s, 863m, 841m, 832m, 791w, 735s, 700s, 640s, 627w, 439m, 312s [$\nu(\text{VCl})$].

N.m.r. [$^1\text{H}(\text{C}_6\text{D}_6)$]: -9.8s (CH_2); -25.9s (CH_3).

Magnetic susceptibility (toluene, 298 K): $\mu_{\text{eff}} = 3.7$ B.M.

2.3. Reaction of $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$ with bis(diphenylphosphino)ethane

To $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$ (1.23 g, 0.76 mmol), in dichloromethane (80 cm³), was added dppe (2.50 g, 6.28 mmol). The reaction mixture was stirred at room temperature for 24 h. Subsequent filtration, concentration and cooling to -20°C yielded a green crystalline powder.

Yield: 2.00 g (95%). m.p. 140°C (dec) [Found: C, 54.1; H, 5.8;

P, 8.3. $\text{C}_{120}\text{H}_{128}\text{Cl}_{12}\text{O}_4\text{P}_4\text{V}_4\text{Zn}_2$ requires: C, 54.5; H, 4.9;

P, 9.4%].

2.4. bis[tri- μ -chlorohexakis(trimethylphosphine)vanadium(II)][hexachlorodizincate]

To a suspension of $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6]_2[\text{Zn}_2\text{Cl}_6]$ (1.49 g, 0.92 mmol), in toluene (50 cm³) at -78°C, was added PMe_3 (2 ml, 20 mmol). Warming to room temperature and stirring for 3 h. resulted in a pink precipitate which was collected, washed with toluene (2 x 20 cm³) and dried. Extraction into dichloromethane, concentration, addition of diethylether and cooling to -20°C yielded a purple crystalline solid. Yield: 0.80 g, 52%, m.p. 180°C (dec). [Found: C, 26.0; H, 6.7;

P, 21.9; Cl, 24.6. $\text{C}_{36}\text{H}_{108}\text{Cl}_{12}\text{P}_{12}\text{V}_4\text{Zn}_2$ requires: C, 25.8; H, 6.5; P, 22.2; Cl, 25.4%].

I.r.: 1435, 1420m, 1305, 1286, 1260, 1095, 1017, 960s, 850, 800,

727, 668w.

2.5. trans-dimethylbis[1,2-bis(dimethylphosphino)ethane]vanadium(II)

To a suspension of trans-VCl₂(dmpe)₂ (1.50 g, 3.55 mmol) in diethylether (50 cm³) was added LiMe (7.12 mmol, 0.89 M in Et₂O). The solution slowly turned dark orange and after 1 h. the solvent was removed. The residue was extracted into hexane (50 cm³), filtered, concentrated and cooled to -20°C, yielding dark yellow needles.

Yield: 0.20 g (48%). m.p. 145°C (dec). [Found: C, 43.7; H, 10.0;

P, 33.3. C₁₄H₃₈P₄V requires: C, 44.1; H, 10.0; P, 32.5%].

I.r.: 2758 [ν(CH)], 1420s, 1290s, 1275s, 1125m, 1100m [δ(CH)], 1074m,

983m, 940vs, 878s, 851m, 822s, 786w, 720s, 690s, 632s, 544m,

435m, 412s.

N.m.r. [¹H (C₆D₆)]: 11.7s (CH₂); -13.5s (CH₃).

Magnetic susceptibility (toluene, 298 K): μ_{eff} = 3.7 B.M.

2.6. [trans-bis(acetonitrile)bis[1,2-bis(dimethylphosphino)ethane]-vanadium(II)]bis[tetraphenylborate]

To trans-VCl₂(dmpe)₂ (0.50 g, 1.19 mmol), in acetonitrile (50 cm³), was added NaBPh₄ (0.82 g, 2.4 mmol). The solution rapidly turned dark red and NaCl precipitated. After stirring for 24 h., the solution was filtered, concentrated and cooled to -20°C to yield red prisms.

Yield: 1.12 g (88%), m.p. 100°C (dec). [Found: C, 70.9; H, 7.3;

N, 2.6; P, 11.4. C₆₄H₇₈B₂N₂P₄V requires: C, 71.7; H, 7.3;

N, 2.6; P, 11.6%].

I.r.: 3060m, 3040m, 2255w, 1580m, 1420s, 1308m, 1292m, 1262m, 1036m,
942s, 930m, 890m, 865w, 845w, 830vw, 800w, 740vs, 709vs, 615s.

Magnetic susceptibility (MeCN, 298 K): $\mu_{\text{eff}} = 3.3$ B.M.

Conductivity (MeCN, 298 K): $\Lambda_M = 249 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

The above complex cation can be obtained as the corresponding hexafluorophosphate by using NaPF_6 in place of NaBPh_4 .

2.7. [trans-bis(propionitrile)bis[1,2-bis(dimethylphosphino)ethane]-vanadium(II)]bis[tetraphenylborate]

To trans- $\text{VCl}_2(\text{dmpe})_2$ (0.79 g, 1.87 mmol), in propionitrile (50 cm^3), was added NaBPh_4 (1.28 g, 3.74 mmol). The solution was refluxed gently for 24 h. and then cooled. The red solution was filtered, concentrated and cooled to -20°C to yield red needles of the complex.

Yield: 1.54 g (75%), m.p. 160°C (dec). [Found: C, 71.9; H, 7.4;

N, 2.4; P, 11.4; B, 2.0. $\text{C}_{66}\text{H}_{82}\text{B}_2\text{N}_2\text{P}_4\text{V}$ requires: C, 72.1; H, 7.5, N, 2.5; P, 11.3; B, 2.0%].

I.r.: 3060m, 3040m, 2240w, 1580m, 1420s, 1308m, 1292m, 1265m, 945s,
930m, 893w, 870vw, 845vw, 802w, 755s, 736vs, 711vs, 615s.

