Cationic Hydrazine and Hydrazone Complexes of Ruthenium(II) Containing Isocyanide Ligands

E. SINGLETON* and H. E. SWANEPOEL

National Chemical Research Laboratory, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria 0001, Republic of South Africa

The hydrazone complexes trans-$[Ru(CNR)_4(NH_2NCMe_2)_2](BPh_4)_2$ (1; CNR = $CNBu^t$, CNC_6H_{11}, $CNCH_2Ph$, $CNC_6H_3Me_2$-2,6) have been prepared from $[Ru(C_8H_{12})(NH_2NH_2)_4](BPh_4)_2$ (2; C_8H_{12} = 1,5-cyclooctadiene) and the appropriate isocyanide in boiling acetone solutions. With ethanol as solvent, (2) and $CNBu^t$ gave mer-$[Ru(CNBu^t)_3(NH_2NH_2)_3](BPh_4)_2$ (3) which converted to trans-$[Ru(CNBu^t)_4(NH_2NH_2)_2](BPh_4)_2$ (4) in cold acetone and mer-$[Ru(CNBu^t)_3(NH_2NCMe_2)_3](BPh_4)_2$ (5) in boiling acetone. Similar reactions with $[Ru(C_8H_{12})(NH_2NHMe)_4](PF_6)_2$ (6) and isocyanides in either acetone or ethanol gave trans-$[Ru(CNR)_4(NH_2NHMe)_2](PF_6)_2$ (7; CNR = $CNBu^t$, $CNCH_2Ph$, $CNC_6H_3Me_2$-2,6). The inertness of the hydrazones (1) to substitution reactions is shown not to be attributable to hydrogen bonding, as previously proposed for the corresponding phosphite complexes [1].

Introduction

Considering the large number of transition metal hydrazine compounds that are known [2], it is surprising that so few metal hydrazone complexes have been prepared. This could be due to the reduced basicity of the amino and imino nitrogen atoms, when compared with hydrazine, through lone pair conjugation with the imine π-system [3]. However in the only two comparable complexes known, *e.g.* $[M(C_5H_5)(CO)_3L]PF_6$ (M = Mo, W; L = NH_2NH_2, NH_2NCMe_2) [4], there appears to be little difference in stabilities between the hydrazine and hydrazone complexes.

In the salts *trans*-$[RuL_4(NH_2NCMe_2)_2](BPh_4)_2$ {1; L = $P(OMe)_2Ph$, $P(OR)_3$, $P(OCH_2)_3CR$, R = Me or Et} the extraordinary inertness of the hydrazone ligands to further substitution was proposed [1b], from crystallographic evidence, to be due to strong hydrogen bonding occurring between the amino

hydrogen atoms of the hydrazone ligands and the oxygen atoms of the phosphite or phosphonite ligands. In continuing our investigation into the formation and stability of metal hydrazone complexes we decided to investigate the formation of (1) with ligands, L, that will be unable to hydrogen bond to the hydrazone amino hydrogen atoms and to this end the reactions of $[Ru(C_8H_{12})(NH_2NH_2)_4](BPh_4)_2$ (2) with isocyanides were investigated. As a comparison corresponding ruthenium hydrazine-isocyanide and 1-methylhydrazine-isocyanide complexes were also prepared.

Results and Discussion

Hydrazone Complexes

Addition of four molar-equivalents of the respective isocyanide to a boiling acetone solution of (2) gave the hydrazone complexes (1; L = CNR; R = Bu^t, C_6H_{11}, CH_2Ph and $C_6H_3Me_2$-2,6) as white powders on addition of ethanol. Corresponding reactions performed with less than four molar equivalents of isocyanide or with aldehydes or other ketones as solvent gave only oily products which could not be purified.

Treatment of (2) with an excess of $CNBu^t$ in acetone solution under reflux gave the known salt $[Ru(CNBu^t)_6](BPh_4)_2$ [5] from ethanol in 24% yield. This complex could not be prepared by refluxing (1; L = $CNBu^t$) in acetone with an excess of $CNBu^t$ even with extended reaction times. In fact the hydrazone ligands in (1; L = CNR) were all inert to substitution by CO, pyridine or the corresponding isocyanide in refluxing acetone or THF. In higher boiling solvents decomposition of the starting material tended to take place. The X-ray crystallographic determination of {1; L = $P(OMe)_3$} showed extensive hydrogen bonding between the amino hydrogen atoms of the hydrazone ligands and the oxygen atoms of the phosphite ligands. As a consequence, the inertness to substitution of the hydrazone ligands in all the complexes {1; L = $P(OMe)_2Ph$, $P(OR)_3$, $P(OCH_2)_3CR$; R = Me, Et} was attributed to this

