

Synthesis and NMR spectral studies of polynuclear complexes of rhodium(I) with bridging benzimidazole derivatives

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Reaction of $[\text{Rh}(\text{diolefin})(\mu\text{-Cl})_2]$ (diolefin = cycloocta-1, 5-diene or norbornadiene) with 2-substituted benzimidazoles (R-bztH; R = H, Me, Et, *n*-Pr or *n*-Bu) in the presence of triethylamine yields trinuclear complexes of the type $[\text{Rh}(\text{diolefin})(\mu\text{-R-bzt})_3]$. The latter compounds undergo displacement of diolefin with CO to give tetranuclear complexes of the formula $[\text{Rh}(\text{CO})_2(\mu\text{-R-bzt})_4]$. NMR spectral studies have been useful in assigning the structures of the complexes.

There has been a growing interest in the study of polynuclear complexes of rhodium in view of their possible use as multicentered catalysts¹⁻⁷. Polynuclear complexes, in general are also of significance, since such systems could function as models for intramolecular electron transfer reactions and could also behave as one dimensional conductors^{8,9}.

Noriaki *et al.*¹⁰ have patented the synthesis of trinuclear complexes of rhodium of the type $[\text{RhL}_2(\mu\text{-N-N})_3]$ (L_2 = cycloocta-1, 5-diene (cod); N-N = imidazole or benzimidazole; L = C_2H_4 ; N-N = imidazolate) which are prepared by reacting $[\text{RhL}_2(\mu\text{-Cl})_2]$ in tetrahydrofuran with an appropriate nitrogen heterocycle in the presence of BuLi at -60°C . Structural assignments for these complexes have not been revealed. Nevertheless the imidazolate complex containing cod has been found to be a hydroformylation catalyst for the conversion of olefins to aldehydes¹¹. Synthesis of some tri and tetra-nuclear complexes of rhodium containing imidazolate and its derivatives have also been described by Uson and co-workers¹². Earlier we have reported^{13,14} a number of binuclear complexes of rhodium containing bridging nitrogen heterocycles. As an extension of our earlier work, synthesis and NMR spectral investigations of polynuclear complexes of rhodium stabilised by substituted benzimidazole derivatives are reported in this paper.

Materials and Methods

The complexes such as $[\text{Rh}(\text{cod})(\mu\text{-X})_2]$, $[\text{Rh}(\text{nbd})(\mu\text{-Cl})_2]$ and $[\text{Rh}(\text{CO})_2(\mu\text{-X})_2]$ were prepared by published methods¹⁵⁻¹⁷. Infrared (in nujol and CH_2Cl_2) and ¹H and ¹³C NMR spectra (in CDCl_3) were recorded on a specord 75 IR spectrophotometer and Bruker WH-270 spectrometer, respectively. Solid state ¹³C

NMR spectrum was recorded on a Bruker MSL-300 spectrometer. Conductivity measurements were carried out using a Toshniwal conductivity bridge type CL 01.02. Molecular weight measurements were made using KNAUER vapour pressure osmometer.

Tris[cycloocta-1, 5-diene (cod) or norbornadiene (nbd)] *tris*- $[\mu\text{-R-benzimidazolato}$ (R-bzt)] *trirhodium* (1) (for cod, R = H, Me, Et, *n*-Pr or *n*-Bu; for nbd, R = Me or *n*-Pr)

The nitrogen heterocycle, R-bztH (1.0 mmole) followed by triethylamine (1.0 ml) was added to a hot solution of $[\text{Rh}(\text{diolefin})(\mu\text{-X})_2]$ (0.5 mmole) in acetone (30 ml). The resultant solution was refluxed for 3 hr, when shining yellow crystals of the desired product separated out. The crystals were filtered off, washed with water, acetone and dried *in vacuo*.

Octacarbonyl tetrakis($\mu\text{-R-benzimidazolato}$)*tettrahodium* (1) $[\text{Rh}(\text{CO})_2(\mu\text{-R-bzt})_4]$ (R = H, Me, Et, *n*-Pr or *n*-Bu): *Method-1*

Carbon monoxide was bubbled through a suspension of $[\text{Rh}(\text{cod})(\mu\text{-R-bzt})_3]$ in benzene (30 ml) for 4-5 hr. The resulting yellow solution was concentrated under reduced pressure to about 0.5 ml and ethanol was added when pale yellow microcrystals of the desired products separated out. The crystals were washed with ethanol and dried *in vacuo*.