Magnetic susceptibility (solid, 298 K): $\mu_{\text{eff}} = 3.4$ B.M.

Conductivity (EtCN, 298 K): $183 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

2.8. [(tert-butylisocyanide)chloro bis[1,2-bis(dimethylphosphino)ethane]vanadium(II)]bis[tetraphenylborate]

To trans- $\text{VCl}_2(\text{dmpe})_2$ (0.39 g, 0.92 mmol) and NaPF_6 (0.31 g, 1.85

mmol), in methanol (50 cm³), was added t-butyliisocyanide (0.25 ml, 2.21 mmol). Stirring the reaction mixture at room temperature for 24 h. resulted in a purple-blue solution and an orange precipitate. The solution was filtered, the solvent removed and the residue extracted into tetrahydrofuran (50 cm³). Subsequent filtration, concentration and cooling to -20°C yielded purple-red crystals of the complex.

Yield: 0.23 g (41%), m.p. 150°C (dec). [Found: C, 34.8; H, 6.9;

N, 2.2; Cl, 4.9; P, 23.7; V, 7.4. C₁₇H₄₁ClF₆NP₅V requires: C, 33.2; H, 6.7; N, 2.3; P, 25.2; Cl, 5.8; V, 8.3%].

I.r.: 2130vs (ν_{CN}), 1421s, 1302m, 1284m, 1260m, 1239w, 1190m, 1095m, 1065m, 1020w, 947s, 930s, 892m, 835vs, 735m, 705m, 645m, 561s.

Conductivity (MeCN, 298 K): Λ_M = 114 Ω⁻¹ cm² mol⁻¹.

Mass spectrum: M/e = 469 (M⁺, 0.6%).

2.9. trans-bis(thiocyanato)bis[1,2-bis(dimethylphosphino)ethane]-vanadium(II)

To a solution of trans-VCl₂(dmpe)₂ (0.29 g, 0.69 mmol), in acetonitrile (40 cm³) at -40°C, was added a methanolic solution of KNCS (0.14 g, 1.44 mmol). Slow warming to room temperature and stirring of the reaction mixture resulted in an initial pink precipitate. After 24 h. the solvent was removed and the residue extracted into tetrahydrofuran (50 cm³). Subsequent filtration, concentration and cooling to -20°C yielded dark red prisms.

Yield: 0.27 g (85%), m.p. 130°C (dec). [Found; C, 35.8; H, 6.9;

N, 6.3; S, 13.6; P, 27.0. C₁₄H₃₂N₂P₄S₂V requires: C, 36.0; H, 6.9; N, 6.0; S, 13.7; P, 26.6%].

I.r.: 2055vs (ν_{CN}), 1420s, 1301m, 1287m, 1260m, 1135m, 1083m, 1015w, 990w, 947vs, 928s, 892s, 869m, 838m, 800s, 738s, 705s, 642m, 629w, 480w (δ_{NCS}), 440w.

Magnetic susceptibility (solid, 298 K): $\mu_{\text{eff}} = 3.7$ B.M.

Mass spectrum: $M/e = 467$ (M^+ , 3.3%).

2.10. trans-dicyanobis[1,2-bis(dimethylphosphino)ethane]vanadium(II)

To trans- $\text{VCl}_2(\text{dmpe})_2$ (0.38 g, 0.9 mmol), in acetonitrile (50 cm^3) at room temperature, was added a methanolic solution of KCN (0.12 g, 0.9 mmol). After stirring for 24 h., the solvent was removed in vacuo. Extraction into tetrahydrofuran, concentration to ca. 35 cm^3 and then careful addition of hexane yielded an orange-yellow solid, which was isolated, washed with hexane and dried.

Yield: 0.20 g (55%), m.p. 150°C (dec). [Found: C, 41.8; H, 8.0;

N, 7.0; P, 29.1. $\text{C}_{14}\text{H}_{32}\text{N}_2\text{P}_4\text{V}$ requires: C, 41.7; H, 8.0;

N, 7.0; P, 30.8%].

I.r.: 2060s (ν_{CN}), 1427s, 1301w, 1295w, 1282m, 1262m, 1150w, 1093w, 1020w, 995w, 954vs, 929s, 893m, 840m, 805m, 735s, 707s, 645m.

Magnetic susceptibility (MeCN, 298 K): $\mu_{\text{eff}} = 3.7$ B.M.

Mass spectrum: $M/e = 406$ (H^+ , 1.6%).

2.11. trans-dicarbonylbis[1,2-bis(dimethylphosphino)ethane]vanadium(0)

A pressure bottle containing sodium amalgam (5 equivalents of Na per V) and trans- $\text{VCl}_2(\text{dmpe})_2$ (0.50 g, 1.18 mmol) in tetrahydrofuran (70 cm^3) at -78°C was pressurised with CO to 2 atm. The mixture was

vigorously stirred and allowed to warm to room temperature. The initial purple solution became red and finally orange. The solution was filtered, evaporated and the residue extracted with hexane (40 cm³). Filtration, concentration to ca. 10 cm³ and cooling to -20°C gave small orange-red prisms which were collected, and dried in vacuo.

Yield: 0.25 g (50%), m.p. 247°C (dec). [Found: C, 41.1; H, 8.1;

P, 28.4. C₁₄H₃₂O₂P₄V requires: C, 41.3; H, 7.9; P, 30.4%].

I.r.: 1820s, 1760s (ν_{CO}).

Hexane: 1763s.

Mass spectrum: M/e = 408 (M⁺, 54.2%).

E.s.r. (toluene, 77 K): g_x = 2.1563, g_y = 2.0523, g_z = 1.8379.

Magnetic susceptibility (CH₂Cl₂, 298 K): μ_{eff} = 1.53 B.M.

