Journal of Organometallic Chemistry, 384 (1990) 339–346
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20532

Reactivity of cationic isocyanide iron(II) derivatives towards nucleophilic agents

Victor Riera * **and Javier Ruiz**

Departamento de Química Organometálica, Universidad de Oviedo, 33071 (Spain)

(Received July 24th, 1989)

Abstract

Attack of MeNH_2 on two adjacent isocyanide ligands in $[\text{Fe(dppe)(CNPh)}_4](\text{ClO}_4)_2$ (Ia) gives *cis*-$[\text{Fe(dppe)(CNPh)}_2\{\text{C(NHPh)NMeC=NPh}\}]\text{ClO}_4$ (II). II reacts with concentrated aqueous HClO_4 to give *cis*-$[\text{Fe(dppe)(CNPh)}_2\{\text{C(NHPh)NMeC(NHPh)}\}](\text{ClO}_4)_2$ (III), which contains a chelating diaminocarbene ligand. Refluxing of a dichloromethane solution of III causes opening of the carbene ring to give *mer*-$[\text{Fe(dppe)(CNPh)}_3\{\text{C(NHPh)(NHMe)}\}](\text{ClO}_4)_2$ (IV). Treatment of III or IV with KOH complex regenerates II. Ia also undergoes addition of Me_2NH to give *cis*-$[\text{Fe(dppe)(CNPh)}_2\{\text{C(NMe}_2\text{)NPhC=NPh}\}]\text{ClO}_4$ (V). Reaction of the complexes $[\text{Fe(dppe)(CNR)}_4](\text{ClO}_4)_2$ (Ia: R = phenyl; Ib: R = 4-methylphenyl) with KOH gives the carbonyl derivatives $[\text{Fe(dppe)(CNR)(CO)(RN=CNRC=NR)}]$ (VIa and VIb). Treatment of VIa with dilute aqueous HClO_4 yields $[\text{Fe(dppe)(CNPh)(CO)}\{\text{C(NHPh)NPhC=NPh}\}]\text{ClO}_4$ (VII), which takes up a second proton when treated with concentrated aqueous HClO_4 to give *trans*-$[\text{Fe(dppe)(CNPh)}_2\text{(CO)}\{\text{C(NHPh)}_2\}](\text{ClO}_4)_2$ (VIII).

Introduction

There is much information available of reactions of isocyanide ligands in transition metal complexes [1]. They are known to react with organolithium compounds to give iminoacyl derivatives [2], and reaction of NaBH_4 with two adjacent isocyanide ligands yields a new chelating ligand [3]. They also undergo electrophilic attack to give carbyne derivatives [4,5], and treatment with nucleophilic protic species (amines, alcohols, thiols) give several types of carbene derivatives [1,6].

We report here a study of the reaction of the complex compound $[\text{Fe(dppe)(CNPh)}_4](\text{ClO}_4)_2$ [7] with amines (MeNH_2, Me_2NH). This work has revealed the existence of equilibrium between chelated and terminal carbene derivatives. We have also examined the reaction of $[\text{Fe(dppe)(CNR)}_4](\text{ClO}_4)_2$ with KOH,