---

TABLE I. Physical and Analytical Data for trans-[Ru(CNR)$_4$(NH$_2$NCMe$_2$)$_2$](BPh$_4$) (1), mer-[Ru(CNR)$_3$(NH$_2$NCMe$_2$)$_2$](BPh$_4$)$_2$ (3), trans-[Ru(CNR)$_4$(NH$_2$NH$_2$)$_2$](BPh$_4$)$_2$ (4), mer-[Ru(CNR)$_3$(NH$_2$NH$_2$)$_3$](BPh$_4$)$_2$ (5) and trans-[Ru(CNR)$_4$(NH$_2$NHMe)$_2$](PF$_6$)$_2$ (7).]

Complex	M.p.[a] (°C)	Analysis (%)[b] C	H	N	Infrared data[c,d,e] (cm^{-1}) ν(NH)	δ(NH)	ν(C=N)	ν(NN)	ν(C≡N)
1 R=Bu^t	150–152	73.43(73.03)	7.46(7.62)	9.24(9.21)	3165, 3230, 3290	1600	1655	915	2170
R=C$_6$H$_{11}$	148–150	73.90(74.59)	7.75(7.63)	8.97(8.49)	3230, 3280–3310	f	1655	925, 935	2180
R=CH$_2$Ph	190–192	76.08(76.38) Ru 7.11(7.47) B 1.69(1.60)	6.33(6.26)	8.45(8.29)	3160, 3240, 3290	f	1670	920, 935	2190–2210
R=C$_6$H$_3$Me$_2$-2,6	185–187	75.97(76.75)	6.58(6.58)	7.72(7.96)	3160, 3220, 3260		1650–1660	930	2150
3 R=Bu^t	175–178	68.82(69.73)	7.58(7.34)	11.98(11.62)	3160, 3230, 3270	1600		925	2110, 2170
4 R=Bu^t	178–180	71.97(71.88)	7.54(7.45)	9.89(9.86)	3170, 3230, 3270, 3300, 3370	1605		920	2160
5 R=Bu^t	175–177	71.32(71.75)	7.37(7.61)	11.10(10.46)	3160–3310	1605	g	935	2120
7 R=Bu^t	188–190	32.48(32.39)	5.86(5.93)	13.69(13.74)	3190, 3250, 3320, 3340	1610		940	2180
R=CH$_2$Ph	175–180	42.53(42.91)	4.53(4.24)	11.86(11.77)	3190, 3260–3330	1605–1615		g	2200
R=C$_6$H$_3$Me$_2$-2,6	212–214	44.74(45.28)	4.88(4.80)	11.31(11.12)	3190, 3260, 3320, 3340	1615		930	2150

[a]In air. [b]Calculated values are in parenthesis. Additional analyses are given below C, H, N values. [c]Nujol mulls. [d]ν(NH), δ(NH), ν(C=N) and ν(NN) frequencies are weak, ν(C≡N) frequencies are strong. [e]Vibrations due to BPh$_4$ anion observed at 710, 735 and 750 cm^{-1} and PF$_6$ anion observed at 830–855 cm^{-1}. [f]Not observed; possibly obscured by band at 1580 cm^{-1} due to BPh$_4$ anion. [g]Not observed.

bonding [1]. In the isocyanide complexes no hydrogen bonding can take place between the hydrazone and isocyanide ligands and whilst we cannot comment on the electronic factors governing the stability of these salts it does appear as if hydrogen bonding in the tertiary phosphorus complexes plays an insignificant role in their inertness to substitution.

From the few hydrazone complexes previously reported it is uncertain when condensation of acetone and hydrazine occurs. Dehand and Pfeffer [6] have proposed that condensation in their palladium complexes takes place whilst the hydrazine is bonded to the metal, but no evidence was presented for this proposal. We find that when the salt [Ru(CNBu^t)$_4$-(NH$_2$NH$_2$)$_2$](BPh$_4$)$_2$ is dissolved in acetone-d$_6$ and the formation of water monitored by ^{1}H n.m.r., there is only a 10% conversion to the corresponding hydrazone within 5½ h, at 22% conversion within 22 h and a 70% conversion after 4 days. In contrast addition of CNBu^t to an acetone-d$_6$ solution of (2) gave 80% of (1; L = CNBu^t) within 10 min, from which we deduce that condensation of acetone takes place with uncoordinated hydrazine. Why condensation of acetone with bonded hydrazine is very slow is not, at this stage, clear, but it is possible that steric interaction with other ligands within the coordination sphere prevents close approach of the acetone molecule.