2.12. Bis(carbon disulphide)bis[1,2-bis(dimethylphosphino)ethane]-vanadium(0)

To trans-VCl₂(dmpe)₂ (0.27 g, 0.64 mmol) in tetrahydrofuran (40 cm³) and sodium amalgam (0.7%, 4 ml) at -78°C, was added CS₂ (16.6 mmol). Warming to room temperature and stirring for several hours resulted in the formation of a red solution. The solvent was removed in vacuo and the residue extracted with tetrahydrofuran. Subsequent filtration, concentration and cooling to -20°C for several days yielded an orange powder.

Yield: 0.14 g (43%), m.p. 60°C (dec). [Found: C, 30.6; H, 6.2;

P, 20.8; S, 28.1. C₁₄H₃₂P₄S₄V requires: C, 33.4; H, 6.4;

P, 24.7; S, 25.5%].

I.r.: 1420m, 1305m, 1289s, 1260w, 1192m, 1103vs (ν(CS₂)), 1050s,

1030s, 946vs, 920vs, 854s, 800w, 700s, 719s, 700w, 581s.

Mass spectrum: $M/e = 503 (M^+, 0.3\%)$.

2.13. Reduction of $[V_2(\mu-Cl)_3(thf)_6]_2[Zn_2Cl_6]$ in the presence of CO and PMe_3

To a suspension of $[V_2(\mu-Cl)_3(thf)_6]_2[Zn_2Cl_6]$ (1.00 g, 0.6 mmol) in tetrahydrofuran (50 cm^3) at -78°C , was added trimethylphosphine (1.5 ml, 15 mmol). Stirring and warming to room temperature resulted in a red-brown solution. The reaction mixture was transferred to a pressure bottle containing sodium amalgam (0.7%, 4 ml) at -78°C and then pressurised with CO to 2 atm. After warming to room temperature and stirring vigorously for ca. 2 h. the solution became orange. The solution was filtered, evaporated and extracted into toluene. Subsequent concentration yielded a toluene-insoluble yellow precipitate which was isolated, washed with hexane (2 x 20 ml) and toluene (2 x 20 ml) and then dried in vacuo.

Yield: 0.15 g, m.p. 145°C (dec). [Found: C, 30.7; H, 4.2; O, 17.5;

P, 14.4. $C_{10}H_{18}ClNaO_4P_2V$ requires: C, 32.1; H, 4.8; O, 17.1; P, 16.6%].

I.r. (thf): 1824s (ν_{CO}).

E.s.r. (thf, 77 K): $g_{\parallel} = 1.837$, $g_{\perp} = 1.892$, $A_{\parallel} (^{31}\text{P}) = 0.014$,

$A_{\perp} (^{31}\text{P}) = 0.005\text{ cm}^{-1}$.

2.14. Reaction of trans- $VCl_2(dmpe)_2$ with NO in toluene

Dry NO gas was bubbled slowly through a solution of trans-

-VCl₂(dmpe)₂ (0.50 g, 1.18 mmol) in toluene (50 cm³) for 10 min, resulting in an immediate yellow precipitate. Subsequent extraction into dichloromethane, concentration and cooling to -20°C yielded a yellow powder, which was isolated, washed with toluene (2 x 20 ml) and dried in vacuo.

Yield: 0.18 g. m.p. 130°C (dec). [Found: C, 29.4; H, 6.6; Cl, 16.6; N, 2.1; O, 12.8; P, 22.2].

I.r.: 1565s (v_{NO}), 1415m, 1306m, 1298m, 1283w, 1260s, 1205w, 1160s, 1095vs, 1018s, 948m, 935m, 918w, 902w, 865m, 800s, 763w, 751w, 740w, 721w, 715w, 665w, 620m, 547w, 468m.

EXPERIMENTAL : CHAPTER 3

Spectroscopic data for compounds described in this section can be found in Tables 3.3. and 3.4.

3.1. cis-Dicarbonylchloro bis[1,2-bis(dimethylphosphino)ethane]-vanadium(I)

To trans-V(CO)₂(dmpe)₂ (0.3 g, 0.74 mmol) in diethylether (40 cm³) at -78^oC was added HCl (1.47 mmol, 0.9 M in Et₂O). After stirring for ca. 1 h. at room temperature, the red solution was evaporated and the residue extracted into diethylether. Filtration, concentration and cooling to -20^oC gave red needles which were collected and dried in vacuo.

Yield: 0.2 g (60%), m.p. 200^oC (dec). [Found: C, 37.8; H, 7.3;

P, 27.7; Cl, 8.1; O, 7.5. C₁₄H₃₂ClO₂P₄V requires: C, 38.0; H, 7.2; P, 27.7; Cl, 8.0; O, 7.2%].

Mass spectrum: M/e = 442 (M⁺, 0.1%).

3.2. cis-Dicarbonyltrifluoroacetato bis-[1,2-bis(dimethylphosphino)-ethane]vanadium(I)

To trans-V(CO)₂(dmpe)₂ (0.26 g, 0.64 mmol), in tetrahydrofuran (50 cm³) at -78^oC, was added CF₃CO₂H (1.28 mmol, 1.5 M in Et₂O). The mixture was stirred and allowed to warm to room temperature. Removal of the solvent and extraction of the residue into hexane (50 cm³) gave a red solution. Filtration, concentration and cooling to -20^oC

yielded small red crystals.

Yield: 0.17 g (50%), m.p. 140°C (dec). [Found: C, 36.3; H, 6.1; P, 22.8; O, 13.1; F, 11.5. $C_{16}H_{32}F_3O_4P_4V$ requires: C, 36.9; H, 6.2; P, 23.8; O, 12.3; F, 11.0%].