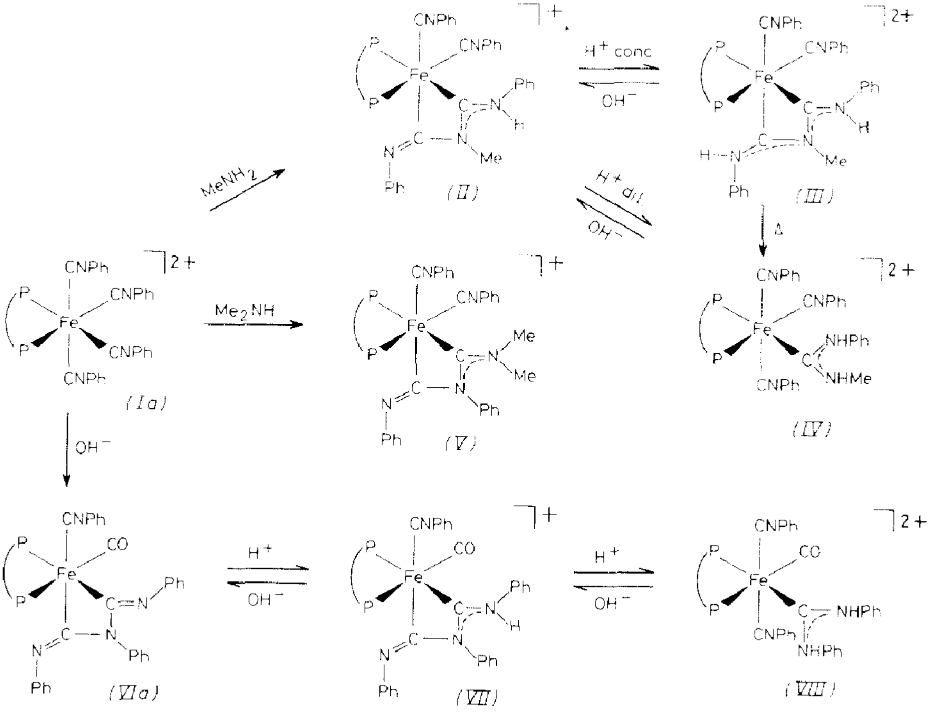
0022-328X/90/$03.50

and observed an interesting conversion of coordinated isocyanide into coordinated carbon monoxide; a preliminary account of these results has appeared [8].

Results and discussion

Reaction of $[Fe(dppe)(CNPh)_4](ClO_4)_2$ (Ia) with an excess of $MeNH_2$ gave the complex *cis*-$[Fe(dppe)(CNPh)_2\{C(NHPh)NMeC{=}NPh\}]ClO_4$ (II), which shows two absorptions of equal intensity at 2115 and 2080 cm^{-1} in its IR spectrum, typical of a *cis*-bis(isocyanide) derivative ($\nu(CN)$).

The ^1H NMR spectrum of II shows a signal at 1.93 ppm which integrates as three protons, suggesting that one molecule of $MeNH_2$ had attached to each of the two adjacent isocyanide ligands. Such an addition is not uncommon; it is well known that $MeNH_2$ reacts with $[Fe(CNMe)_6]^{2+}$ and $[Mn(CNMe)_2(CO)_4]^+$ to give $[Fe(CNMe)_4\{C(NHMe)NMeC(NHMe)\}]^{2+}$ [9] and $[Mn(CO)_4\{C(NHMe)NMeC(NHMe)\}]^+$ [10], respectively. However, in our case, the molar conductivity of II is typical of a 1/1 electrolyte, indicating that the attack of amine has resulted in proton abstraction (see Scheme 1). Moreover its IR spectrum shows bands at 1530 cm^{-1}, characteristic of the C–N stretching vibration in aminocarbene ligands, and at 1615 cm^{-1} assignable to the C=N stretching vibration of the imino group in the new chelating ligand. Deprotonation of aminocarbene ligands has been reported previously thus it has been shown that the complex $[Fe(CNMe)_4\{C(NHMe)NHNHC(NHMe)\}]^{2+}$ acts as a weak acid in aqueous solution [11], and treatment of $[Mn(CO)_4\{C(NHMe)NMeC(NHMe)\}]^+$ with base gives $[Mn(CO)_4\{C(NHMe)NMeC{=}NMe\}]$ [10].