The i.r. and n.m.r. data for the complexes (1; L = CNR) are given in Tables I and II. The N–H stretching frequencies were observed in the region 3160–3310 cm^{-1} for all the isocyanide compounds but only for L = CNBu^t was δ(N–H) at 1600 cm^{-1} unambiguously assigned. In the other isocyanide compounds, as well as for (1; L = phosphite, phosphinite), BPh$_4$ absorption obscured this vibration. In contrast to the tertiary phosphorus hydrazone complexes in which no N–N stretching frequencies were observed, all the isocyanide salts gave unambiguous N–N frequencies in the region 915–935 cm^{-1}. The hydrazone ν(C=N) at 1650–1670 cm^{-1} correspond to those observed for (1; L = phosphite, phosphonite) (1640–1650 cm^{-1}) [1] and [Cr(CO)$_5$(NH$_2$NCMe$_2$)] (1665 cm^{-1}) [7]. Single, strong, broad isocyanide ν(C≡N) vibrations occurred in the region 2150–2210 cm^{-1} for (1; L = CNR). No structural information was obtained from these absorptions.

No resonances could be assigned for the NH protons in the ^{1}H n.m.r. spectra of (1; L = CNR) down to −80 °C. This could be attributed to broadening due to either the quadrupole relaxation of the ^{14}N nucleus or to proton interchange processes. These resonances were also not observed in the corresponding phosphite or phosphonite salts [1]. Two hydrazone methyl peaks for (1; L = CNBu^t, CNC$_6$H$_{11}$, CNC$_6$H$_3$Me$_2$-2,6) were found at 1.93 and 1.95 ppm, 1.87 and 1.90 ppm, and 1.77 and 1.80 ppm

TABLE II. ^{1}H n.m.r. Data for *trans*-[Ru(CNR)$_4$(NH$_2$NCMe$_2$)$_2$](BPh$_4$)$_2$ (1)[a], *mer*-[Ru(CNR)$_3$(NH$_2$NH$_2$)$_3$](BPh$_4$)$_2$ (3)[b], *trans*-[Ru(CNR)$_4$(NH$_2$NH$_2$)$_2$](BPh$_4$)$_2$ (4)[a] and *trans*-[Ru(CNR)$_4$(NH$_2$NHMe)$_2$](PF$_6$)$_2$ (7).[a]

Complex	^{1}H n.m.r. data (ppm)[c,d]
^{1}R=Bu^t	1.53(s) {−CMe$_3$, 36H}; 1.93(s) and 1.95(s) {=CMe$_2$, 12H}
R=C$_6$H$_{11}$	1.40(br), 1.87(s) and 1.90(s) {=CMe$_2$ and −CH$_2$−, 52H}[e]; 4.08(br) {−Ç−H, 4H}
R=CH$_2$Ph	1.63(s), 1.65(s), 1.68(s) and 1.70(s) {=CMe$_2$}[e]; 5.03(s), 5.04(s) and 5.07(s) {−CH$_2$−, 8H}
R=C$_6$H$_3$Me$_2$-2,6	1.77(s) and 1.80(s) {=CMe$_2$}[e]; 2.63(s) {=C(Me)−, 24H}
^{3}R=Bu^t	1.57(s) and 1.60(s) {−CMe$_3$, 27H}; 4.6(br) {−NH$_2$, 6H}
^{4}R=Bu^t	1.57(s) {−CMe$_3$, 36H}; 3.40(br) {−NH$_2$, 4H}[f]; 5.27(br) {−NH$_2$, 4H}[f]
^{7}R=Bu^t	1.60(s) {−CMe$_3$, 36H}; 2.57(br) {−N(Me)−, 6H}; 3.27(br) {−NH−, 2H}[f]; 5.07(br) {−NH$_2$, 4H}
R=CH$_2$Ph	2.47(s) {−N(Me)−, 6H}; 3.47(br) {−NH−, 2H}[f]; 5.20(s) {−CH$_2$−, 8H}; 5.37(br) {−NH$_2$, 4H}
R=C$_6$H$_3$Me$_2$-2,6	2.43(s) {−N(Me)− and =C(Me)−, 30H}; 3.1−6.0(br,m) {−NH$_2$ and −NH−}