3.3. cis-Dicarbonylaceto bis-[1,2-bis(dimethylphosphino)ethane]-vanadium(I)

To trans- $V(CO)_2(dmpe)_2$ (0.34 g, 0.84 mmol), in tetrahydrofuran (50 cm³) at -78°C, was added CH_3CO_2H (3.95 mmol, 2.6 M in Et_2O). After stirring for 24 h. at room temperature, the solvent was removed in vacuo, and the residue extracted and recrystallised from diethylether, yielding red crystals.

Yield: 0.2 g (50%), m.p. 130°C (dec). [Found: C, 41.3; H, 7.6; P, 24.2; O, 13.8. $C_{16}H_{35}O_4P_4V$ requires: C, 41.2; H, 7.5; P, 26.6; O, 13.7%].

3.4. cis-Dicarbonylpropionato bis-[1,2-bis(dimethylphosphino)ethane]-vanadium(I)

To trans- $V(CO)_2(dmpe)_2$ (0.48 g, 1.18 mmol), in diethylether (50 cm³) at -78°C, was added $EtCO_2H$ (2.5 mmol, 1.8 M in Et_2O). After stirring at room temperature for 24 h., the solvent was removed in vacuo, and the residue extracted and recrystallised from hexane, yielding red needles.

Yield: 0.28 g (50%), m.p. 135°C (dec). [Found: C, 42.6; H, 7.9; P, 25.2; O, 12.9. $C_{17}H_{37}O_4P_4V$ requires: C, 42.5; H, 7.7; P,

25.8; O, 13.3%].

3.5. cis-Dicarbonylphenylphosphinato bis-[1,2-bis(dimethylphosphino)-ethane]vanadium(I)

To trans-V(CO)₂(dmpe)₂ (0.16 g, 0.39 mmol), in toluene (40 cm³) at -78°C, was added PhPO₂H₂ (56.6 mg, 0.4 mmol). After stirring for 24 h. at room temperature, the solvent was removed in vacuo and the residue extracted and recrystallised from diethylether, yielding red crystals.

Yield: 0.13 g (65%), m.p. 140°C (dec). [Found: C, 44.0; H, 6.7;

P, 27.9; O, 11.4. C₂₀H₃₈O₄P₅V requires: C, 43.8; H, 6.9; P, 28.3; O, 11.7%].

3.6. cis-Dicarbonylsulphamato bis-[1,2-bis(dimethylphosphino)ethane]-vanadium(I)

To trans-V(CO)₂(dmpe)₂ (0.39 g, 0.96 mmol), in tetrahydrofuran (60 cm³) at room temperature, was added NH₂SO₃H (97.4 mg, 1 mmol). After stirring for 24 h., the solvent was evaporated and the residue extracted into toluene (40 cm³). Concentration and cooling to -20°C of the solution gave red needles.

Yield: 0.35 g (70%), m.p. 150°C (dec). [Found: C, 33.6; H, 6.9;

P, 24.5; O, 16.0; N, 2.8. C₁₄H₃₄NO₅P₄SV requires: C, 33.4; H, 6.8; P, 24.7; O, 15.9; N, 2.8%].

3.7. cis-Dicarbonylazido bis-[1,2-bis(dimethylphosphino)ethane]-vanadium(I)

(i) To trans-V(CO)₂(dmpe)₂ (0.47 g, 1.15 mmol), in hexane (50 cm³) at -78°C, was added Me₃SiN₃ (3 mmol, 0.5 M in hexane). After stirring at room temperature for 24 h., the resulting yellow precipitate was collected, washed with hexane (2 x 10 cm³), filtered and dried. Subsequent extraction into diethylether (50 cm³), filtration and cooling to -20°C gave orange needles which were collected and dried in vacuo.

Yield: 0.2 g (40%).

(ii) A methanolic solution of NaN₃ (0.1 g, 1.54 mmol) was added to cis-V(CO)₂(dmpe)₂Cl (0.31 g, 0.7 mmol) in methanol (30 cm³) at -78°C. After stirring for 24 h. at room temperature, the solvent was removed and the residue extracted into diethylether (50 cm³). Crystallization as above gave orange needles.

Yield: 0.25 g (80%), m.p. 140°C (dec). [Found: C, 37.9; H, 7.1;

N, 8.7. C₁₄H₃₂N₃O₂P₄V requires: C, 37.4; H, 7.1; N, 9.3%].

3.8. cis-Dicarbonylcyno bis-[1,2-bis(dimethylphosphino)ethane]-vanadium(I)

A methanolic solution of KCN (84.0 mg, 1.29 mmol) was added to cis-V(CO)₂(dmpe)₂Cl (0.15 g, 1.15 mmol) in methanol (50 cm³) at -78°C. After stirring at room temperature for 24 h., the solvent was removed and the residue extracted into acetonitrile (60 cm³). Subsequent filtration, concentration and cooling to -20°C gave yellow needles.

Yield: 0.37 g (75%), m.p. 200°C (dec). [Found: C, 41.9; H, 7.6;

P, 28.5; N, 3.3; O, 7.4. $C_{15}H_{32}NO_2P_4V$ requires: C, 41.6; H, 7.9; P, 28.6; N, 3.2; O, 7.4%].

Mass spectrum: $M/e = 434 (M^+, 6.8\%)$.

3.9. Salts of the cation $[HV(CO)_2(dmpe)_2]_2^{2+}$

(a) To trans- $V(CO)_2(dmpe)_2$ (0.24 g, 0.59 mmol), in methanol (40 cm^3) at $-78^\circ C$, was added tetrafluoroboric acid (0.6 mmol, 0.67 M in Et_2O). After allowing the red solution to warm, with stirring at room temperature for 24 h., the final orange solution was filtered, concentrated and cooled to $-20^\circ C$, yielding orange crystals of the tetrafluoroborate as methanol solvate.