Scheme 1

Table 1

Infrared and analytical data

Compound	Λ_m [a]	(Found (calcd.) (%))			$\nu(CN)$ [c] (cm^{-1})	$\nu(CO)$ [c] (cm^{-1})
		C	H	N		
II	133	65.6	5.0	7.2	2115s	
		(66.3)	(4.8)	(7.0)	2080s	
III	230	59.5	4.3	6.1	2137s	
		(60.2)	(4.4)	(6.3)	2109s	
IV	220	59.1	4.0	6.0	2170w	
		(60.2)	(4.4)	(6.3)	2140sh	
					2126s	
V	120	65.8	4.7	6.8	2120s	
		(66.5)	(4.9)	(6.9)	2085s	
VIa		71.0 [b]	4.9	5.9	2090s	1950s
		(73.4)	(4.9)	(6.3)		
VIb		73.5	6.0	5.6	2090s	1950s
		(74.2)	(5.5)	(5.9)		
VII	122	64.8	4.6	5.7	2125s	1982s
		(65.9)	(4.6)	(5.7)		
VIII	220	59.4	4.2	5.1	2178w	2048s
		(59.8)	(4.2)	(5.1)	2148s	

[a] In acetone (5×10^{-4} mol dm^{-3}), values in Ω^{-1} cm^2 mol^{-1}. [b] Purification was difficult owing to its low solubility. [c] In CH_2Cl_2.

Restricted rotation around the C–N bonds of the imino and carbene groups in the chelating ligand gives rise to the existence of various isomers of II, differing in the relative positions of the nitrogen substituents. However the $^{31}P\{^1H\}$ NMR spectrum of the compound, consisting of an AB quartet (see Table 2), indicated the presence of only one isomer. In view of the structure of the chelating ligand in compound VI (described later) the most probable structure for II is that shown in

Table 2

^1H and $^{31}P\{^1H\}$ NMR data

Compound	$^{31}P\{^1H\}$ [a]	$J(PP)$ (Hz)	^1H [b]
II	76.6(qAB)	15	1.93(d, 3H, $^5J(PH)$ 1.5 Hz)
III	77.3(s)		2.05(s, 3H)
IV	72.92(qAB)	16	2.84(d, $J(HH)$ 4.7)
	72.65(qAB)	16	3.60(d, $J(HH)$ 4.7)
V	75.7(d)	15	1.77(s, 3H)
	71.8(d)		2.40(s, 3H)
VIb	79.8(d)	20	
	74.5(d)		
VII	71.87(d)	19	
	75.45(d)		
VIII	68.15(d)	18	
	71.71(d)		

[a] In CH_2Cl_2 as solvent; chemical shifts (ppm) are positive to high frequencies relative to 85% H_3PO_4. [b] In $CDCl_3$ as solvent.

Scheme 1, in which the phenyl substituent in the carbene group (C–NHPh) lies "*anti*" to the N–Me group, and the phenyl substituent in the imino group (C=NPh) "*syn*" to the N–Me group. Steric effects of the bulky diphosphine ligand seems to be responsible for this arrangement.

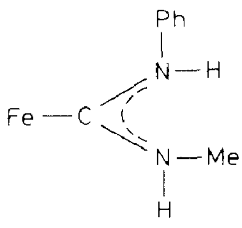
As expected, compound II was found to be protonated by concentrated aqueous $HClO_4$ to give the chelated diaminocarbene derivative *cis*-[Fe(dppe)$(CNPh)_2$\{C(NHPh)NMeC(NHPh)\}]$(ClO_4)_2$ (III) (see Scheme 1). III also gave two bands of equal intensity in its IR spectrum arising from the CN stretching vibrations of the isocyanides, but at higher frequency than observed for its precursor (see Table 1). There was a strong band at 1525 cm^{-1} for the stretching CN in the carbene ligand. Surprisingly the $^{31}P\{^1H\}$ NMR spectrum of III gave only one signal for the two phosphorus of the diphosphine at 77.3 ppm.

Compound II was regenerated when III was treated with KOH or NMe_3 in CH_2Cl_2.