[a]In acetone-d$_6$. [b]In acetonitrile-d$_3$. [c]Values relative to internal TMS. Aromatic protons between 6.5 and 7.5 ppm. [d]s = singlet, br = broad, br,m = broad multiplet. [e]Accurate integration precluded by overlapping solvent resonances and acetone of crystallisation. [f]Disappear on addition of D$_2$O. No ^{1}H n.m.r. spectra could be recorded of *mer*-[Ru(CNBu^t)$_3$(NH$_2$NCMe$_2$)$_3$]-(BPh$_4$)$_2$ (5) because of insufficient material.

TABLE III. ^{13}C N.m.r. Data.

Complex		Solvent	Carbon atom			δ in ppm[a,b,c]
[RuCNCH$_2$Ph)$_4$(NH$_2$NCMe$_2$)$_2$](BPh$_4$)$_2$	(1)	Acetone-d$_6$	Hydrazone ligand:	CH$_3$		16.3 and 25.4
			Isocyanide ligand:	CN		163.8
				NCH$_2$		49.0
				Ph		133.1
					ortho	130.0
					meta	129.8
					para	128.1
[Ru(CNBu^t)$_3$(NH$_2$NH$_2$)$_3$](BPh$_4$)$_2$	(3)	Acetonitrile-d$_3$	Isocyanide ligand:	CH$_3$		30.5 and 30.7
[Ru(CNBu^t)$_4$(NH$_2$NH$_2$)$_2$](BPh$_4$)$_2$	(4)	Acetonitrile-d$_3$	Isocyanide ligand:	CH$_3$		30.4
[Ru(CNC$_6$H$_3$Me$_2$-2,6)$_4$(NH$_2$NHMe)$_2$](PF$_6$)$_2$	(7)	Acetone-d$_6$	Hydrazine ligand:	CH$_3$		42.0
			Isocyanide ligand:	Ph	*ortho*	137.0
					meta	129.1
					para	130.9
				CH$_3$		19.0

[a]Relative to TMS. [b]Other ^{13}C-peaks not observed. [c]Anions excluded.

respectively, as expected for equivalent hydrazone ligands containing asymmetrical methyl groups. For (1; L = CNCH$_2$Ph) four methyl resonances of equivalent intensity were observed at 1.63, 1.65, 1.68 and 1.70 ppm, and this can be accounted for by the orientation of the phenyl rings causing either asymmetry in the molecule, or anisotropic shielding of the methyl groups. The butyl and xylyl methyl resonances appeared as singlets indicating equivalent magnetic environments as would be expected for a *trans*-configuration.

The assignment of a *trans*-configuration is further confirmed by the ^{13}C n.m.r. spectrum (Table III)

of (1; L = CNCH$_2$Ph) which contained a single peak for each type of carbon atom of the isocyanide ligands. The isocyanide carbon resonance at 163.8 ppm is somewhat higher than those observed in [Fe(CN)(CNCH$_2$Ph)$_5$]Br {149.0 (*trans*), 149.5 (*cis*) ppm} [8], [Fe(C$_5$H$_5$)(CNCH$_2$Ph)$_2$CO]Br (147.4 ppm) [8] and [RuCl$_2$(CNCH$_2$Ph)$_2$(PMe$_2$Ph)$_2$] (149.9 ppm) [9], whereas the isocyanide methylene resonance at 49.0 ppm and the phenyl carbons at 128.1, 129.8, 130.0 and 133.1 ppm are comparable with those in [FeCN(CNCH$_2$Ph)$_5$]Br and [Fe(C$_5$H$_5$)-(CNCH$_2$Ph)$_2$CO]Br at 48.0 and 51.4 and 125.6−130.9 and 128.0−132.5 ppm respectively [8]. The

methyls of the hydrazone appeared at 16.3 and 25.4 ppm.