Yield: 0.25 g (42%), m.p. $135^\circ C$ (dec).

Conductivity (MeOH, $25^\circ C$): $\Lambda_M = 90 \Omega^{-1} cm^2 mol^{-1}$.

(b) To trans- $V(CO)_2(dmpe)_2$ (0.22 g, 0.54 mmol), in toluene (40 cm^3) at room temperature, was added a toluene solution of $HCP(SO_2CF_3)_2$ (0.19 g, 0.54 mmol) giving an orange precipitate. The reaction mixture was stirred for about 2 h. and the solid collected, washed with toluene ($2 \times 20 cm^3$), and dried in vacuo.

Yield: 0.6 g (79%).

Conductivity (MeOH, $25^\circ C$): $\Lambda_M = 79 \Omega^{-1} cm^2 mol^{-1}$.

(c) The tetrafluoroborate can be converted to the tetraphenylborate by the addition of $NaBPh_4$ in methanol. However attempts to recrystallise this salt from acetonitrile lead to the isolation of $[V(CO)_2(dmpe)_2MeCN][BPh_4]$.

Analytical and spectroscopic data for these salts can be found in Table 3.5.

3.10. cis-Dicarbonylbis[1,2-bis(dimethylphosphino)ethane]acetonitrile
vanadium(I) tetraphenylborate

To trans-V(CO)₂(dmpe)₂ (0.4 g, 0.98 mmol), in acetonitrile (30 cm³) at -30°C, was added AgSO₃CF₃ (1 equivalent, 0.98 mmol) in the dark. After about 15 min the resultant red-brown solution was filtered and the solvent removed in vacuo. Addition of a methanolic solution of NaBPh₄ gave an orange precipitate which was collected, washed with methanol (2 x 10 cm³) and dried. Subsequent extraction into acetonitrile (30 cm³) gave an orange-brown solution, which was stirred with a small amount of mercury to collect the finely-divided silver suspended in solution. After several minutes the orange solution was filtered, concentrated and cooled to -20°C yielding orange-red prisms.

Yield: 0.5 g (50%), m.p. 170°C (dec). [Found: C, 62.4; H, 7.3;

P, 16.2; N, 1.9; O, 3.7. C₄₀H₅₅BNO₂P₄V requires: C, 62.6;

H, 7.2; P, 16.2; N, 1.8; O, 4.2%].

Conductivity (MeCN, 25°C): $\Lambda_M = 61 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$.

I.r.: 2250w (ν_{CN}); 1836s, 1779s (ν_{CO}).

(MeCN): 1839s, 1776s (ν_{CO}).

N.m.r. [¹H (CD₂Cl₂)]: 7.3s, 7.0s, 6.9s (phenyl); 1.95 (CH₂);

1.5 (CH₃).

EXPERIMENTAL : CHAPTER 4

4.1. [Hexakis(acetonitrile)vanadium(II)]bis[tetraphenylborate]

(a) To a solution of [trans-V(MeCN)₂(dmpe)₂][BPh₄]₂ (0.31 g, 0.29 mmol) in acetonitrile (40 cm³) at -30°C was added a solution of HCPPh(SO₂CF₃)₂ (0.21 g, 0.59 mmol) in acetonitrile (20 cm³). Warming to room temperature and stirring for 24 h. resulted in the formation of a green solution. The solvent was removed in vacuo and the residue washed with toluene (2 x 20 ml) to remove any unreacted acid. Subsequent extraction into acetonitrile, filtration and cooling to -20°C yielded green and white crystals.

Yield (green crystals): 0.03 g (10%), m.p. 190°C (dec).

I.r. (green crystals): 2310w, 2280 [v(C≡N)], 3055m, 1581m (BPh₄⁻).

(b) To a solution of VCl₃(MeCN)₃ (0.78 g, 2.78 mmol) in acetonitrile (40 cm³) was added a solution of NaBPh₄ (2.90 g, 8.34 mmol) in acetonitrile (20 cm³), and the reaction mixture stirred at room temperature for 24 h. The resulting green solution was filtered, concentrated and cooled to -20°C, producing large quantities of pale green plate-like crystals.

Yield: 2.46 g (95%), m.p. 196°C (dec). [Found: C, 77.1; H, 6.3;

N, 9.0; V, 5.7. C₆₀H₅₈B₂N₆V requires: C, 77.0; H, 6.2; N, 9.0; V, 5.5%].

I.r.: 3055m, 2310w, 2280m, 1580w, 1426m, 1299w, 1260s, 1145m, 1095s, 1027s, 845w, 800s, 739m, 726s, 698s, 624w, 615m, 600s, 485w, 462w, 417w.

Magnetic susceptibility (solid, 298 K): 4.0 B.M.

Conductivity (MeCN, 298 K): $\Lambda_M = 158 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

4.2. [trans-bis(acetonitrile)bis[1,2-bis(dimethylphosphino)ethane]]-vanadium(II)]bis[tetraphenylborate]

To a solution of $[\text{V}(\text{MeCN})_6][\text{BPh}_4]_2$ (0.35 g, 0.37 mmol) in acetonitrile (50 cm^3) was added dmpe (0.7 ml, 4.67 mmol), resulting in an immediate dark green solution. Stirring at room temperature for 24 h. produced an orange-red solution. Filtration, concentration to ca. 5 cm^3 and cooling to -20°C yielded red crystals.

Yield: 0.30 g (75%), m.p. 105°C (dec). [Found: C, 71.7; H, 7.3;

N, 2.6; P, 11.7. $\text{C}_{64}\text{H}_{78}\text{B}_2\text{N}_2\text{P}_4\text{V}$ requires: C, 71.7; H, 7.3; N, 2.6; P, 11.4%].

I.r.: 2250w (ν_{CN}).