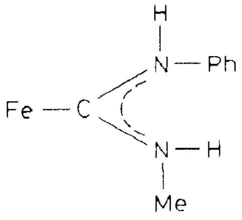
When a dichloromethane solution of compound III was treated under reflux, opening of the diaminocarbene ring occurred, and *mer*-[Fe(dppe)$(CNPh)_3$\{C(NHMe)(NHPh)\}]$(ClO_4)_2$ (IV) was obtained (see Scheme 1). Treatment of IV with a base (KOH or NMe_3) reformed the carbene ring regenerating compound II. Compound IV was obtained directly from II by reaction with dilute $HClO_4$ in CH_2Cl_2.

There are other examples of terminal/chelating carbene conversion in the literature [10,12]; the factors favouring formation of one or other configuration were studied by Balch and Doonan [13,14].

In the case of compound IV two isomers were detected by NMR spectroscopy. These probably originated in the restricted rotation around the C–N bonds in the carbene ligand. Thus, the ^1H NMR spectrum of IV showed two doublets at δ 3.6 and 2.84 ppm (J(HH) 4.5 Hz) in an approximate ratio of 1/3. The two most probable isomers are those in which the methyl and phenyl substituents of the carbene ligand have interchanged positions, as represented in *a* and *b*. Because signal from the methyl groups *cis* to a metal appears at lower field than that *trans* [14,15], the doublet at δ 3.6 ppm is probably due to the isomer *b*, and the other doublet to the isomer *a*. Angelici observed two analogous isomers in the cation $[CpFe(CNC_6H_4OMe\text{-}4)_2\{C(NHC_6H_4OMe\text{-}4)(NHMe)\}]^+$ [16].



(a)



(b)

The presence of two isomers for IV was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy; thus two AB quartets were found in a ratio of 1/3 (see Table 2).

The IR spectrum of IV showed a pattern of bands in the ν(CN) region typical of a *mer* arrangement of the isocyanide ligands (see Table 1). As expected, there was also a band at 1530 cm^{-1} was present for the stretching C–N in the carbene ligand

and two bands at 3400 and 3250 cm^{-1} for the ν(N–H) vibrations in this ligand.

When compound Ia was treated with Me_2NH instead of $MeNH_2$ a new chelating ligand was obtained (compound V in Scheme 1). The presence of two signals at δ 2.4 and 1.77 ppm in the ^1H NMR spectrum of V each integrating as three protons, confirmed that only one Me_2NH molecule had added to Ia. A conductivity typical of an 1/1 electrolyte indicated that deprotonation had also occurred. The *cis* arrangement of the isocyanide ligands was inferred from the IR spectrum which showed two bands of equal intensity in the ν(CN) region (see Table 1). Furthermore, bands at 1620 and 1555 cm^{-1} for the ν(C–N) of the imino and amino groups of the chelating ligand were observed. In the light of these data the most probable structure for V is that shown in Scheme 1.

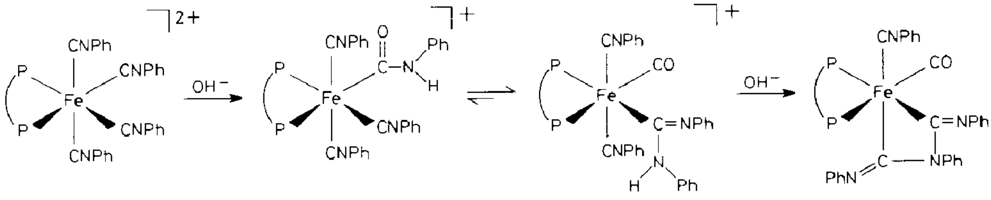
Attempts to obtain the protonated derivatives of V analogous to III and IV were unsuccessful; thus treatment of V with $HClO_4$ caused decomposition, and a small amount of complex IV was the only product isolated.