Method-2

To an alcoholic solution (25 ml) of $[\text{Rh}(\text{CO})_2(\mu\text{-X})_2]$ (0.4 mmole), R-bztH (0.8 mmole) was added and the mixture was stirred for 1.5 hr in the presence of triethylamine (1.0 ml) to get pale yellow crystals of the desired product. The crystals were filtered off, washed with water, ethanol and dried *in vacuo*.

Table 1—Physical properties and elemental analyses of polynuclear complexes

[All the complexes are yellow crystalline solids]

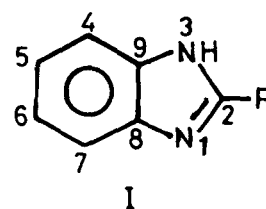
Complex	m.p. (°C)	Mol. weight ^a	Found (%) (calc.)		
			C	H	N
I [Rh(cod)(μ-bzt)] ₃	200	—	54.19 (54.88)	5.91 (5.22)	8.26 (8.53)
II [Rh(cod)(μ-2-Me-bzt)] ₃	250	897 (1026)	56.13 (56.14)	5.76 (5.59)	7.86 (8.18)
III [Rh(cod)(μ-2-Et-bzt)] ₃	164	—	56.20 (57.17)	5.62 (5.92)	7.54 (7.84)
IV [Rh(cod)(μ-2-n-Pr-bzt)] ₃	200	1076 (1110)	58.45 (58.37)	6.10 (6.26)	7.54 (7.56)
V [Rh(cod)(μ-2-n-Bu-bzt)] ₃	164	—	58.80 (59.40)	6.37 (6.54)	7.15 (7.29)
VI [Rh(nbd)(μ-2-Me-bzt)] ₃	172	—	54.96 (55.23)	5.04 (4.63)	8.58 (8.58)
VII [Rh(nbd)(μ-2-n-Pr-bzt)] ₃	186	—	57.45 (57.63)	5.50 (5.40)	7.76 (7.91)
VIII [Rh(CO) ₂ (μ-bzt)] ₄	160	—	38.00 (39.15)	2.37 (1.83)	9.15 (10.14)
IX [Rh(CO) ₂ (μ-2-Me-bzt)] ₄	156	1346 (1160)	41.39 (41.40)	2.28 (2.43)	9.40 (9.67)
X [Rh(CO) ₂ (μ-2-n-Bu-bzt)] ₄	164	—	47.65 (46.96)	4.07 (3.91)	8.13 (8.43)

^a Calculated value in parentheses

Results and Discussion

The halo-bridged binuclear complexes of the type [Rh(cod)(μ-X)]₂ (X = Cl or Br) react with benzimidazole or its 2-substituted derivatives (R = H, Me, Et, *n*-Pr or *n*-Bu) to give pale yellow products the elemental analyses of which correspond to the composition Rh(cod)X(R-bztH). Obviously the benzimidazole derivative cleaves the halo-bridges of the dimer to give simple mononuclear derivatives (these systems are being investigated). On the contrary, if the pH of the above reaction system is raised by using triethylamine (Et₃N) yellow crystalline products are obtained, the analytical data and other physical properties of which suggest that these should be formulated as [Rh(diolefin)(μ-R-bzt)]_n for cod, R = H, Me, Et, *n*-Pr or *n*-Bu; for nbd, R = Me or *n*-Pr). Some physical properties and analytical data of the isolated compounds are listed in Table 1.

The complexes are soluble in common organic solvents (excepting the Et-bzt containing complex) and are non-electrolytes in nitrobenzene. The IR spectra of these complexes either in nujol or in dichloromethane do not exhibit any peak assignable to νNH implying that the R-bztH ligand undergoes deprotonation at the pyrrole nitrogen during the reaction in the presence of Et₃N. This is further confirmed



by their ¹H NMR spectra which do not exhibit the presence of NH resonance signal around δ11.0. The resonance signals due to the coordinated diolefin and R-bzt groups are easily discernible. Each of these [Rh(cod)(μ-R-bzt)]_n complexes (except when R = H) shows six sets of resonance signals (Fig. 1), three of these sets (which are complex) in the range of δ1.2 to 3.0 correspond to the diolefin ligands and the other three (labelled as a, b and c)† in the range δ6.8 to 8.4 due to the bzt groups (Table 2). These results suggest that not only there are three diolefin molecules and three R-bzt groups per molecule of the complex but also the groups are in three different chemical environments (probably oriented in different directions caused by steric effects arising from the R group). On the basis of these results the complexes may be proposed