4.3. [trans-bis(tert-butylisocyanide)bis[1,2-bis(dimethylphosphino)ethane]]vanadium(II)]bis[hexafluorophosphate]

To a suspension of [trans-V(MeCN)₂(dmpe)₂][PF₆]₂ (0.30 g, 0.42 mmol) in methanol (50 cm^3) was added t-BuNC (0.29 M in Et₂O, 0.93 mmol). The reaction mixture was gently refluxed for 24 h., resulting in an orange precipitate and colourless solution. The orange precipitate was isolated, washed with Et₂O (2 x 20 ml) and dried in vacuo.

Yield: 0.27 g (82%), m.p. 170°C (dec). [Found: C, 32.6; H, 6.3;

N, 3.7; F, 27.6; P, 23.2. $\text{C}_{22}\text{H}_{50}\text{F}_{12}\text{N}_2\text{P}_6\text{V}$ requires: C, 32.7; H, 6.2; N, 3.5; F, 28.3; P, 23.1%].

I.r.: 2150vs (ν_{CN}), 1426s, 1311m, 1306w, 1298m, 1260m, 1240m,

1189s, 1095m, 1020m, 952s, 936s, 898m, 875s, 836vs, 745m, 715m,

647w, 565s, 526w, 446w.

Magnetic susceptibility (solid, 298 K): $\mu_{\text{eff}} = 3.6 \text{ B.M.}$

Conductivity (MeCN, 298 K): $\Lambda_{\text{M}} = 270 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

REFERENCES

1. F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, (5th. Edition), in press.
2. E.M. Page, *Coord. Chem. Revs.*, 1984, 57, 237.
3. D.A. Rice, *Coord. Chem. Revs.*, 1982, 45, 67.
4. N.G. Connelly, *Comprehensive Organometallic Chemistry*, 1982, Vol. 3, Chap. 24, Pergamon Press, Oxford.
5. M. Schoenherr, *Z. Chem.*, 1980, 20, 155.
6. K.M. Sharma and S.K. Anand, *J. Inst. Chem. (India)*, 1979, 51, 208.
7. K.H. Thiele, W. Schmann, S. Wagner and W. Brüser, *Z. Anorg. Allg. Chem.*, 1972, 390, 280.
8. A. Lachouiez and K.H. Thiele, *Z. Anorg. Allg. Chem.*, 1977, 431, 88.
9. R. Choukroun and D. Gervais, *J. Chem. Soc., Dalton Trans.*, 1980, 1800.
10. F. Bottomley, J. Darwka, L. Sutlin and P.S. White, *Organometallics*, 1986, 5, 2165.
11. (a) E.O. Fischer, S. Vigoureux and P. Kuzel, *Chem. Ber.*, 1960, 93, 701; (b) V.N. Latyaeva, V.V. Pereskein and A.N. Lineva, *Tr. Khim. Khim. Teknol.*, 1974, 32 (Chem. Abstr., 1975, 83, 179, 261).
12. P. Petrovic and M. Maga, *Proc. Conf. Coord. Chem.*, 1980, 8th., 337.
13. O. Bortolini, F. di Furia and G. Modena, *J. Am. Chem. Soc.*, 1981, 103, 3925.

14. D.C. Bradley, M.B. Hursthouse, K.M.A. Malik and G.B.C. Vuru, *Inorg. Chim. Acta*, 1980, 44, L5.
15. P. Schwendt and M. Sivac, *Proc. Conf. Coord. Chem.*, 1980, 8th., 363.
16. M.K. Chandhuri and S.K. Ghosh, *Inorg. Chem.*, 1984, 23, 534.
17. M. Siroki, L. Maric and Z. Stefanac, *J. Inorg. Nucl. Chem.*, 1981, 43, 1151.
18. L. Saussine, H. Mimoun, A. Mitschler and J. Fischer, *J. Nouv. Chem.*, 1980, 4, 235.
19. E.A. Maatta, *Inorg. Chem.*, 1984, 23, 2560.
20. F. Preuss and W. Towae, *Z. Naturforsch.*, 1981, 36B, 1130.
21. H.J. de Liefde Meijer, M.J. Janssen and G.J.M. van der Kerk, *Chem. Ind. (London)*, 1960, 79, 119.
22. T.M. Vogelaar van der Huizen and J.H. Teuben, *J. Organomet. Chem.*, 1976, 105, 321.
23. M.F. Rettig and R.M. Wing, *Inorg. Chem.*, 1969, 8, 2685.
24. M. Pasquali, F. Marchetti, C. Floriani, *Inorg. Chem.*, 1979, 18, 2401.
25. A. Jezierski, J.B. Raynor, *J. Chem. Soc., Dalton Trans.*, 1981, 1.
26. K.P. Callahan and P.J. Durand, *Inorg. Chem.*, 1980, 19, 3211.
27. J.K. Money, J.C. Huffman and G. Christou, *Inorg. Chem.*, 1985, 24, 3297.
28. R. Seangprasertkij and T.L. Riechel, *Inorg. Chem.*, 1986, 25, 3121.
29. O. Pioversana and G. Cappuccilli, *Inorg. Chem.*, 1972, 11, 1543.
30. F.A. Cotton, G.E. Lewis and G.N. Mott, *Inorg. Chem.*, 1982, 21, 3127.
31. H.J. de Liefde Meijer and F. Jellinek, *Inorg. Chim. Acta*, 1970,