We examined the reactions of compound Ia with KOH. When a dichloromethane solution of Ia was treated with an excess of KOH a neutral compound VIa was obtained (see Scheme 1). A band at 1950 cm^{-1} in the IR spectrum of VIa revealed that a carbon monoxide ligand had been formed. Formation of coordinated carbon monoxide from isocyanide has been observed previously in the reaction of $(PPh_3)_2Rh(CNMe)Cl$ with THF/H_2O to give $(PPh_3)_2Rh(CO)Cl$ [17]. It has also been postulated that the intermediate $[(PPh_3)_2Pt(CNMe)(CO)]^+$ is formed in the reaction with acids of $[(PPh_3)_2Pt(CNMe)\{C(O)NHMe\}]^+$ (obtained by treating $[(PPh_3)_2Pt(CNMe)_2]^{2+}$ with KOH [18]) in the presence of acetonitrile to give $[(PPh_3)_2Pt(CNMe)(NCMe)]^{2+}$ [19].

The IR spectrum of VIa showed a band at 2090 cm^{-1} for the terminal isocyanide ligand and bands at 1630 and 1560 cm^{-1} in the region for C=N stretching frequencies.

As we were unable to obtain suitable crystals of VIa for an X-ray study, we prepared the related compound $[Fe(dppe)(CNC_6H_4Me\text{-}4)(CO)\{(C_6H_4Me\text{-}4)N{=}C(NC_6H_4Me\text{-}4)C{=}N(C_6H_4Me\text{-}4\}]$ (VIb) from $[Fe(dppe)(CNC_6H_4Me\text{-}4)_4](ClO_4)_2$ (Ib) and KOH. The results of an X-ray study on VIb have been published elsewhere [8]; the structure known for VIa in Scheme 1 is based on that of VIb.

For the formation of complex VI we propose the mechanism drawn in Scheme 2. It is known that attack of KOH on an isocyanide ligand usually gives the corresponding carbamoyl derivative [18] (compound IX in Scheme 2), which may be in equilibrium with the more stable amidinium compound (X) [10]. A further attack by KOH can close the ring to give compound VI.



(Ia) (IX) (X) (VIa)

Scheme 2

Compound VIa was found to be protonated by 1% aqueous perchloric acid to give [Fe(dppe)(CNPh)(CO){C(NHPh)NPhC=NPh}]ClO$_4$ (VII). The conductivity of VII was typical of an uni-univalent electrolyte. Its IR spectrum shows a ν(CO) band and a ν(CN) band, at higher frequencies than those for its precursor (see Table 1). The ν(C–N) bands of the chelating ligand appear at 1630 and 1530 cm^{-1}, and a band at 3340 cm^{-1} is due to the ν(N–H) in the same ligand.

Protonation of complex VII with concentrated aqueous perchloric acid resulted in opening of the chelating ligand to give the terminal carbene derivative VIII (Scheme 1). The IR spectrum of VIII showed a ν(CO) band at 2048 cm^{-1} and two ν(CN) bands at 2078w and 2148vs cm^{-1} probably due to the A′ and A″ modes (C_s symmetry) in a *trans* arrangement of the isocyanide ligands. The ν(C–N) band of the carbene ligand appeared at 1530 cm^{-1}. Two ν(N–H) bands at 3380 and 3270 cm^{-1} were observed for the two amine groups of the same ligand. As expected, the conductivity value of VIII was typical of a uni-bivalent electrolyte.

Both protonations were reversible; thus treatment of VIII with KOH gave initially VII, and then VIa upon more prolonged reaction.

Experimental

All reactions were carried out under dry oxygen-free argon, with solvents dried and distilled under argon prior to use. Infrared spectra were recorded on a Perkin Elmer 298 spectrophotometer, and NMR spectra (^{1}H and ^{31}P{^{1}H}) on a Varian FT-80 instrument. The complexes [Fe(dppe)(CNR)$_4$](ClO$_4$)$_2$ (Ia and Ib) were made as described previously [7].