† Assignments a, b etc are tentative

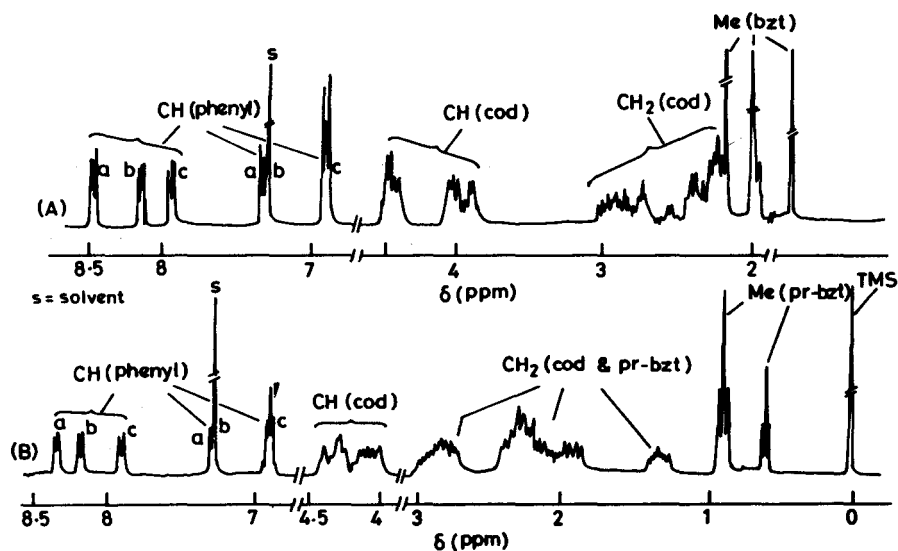


Fig. 1— ^1H NMR spectra (in CDCl_3) of (a) $[\text{Rh}(\text{cod})(\mu\text{-Me-bzt})_3]$ and (b) $[\text{Rh}(\text{cod})(\mu\text{-Pr-bzt})_3]$

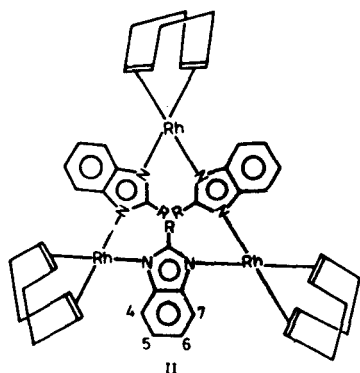
Complex	Table 2—IR (cm^{-1}) and ^1H NMR (δ in ppm) spectral data					
	$\nu\text{C}=\text{C}$ $\nu\text{C}=\text{N}$	$\nu\text{CH}(\text{def})$	Diolefin/ νCO	cod		Nitrogen heterocycle
				CH_2	CH	
I	1600	735, 715	1285, 1232, 1160 1067	1.89m 2.53m	4.28s	6.78s(CH), 6.97m and 7.8m (phenyl)
II	1600	735, 730	1270, 1200, 1140 1060, 620	1.25-2.5m 2.73-3.0m	3.8-4.0m 4.36-4.46m	0.95s, 1.96s, 2.15s (Me) 6.8m, 6.9m, 7.3m, 7.9m, 8.12m and 8.42m (phenyl)
III	1595	740, 730	1270, 1150, 1060 960, 620			
IV	1510	735, 720	1270, 1140, 980 940, 620	1.82-2.53m 2.75-2.91m	3.98-4.13m 4.25-4.36m	0.58, 0.71m and 0.88m (propyl) 6.9m, 7.26m, 7.88m, 8.18m and 8.35m (phenyl)
V	1600	750, 720				
VIII	1605	735, 705	2010, 2090			6.53s(CH) 7.23m and 7.72m (phenyl)
IX	1605	732, 710	2010, 2070			0.42s, 1.56s, 1.91s (Me) 7.0m, 7.18m, 7.31m, 7.48m, 7.7m and 7.88m (phenyl)
X	1605	735, 710	2005, 2080			
$[\text{Rh}(\text{CO})_2(\mu\text{-2-Et-bzt})_4]$	1596	715	2005, 2070			

to have a trinuclear structure(II). The ^{13}C NMR spectrum of $[\text{Rh}(\text{cod})(\mu\text{-Me-bzt})_3]$ complex (Fig. 2) \ddagger in CDCl_3 also exhibits six sets of resonance signals, three of these due to the diolefin ligands and the other three due to Me-bzt groups (Table 3) supporting the trimeric formula for the complex. The solid state ^{13}C NMR spectrum of this compound (Fig. 3) also exhibits spectral features which are more or less comparable to those in the solution spectrum implying that the trim-

eric form exists both in the solid state and in solution. Molecular weight measurements in chloroform further support the trimeric nature of the complexes (Table 1).