Hydrazine Complexes

Treatment 6f (2) with three or more molar equivalents of CNBu^t in refluxing ethanol gave *mer*-[Ru(CNBu^t)$_3$(NH$_2$NH$_2$)$_3$](BPh$_4$)$_2$ (3) as the only isolable product. Less than three molar equivalents produced intractable oils which were not further investigated. Surprisingly *trans*-[Ru(CNBu^t)$_4$(NH$_2$-NH$_2$)$_2$](BPh$_4$)$_2$ (4) could not be synthesised directly from (2) with an excess of CNBu^t but was obtained in 45% yield as the sole product of attempted recrystallizations of (3) from either cold acetone--ethanol or dichloromethane--ethanol mixtures. The hydrazone complex [Ru(CNBu^t)$_3$(NH$_2$NCMe$_2$)$_3$](BPh$_4$)$_2$ (5) was isolated in 4% yield from boiling acetone--ethanol mixtures. With the N-methylhydrazine compound [Ru(C$_8$H$_{12}$)(NH$_2$NHMe)$_4$](PF$_6$)$_2$ (6), the reaction with isocyanides in either boiling acetone or ethanol gave the salts [Ru(CNR)$_4$(NH$_2$NHMe)$_2$]·(PF$_6$)$_2$ (7; R = Bu^t, CH$_2$Ph, C$_6$H$_3$Me$_2$-2,6) as white powders.

The i.r. spectra of compounds (3), (4), (5) and (7) contain characteristic ν(N--H) frequencies between 3160--3370 cm^{-1}, δ(N--H) frequencies between 1600--1615 cm^{-1} and ν(N--N) frequencies between 920--940 cm^{-1}, and are comparable with those reported for [Ru(C$_8$H$_{12}$)(NH$_2$NH$_2$)$_4$](BPh$_4$)$_2$ [1] and [Ru(arene)(NH$_2$NH$_2$)$_3$](BPh$_4$)$_2$ (arene = C$_6$H$_6$, *p*-MeC$_6$H$_4$CHMe$_2$) [10]. For (5), δ(N--H) was assigned at 1605 cm^{-1}. Surprisingly no vibrations in the i.r. in the region 1650--1670 cm^{-1} corresponding to ν(C=N) were observed in (5). The isocyanide ν(C≡N) vibrations for (3), (4), (5) and (7) all appeared as broad singlets in the region 1220--1270 cm^{-1}.

The ^{1}H n.m.r. spectra of (3) contained a broad singlet at 4.60 ppm and (4) contained broad singlets at 3.40 ppm and 5.27 ppm for the amino protons, which disappeared on addition of D$_2$O. The *tert*-butyl methyl resonances in (3) were observed as two singlets at 1.57 and 1.60 ppm indicative of a *mer*-configuration. For (4) the singlet isocyanide resonance at 1.57 ppm confirmed the *trans*-configuration for this compound. Further confirmation of these assignments came from the ^{13}C n.m.r. which contained 2 singlets for the isocyanide methyl carbon atoms for (3) at 30.5 ppm for the isocyanide *trans* to a hydrazine and at 30.7 ppm for the isocyanides *trans* to each other. The isocyanide methyls for (4) appeared as a singlet at 30.4 ppm. We were unable to record satisfactory ^{1}H and ^{13}C n.m.r. spectra for (5) because of the low yield obtained. For (7; R = Bu^t and CH$_2$Ph) amino protons appeared at 5.07 and 5.37 ppm respectively and imino resonances were at 3.27 and 3.47 ppm respectively. The NMe resonances were recorded as singlets at 2.57

and 2.47 ppm respectively, the butyl methyls and the CH$_2$ protons as singlets at 1.60 ppm and 5.20 ppm respectively. From symmetry considerations a *trans* configuration is thus proposed. For (7; R = C$_6$H$_3$-Me$_2$-2,6) only one singlet is observed at 2.43 ppm for the overlapping resonances of the NMe and xylyl methyl resonances. The NH$_2$ and --NH-- protons were observed as a broad multiplet in the region 3.1--6.0 ppm. Confirmation for a *trans*-configuration for (7; R = C$_6$H$_3$Me$_2$-2,6) came however from the ^{13}C n.m.r. spectrum which showed one peak at 42.0 ppm for the hydrazine methyl and one at 19.0 ppm for the xylyl methyl resonances.

Experimental

Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 457 spectrophotometer, ^{1}H n.m.r. spectra on a Varian EM 390 instrument and ^{13}C n.m.r. spectra on a Varian CFT-20. The complexes [Ru(C$_8$H$_{12}$)(NH$_2$NH$_2$)$_4$](BPh$_4$)$_2$ (2) and [Ru(C$_8$H$_{12}$)(NH$_2$NHMe)$_4$](PF$_6$)$_2$ (6) were prepared as previously reported [1a]. Isocyanides were obtained commercially from Fluka and were not further purified. All reactions were performed in air.