- 4, 651.
32. G.A. Razuvaev, V.N. Latyaeva, E.N. Gladyshev, E.V. Krasilnikova, A.N. Lineva and A.P. Kozina, *Inorg. Chim. Acta*, 1978, 31, L357.
 33. G. Wilkinson and J.M. Birmingham, *J. Am. Chem. Soc.*, 1954, 76, 4281.
 34. J.L. Robbins, N. Edelstrein, B. Spencer and J.C. Smart, *J. Am. Chem. Soc.*, 1982, 104, 1882.
 35. J. Nieman, J.H. Teuben, J.C. Huffman and K.G. Caulton, *J. Organomet. Chem.*, 1983, 255, 193.
 36. B. Hessen, J.H. Teuben, T.H. Lemmen, J.C. Huffman and K.G. Caulton, *Organometallics*, 1985, 4, 946.
 37. R.L. Bausemer, J.C. Huffman and K.G. Caulton, *Inorg. Chem.*, 1985, 24, 3003.
 38. L.F. Larkworthy and M.W. O'Donoghue, *Inorg. Chim. Acta*, 1983, 74, 155.
 39. J.R. Dorfman and R.H. Holm, *Inorg. Chem.*, 1983, 22, 3179.
 40. R.L.R. Towns and R.A. Levenson, *Inorg. Chem.*, 1974, 13, 105.
 41. F.A. Cotton, M.W. Extine, L.R. Falvello, D.B. Lewis, G.E. Lewis, C.A. Murillo, W. Schwotzer, H. Tomas and J.M. Troup, *Inorg. Chem.*, 1986, 25, 3505.
 42. J.K. Money, K. Folting, J.C. Huffman and G. Christou, *Inorg. Chem.*, 1987, 26, 944.
 43. S. Herzog, *Z. Anorg. Allg. Chem.*, 1958, 294, 155.
 44. P. Dapporto, F. Mani and C. Mealli, *Inorg. Chem.*, 1978, 17, 1323.
 45. V.M. Hall, C.D. Schmulbach and W.N. Soby, *J. Organomet. Chem.*, 1981, 209, 69.
 46. F.A. Cotton, S.A. Duraj and W.J. Roth, *Inorg. Chem.*, 1984, 23, 4113.

47. F.A. Cotton, S.A. Duraj, L.R. Falvello and W.J. Roth, *Inorg. Chem.*, 1985, 24, 4389.
48. F.A. Cotton, S.A. Duraj, W.J. Roth and C.D. Schmulbach, *Inorg. Chem.*, 1985, 24, 525.
49. F.A. Cotton, S.A. Duraj, L.E. Manzer and W.J. Roth, *J. Am. Chem. Soc.*, 1985, 107, 3850.
50. J.L. Poncet, J.-M. Barbe, R. Guilard, H. Oumous, C. Lecomte and J. Protas, *J. Chem. Soc., Chem. Commun.*, 1982, 1421.
51. W. Seidel, K. Kreisel and H. Mennenga, *Z. Chem.*, 1976, 16, 492.
52. S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *Inorg. Chem.*, 1984, 23, 1739.
53. R.M. Kowalski, A.L. Rheingold, W.C. Trogler, F. Basolo, *J. Am. Chem. Soc.*, 1986, 108, 2460.
54. Ch. Elschenbroich and J. Heck, *Angew. Chem.*, 1981, 93, 278.
55. J.C. Smart, B.L. Pinsky, M.F. Fredrich and V.W. Day, *J. Am. Chem. Soc.*, 1979, 101, 4371.
56. Ch. Elschenbroich, J. Heck, W. Massa, E. Nun and R. Schmidt, *J. Am. Chem. Soc.*, 1983, 105, 2905.
57. J. Nieman and J.H. Teuben, *Organometallics*, 1986, 5, 1149.
58. K. Ihmels and D. Rehder, *Organometallics*, 1985, 4, 1340.
59. K.L. Fjare and J.E. Ellis, *J. Am. Chem. Soc.*, 1983, 105, 2303.
60. J.E. Ellis and R.A. Faltynek, *J. Organomet. Chem.*, 1975, 93, 205.
61. W. Heilser, E. Winter and E. Schubert, *Chem. Ber.*, 1962, 95, 3070.
62. J.E. Ellis, R.A. Faltynek and S.G. Hentges, *J. Am. Chem. Soc.*, 1977, 99, 626.
63. R.B. King, *Organometallic Syntheses*, Academic Press, New York,

- 1965, Vol. 1, p. 105.
64. M. Hoch and D. Rehder, *J. Organomet. Chem.*, 1985, 288, C25.
 65. R.M. Kowalski, D.O. Kipp, K.J. Stauffer, P.N. Swepston and F. Basolo, *Inorg. Chem.*, 1985, 24, 3750.
 66. E.O. Fischer and K. Plesske, *Chem. Ber.*, 1960, 93, 1006.
 67. T. Saji and S. Aoyagui, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, 63, 405.
 68. J. Quirk and G. Wilkinson, *Polyhedron*, 1982, 1, 209.
 69. F. Näumann, D. Rehder and V. Pank, *Inorg. Chim. Acta*, 1984, 84, 117.
 70. M. Herberhold and H. Trampisch, *Inorg. Chim. Acta*, 1983, 70, 143.
 71. F.G.N. Cloke, P.J. Fyne, V.C. Gibson, M.L.H. Green, M.J. Ledoux, R.N. Perutz, A. Dix, A. Gourdon and K. Proust, *J. Organomet. Chem.*, 1984, 277, 61.
 72. H. Schmidt and D. Rehder, *Transition Met. Chem. (Weinheim, Ger.)*, 1980, 5, 214.
 73. R.L. Bansemer, J.C. Huffman and K.G. Caulton, *J. Am. Chem. Soc.*, 1983, 105, 6163.
 74. W.-L. Kwik and E.I. Stiefel, *Inorg. Chem.*, 1973, 12, 2337.
 75. J. Chatt, W. Hussain, G.J. Leigh, H. Motid, C.J. Pickett and D.A. Rankin, *J. Chem. Soc., Dalton Trans.*, 1985, 1131.
 76. Z. Dawoodi, M.L.H. Green, V.S.B. Mtetwa and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1982, 802.
 77. R.P. Tooze, Ph. D. Thesis, University of London, 1985, p. 110.
 78. C.A. Tolman, S.D. Ittel, A.D. English and J.P. Jesson, *J. Am. Chem. Soc.*, 1978, 100, 4080.
 79. M.L. Luetkens, W.L. Elcesser, J.C. Huffman and A.P. Sattelberger, *Inorg. Chem.*, 1984, 23, 1718.