Surprisingly both the ^1H (Fig. 1B) and ^{13}C NMR spectra of the benzimidazolate complex exhibit only two sets of resonance signals, one set assignable to the diolefin ligands and the other to the bzt groups (Table 2). Presumably the bzt complex also has a trimeric structure and in this case it is likely that all the three diolefin ligands are in identical chemical environments, so also all the three bzt groups owing to the reduced steric hindrance by hydrogen on C-2 (I, R = H).

\ddagger For comparison the ^{13}C NMR spectra of $[\text{Rh}(\text{cod})(\mu\text{-bzt})_3]$, $[\text{Rh}(\text{cod})(\mu\text{-Cl})_2]$ and Me-bztH along with assignments are also included

Table 3— ^{13}C NMR spectra (δ in ppm)

Compound	cod		Nitrogen heterocycle*
	CH ₂	CH	
2-Me-bztH	—	—	14.82(R) 114.59(5,6) 122.23(4, 7) 138.99(8, 9), 151.63(2)
[Rh(cod)(μ -Cl)] ₂	30.97	78.62	—
[Rh(cod)(μ -bzt)] ₃	31.8	80.48	116.69(5,6), 120.10(4, 7) 149.20(2), 143.25(8, 9)
[Rh(cod)(μ -2-Me-bzt)] ₃	28.22	75.76	19.49, 18.52 (Me) 115.64, 117.41 and 118.01 (5,6) 31.14 79.83 118.39, 119.30 and 119.50 (4,7) 34.50 84.04 143.20, 143.72 and 144.52 (8,9) 148.67, 158.13 and 161.02(2)

* Numbers in parentheses correspond to the labellings

That is the bzt groups are oriented in such a way that all of them experience an equivalent chemical environment in the complex. Molecular model studies on the complexes containing benzimidazolate and methylbenzimidazolate groups support the above deductions.

It has been found earlier¹⁴ that the nitrogen heterocycle-bridged dinuclear complexes of the type $[\{\text{Rh}(\text{diolefin})(\text{X})\}_2(\mu\text{-N-N})]$ react with CO to give carbonyl complexes of the type $[\{\text{Rh}(\text{CO})_2\text{X}\}_2(\mu\text{-N-N})]$ by the displacement of each of the diolefin group by two CO molecules. Carbonyl complexes of the formula $[\text{Rh}(\text{CO})_2(\mu\text{-R-bzt})]_n$ have also been obtained presently by bubbling CO through benzene solution of trimers. These carbonyl complexes could also be obtained by treating halo-bridged carbonyl dimers of the type $[\text{Rh}(\text{CO})_2(\mu\text{-X})_2]$ (X = Cl

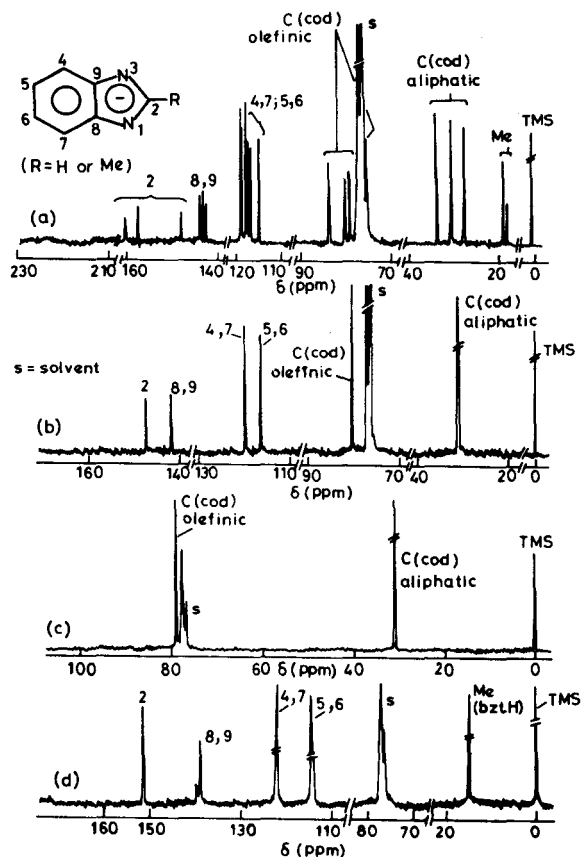


Fig. 2— ^{13}C NMR spectra (in CDCl_3) of (a) $[\text{Rh}(\text{cod})(\mu\text{-Me-bzt})]_3$, (b) $[\text{Rh}(\text{cod})(\mu\text{-bzt})]_3$, (c) $[\text{Rh}(\text{cod})(\mu\text{-Cl})]_2$, (d) Me-bztH

or Br) with benzimidazole derivatives in ethanol in the presence of Et_3N .