Preparation of [Ru(CNR)$_4$(NH$_2$NCMe$_2$)$_2$](BPh$_4$)$_2$ (1, R = Bu^t)

t-Butylisocyanide (0.3 g; 4 mmol) was added to a solution of (2) (1.0 g; 1 mmol) in boiling acetone (20 ml). Addition of ethanol and removal of acetone produced at 0 °C a white precipitate, which after recrystallization from dichloromethane--ethanol gave the required product as a white powder (0.4 g; 38%).

The following compounds were prepared in a similar way:

(1; R = C$_6$H$_{11}$) as a white powder (0.9 g; 71%).

(1; R = CH$_2$Ph) as a white powder (1.1 g; 95%).

(1: R = C$_6$H$_3$Me$_2$-2,6) as a white powder (0.9 g; 67%).

Preparation of [Ru(CNBu^t)$_3$(NH$_2$NH$_2$)$_3$](BPh$_4$)$_2$ (3)

Addition of CNBu^t (0.3 g; 4 mmol) to a suspension of (2) (1.0 g; 1 mmol) in ethanol (20 ml) gave a solution on refluxing overnight which produced the required product as a white powder (0.8 g; 75%) on cooling to 0 °C.

Preparation of [Ru(CNBu^t)$_4$(NH$_2$NH$_2$)$_2$](BPh$_4$)$_2$ (4)

Addition of ethanol to a solution of (3) (1.1 g; 1 mmol) in acetone or CH$_2$Cl$_2$ gave the required product (4) as a white powder (0.5 g; 45%).

Preparation of [Ru(CNBu^t)$_3$(NH$_2$NCMe$_2$)$_3$] (BPh$_4$)$_2$ (5)

A solution of [Ru(CNBu^t)$_3$(NH$_2$NH$_2$)$_3$] (BPh$_4$)$_2$ (1.1 g, 1 mmol) in acetone was boiled for 30 min. Ethanol was then added and the acetone removed to give [Ru(CNBu^t)$_4$(NH$_2$NH$_2$)$_2$] (BPh$_4$)$_2$ (4) (0.5 g, 45%). Reduction of the ethanol mother liquor to low volume and saturation with ether gave the required product which on recrystallization from acetone/ethanol mixtures formed a white powder (0.05 g, 4%).

Preparation of [Ru(CNR)$_4$(NH$_2$NHMe)$_2$] (PF$_6$)$_2$ (7; R = Bu^t)

CNBu^t (0.3 g; 4 mmol) was added to a solution of (6) (0.5 g; 1 mmol) in acetone (10 ml). The solution was boiled for 10 min then ethanol added and the acetone boiled off. The white precipitate formed was recrystallized from acetone/ethanol to give the required product as a white powder (0.4 g; 47%).

The following complexes were prepared in a similar way:

(7; R = CH$_2$Ph) as a white powder (0.3 g; 36%).

(7; R = C$_6$H$_3$Me$_2$-2,6) as a white powder (0.2 g; 24%).

References

1 a) T. V. Ashworth, E. Singleton and J. J. Hough, *J. Chem. Soc. Dalton*, 1809 (1977);
   b) M. J. Nolte and E. Singleton, *J. Chem. Soc. Dalton*, 2406 (1974).
2 a) F. Bottomley, *Chem. Soc. Quart. Rev.*, 24, 617 (1970);
   b) J. R. Dilworth, *Co-ordination Chem. Rev.*, 21, 29 (1976).
3 Yu. P. Kitaev and B. 1. Buzykin, *Russ. Chem. Rev.*, 41, 495 (1972).
4 M. J. Nolte and R. H. Reimann, *J. Chem. Soc. Dalton*, 932 (1978).
5 H. E. Swanepoel, *Ph.D. Thesis*, Randse Afrikaans University, 1980.
6 J. Dehand and M. Pfeffer, *Bull. Soc. Chim. France*, 2782 (1974).
7 D. Sellmann, A. Brandl and R. Endell, *J. Organometal. Chem.*, 111, 303 (1976).
8 D. L. Cronin, J. R. Wilkinson and L. J. Todd, *J. Magn. Resonance*, 17, 353 (1975).
9 B. Crociani and R. L. Richards, *J. Organometal. Chem.*, 144, 85 (1978).
10 R. H. Crabtree and A. J. Pearman, *J. Organometal. Chem.*, 141, 325 (1977).