80. S.S. Wreford and J.F. Whitney, *Inorg. Chem.*, 1981, 20, 3918.
81. C.A. McAuliffe and W. Levason, *Phosphine, Arsine and Stibine Complexes of the Transition Elements*, Elsevier, New York, 1979.
82. R.J. Bouma, J.H. Teuben, W.R. Beukema, R.L. Bansemer, J.C. Huffman and K.G. Caulton, *Inorg. Chem.*, 1984, 23, 2715.
83. G.S. Girolami, G. Wilkinson, A.M.R. Galas, M. Thornton-Pett and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 339.
84. J.E. Salt, G.S. Girolami, G. Wilkinson, M. Motevalli, M. Thornton-Pett and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 685.
85. J.E. Salt, G. Wilkinson, M. Motevalli and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1986, 1141.
86. R.J. Burt, G.J. Leigh and D.L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1981, 793.
87. K. Jacob, *Z. Chem.*, 1978, 18, 227.
88. F.W.B. Einstein, E. Enwall, D.M. Morris and D. Sultan, *Inorg. Chem.*, 1971, 10, 678.
89. P. Chandrasekar and P.H. Bird, *Inorg. Chim. Acta*, 1985, 97, L31.
90. M.B. Hursthouse, personal communication.
91. A.R. Barron, J.E. Salt, G. Wilkinson, M. Motevalli and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, in press.
92. L.D. Silverman, J.C. Dewan, C.M. Giandomenico and S.J. Lippard, *Inorg. Chem.*, 1980, 19, 3379.
93. R.J. Angelici, *Organomet. Chem. Rev., Sect. A*, 1968, 3, 173.
94. A.B. Erofeev, B.M. Bulychev and G.L. Soloveichik, *Zh. Neorg. Khim.*, 1980, 25, 2634.
95. D.M.P. Mingos, *J. Organomet. Chem.*, 1979, 179, C29.
96. I.S. Butler and A.E. Fenster, *J. Organomet. Chem.*, 1974, 66, 161.

97. G. Fachinetti, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1979, 1612.
98. A.B.P. Lever and G.A. Ozin, *Inorg. Chem.*, 1977, 16, 2012.
99. J.E. Salt, Ph.D. Thesis, University of London, 1985.
100. F. Basolo and R.G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd. Edition, John Wiley and Sons, New York, 1967.
101. Van H. Behrens and K. Lutz, *Z. Anorg. Allg. Chem.*, 1968, 356, 226.
102. (a) J.A. Connor and P.I. Riley, *J. Chem. Soc., Dalton Trans.*, 1979, 1318; (b) A.M. Bond, R. Colton and J.J. Jackowski, *Inorg. Chem.*, 1975, 14, 2526; (c) B.D. Dombeck and R.J. Angelici, *Inorg. Chem.*, 1976, 15, 2397; (d) M. Green, J.A.K. Howard, J. Proud, J.L. Spencer, F.G.A. Stone and C.A. Tsipis, *J. Chem. Soc., Chem. Commun.*, 1976, 671.
103. R.C. Mehrotra and R. Bohra, *Metal Carboxylates*, Academic Press (London), 1983.
104. I. Agrell, *Acta Chem. Scand.*, 1971, 25, 2965.
105. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th. Edition, John Wiley and Sons, 1986.
106. R. Garth Kidd, *Annual Reports on N.M.R. Spectroscopy*, Vol. 10A, Academic Press, 1980.
107. K. Ihmels and D. Rehder, *Organometallics*, 1985, 4, 1334.
108. D. Rehder, W.L. Dorn and J. Schmidt, *Trans. Met. Chem.* (Weinheim, Ger.), 1976, 1, 233.
109. M. Herberhold and H. Trampisch, *Z. Naturforsch, B : Anorg. Chem., Org. Chem.*, 1982, 37B, 614.
110. J.A. Connor, P.I. Riley and C.J. Rix, *J. Chem. Soc., Dalton Trans.*, 1977, 1317.

111. F.A. Cotton, M.P. Diebold and I. Shim, *Inorg. Chem.*, 1985, 24, 1510.
112. R.A. Walton, *Spectrochim. Acta*, 1965, 21, 1795.
113. P.C. Ford and R.E. Clarke, *J. Chem. Soc., Chem. Commun.*, 1968, 1109.
114. W. Geeray, *Coord. Chem. Rev.*, 1971, 7, 81.
115. S. Datta and S.S. Wreford, *Inorg. Chem.*, 1977, 16, 1134.
116. F.G.N. Cloke, P.J. Fyne, M.L.H. Green, M.J. Ledoux, A. Gourdon and C.K. Prout, *J. Organomet. Chem.*, 1980, 198, C69.
117. F.N. Tebbe, *J. Am. Chem. Soc.*, 1973, 95, 5823.
118. M.W. Duckworth, G.W.A. Fowles and R.A. Hoodless, *J. Chem. Soc.*, 1963, 5665.
119. L.D. Silverman, P.W.R. Corfield and S.J. Lippard, *Inorg. Chem.*, 1981, 20, 3106.
120. J.C. Hempel, L.O. Morgan and W.B. Lewis, *Inorg. Chem.*, 1970, 9, 2064.
121. K.F. Purcell and J.C. Kotz, *Inorganic Chemistry*, Saunders, 1977.