The carbonyl complexes are freely soluble in common organic solvents and behave as non-electrolytes in nitrobenzene. Satisfactory elemental analyses have been obtained for all the complexes and the analytical data along with some physical properties are given in Table 1. The IR spectra of the complexes exhibit, in addition to bands due to the coordinated bzt groups, two very intense bands around 2000 cm^{-1} assignable to *cis* carbonyl groups (Table 2).

The ^1H NMR spectra of the carbonyl complexes do not exhibit peaks due to the diolefin ligands, but exhibit four sets of resonance signals due to the R-bzt groups suggesting the presence of at least four such heterocyclic groups per molecule of the complex situated in different chemical environments (Table 2). In the case of the benzimidazolate complex only one set of resonance signals have been observed (Table 2) suggesting that the bzt groups are oriented in such a way that they experience an equivalent chemical environment as in the case of the parent diolefin complex. On the basis of these results, a tetrameric structure

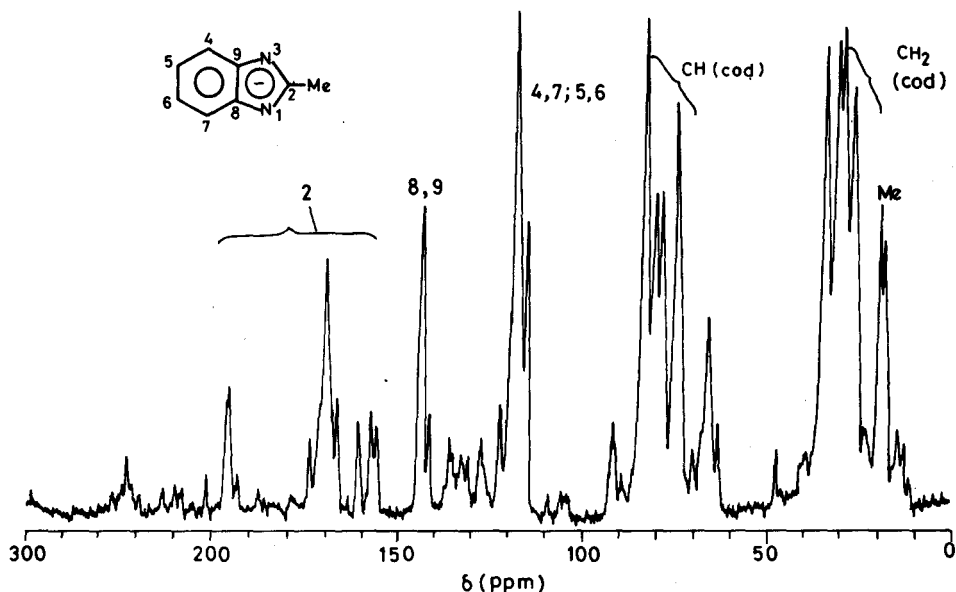
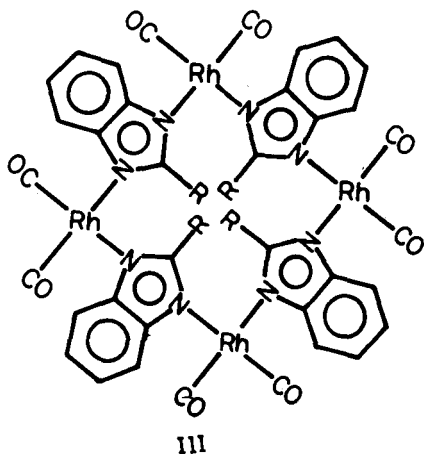


Fig. 3— ^{13}C NMR spectrum (solid state) of $[\text{Rh}(\text{cod})(\mu\text{-Me-bzt})]_3$



(III) may be proposed for the complexes. Molecular weight measurements in chloroform also support the tetrameric nature of the complexes (Table 1). The above results indicate that the trinuclear diolefin complexes on carbonyl substitution get converted into tetranuclear complexes. Such a conversion is perhaps due to changing the terminal ligand from cod to carbonyls. This modifies the electron density on the metal atom in such a way that a change in the molecular geometry is necessary for stabilising the system¹⁸. Formation of such tetranuclear structures has been confirmed by Uson and co-workers¹² and Rasmussen and co-workers¹⁸ by X-ray crystal structure studies.

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