cis-$[\overline{Fe(dppe)(CNPh)_2\{C}(NHPh)NMe\overline{C}{=}NPh\}]ClO_4$ *(II)*

Methylamine was bubbled through a solution of [Fe(dppe)(CNPh)$_4$](ClO$_4$)$_2$ (Ia) (0.5 g, 0.47 mmol) in CH$_2$Cl$_2$ (30 cm^3), for 10 min. The solvent was then evaporated to dryness and the residue washed with diethyl ether (30 cm^3) to give a yellow solid. This was dissolved in CH$_2$Cl$_2$ (40 cm^3), and the solution was filtered and the solvent evaporated off. The residual oil was washed with petroleum ether (40 cm^3) until a yellow solid (II) was obtained (yield 0.33 g, 70%). The product can be recrystallized from a CH$_2$Cl$_2$/MeOH mixture.

cis-$[\overline{Fe(dppe)(CNPh)_2\{C}(NHPh)NMe\overline{C}(NHPh)\}](ClO_4)_2$ *(III)*

To a solution of II (0.1 g, 0.1 mmol) in CH$_2$Cl$_2$ (20 cm^3) was added 70% aqueous perchloric acid (1 cm^3). The mixture was stirred at room temperature for 10 min, and the organic layer was then filtered through a column of diatomaceous earth. The addition of petroleum ether (20 cm^3) to the solution caused the precipitation of III as a yellow solid (yield 0.098 g, 90%).

mer-$[Fe(dppe)(CNPh)_3\{C(NHPh)(NHMe)\}](ClO_4)_2$ *(IV)*

1% aqueous perchloric acid (20 cm^3) was added to a solution of 0.4 g (0.4 mmol) of II in 30 cm^3 of CH$_2$Cl$_2$. The mixture was stirred for 5 h. The organic layer was washed with several portions (30 cm^3) of water and then filtered. Methanol (10 cm^3) was added, and the solution concentrated in vacuum until yellow crystals of IV separated (yield 0.35 g, 80%).

$cis\text{-}[\overline{Fe(dppe)(CNPh)_2\{C}(NMe_2)NPh\overline{C}=NPh\}]ClO_4$ *(V)*

40% aqueous Me_2NH (10 cm^3) was added to a solution of 0.22 g (0.2 mmol) of Ia in CH_2Cl_2 (30 cm^3). After 3 h stirring the organic layer was washed with several portions of water (30 cm^3) and then filtered. The solvent was then evaporated off and the residual oil washed with petroleum ether (40 cm^3) until an orange solid was obtained (yield 0.17 g, 84%).

$[\overline{Fe(dppe)(CNPh)(CO)\{PhN=CNPhC}=NPh\}]$ *(VIa)*

To a solution of Ia (0.3 g, 0.28 mmol) in CH_2Cl_2 (30 cm^3) was added an excess of KOH (2 g). After 4 h stirring the solution was filtered and diethyl ether (20 cm^3) was added. Compound VIa separated as a yellow solid (yield 0.1 g, 40%).

$[\overline{Fe(dppe)(CNC_6H_4Me\text{-}4)(CO)\{(C_6H_4Me\text{-}4)N=CN(C_6H_4Me\text{-}4)C}=N(C_6H_4Me\text{-}4)\}]$ *(VIb)*

This was prepared in the same way as VIa from Ib (0.2 g, 0.178 mmol) and KOH (2 g). Yield 0.12 g, 72%.

$[\overline{Fe(dppe)(CNPh)(CO)\{C(NHPh)NPhC}=NPh\}]ClO_4$ *(VII)*

To a suspension of VIa (0.3 g, 0.34 mmol) in CH_2Cl_2 (30 cm^3) was added 2% aqueous perchloric acid (3 cm^3). The mixture was stirred for 30 min and the organic layer was then filtered and ethanol (10 cm^3) added. Concentration of the solution in vacuo gave yellow crystals of VII (yield 0.12 g, 36%).

$trans\text{-}[Fe(dppe)(CNPh)_2(CO)\{C(NHPh)_2\}](ClO_4)_2$ *(VIII)*

To a solution of VII (0.3 g, 0.30 mmol) in CH_2Cl_2 (30 cm^3) was added 70% aqueous perchloric acid (1 cm^3). The mixture was stirred for 1 h and the organic layer then washed with several portions (30 cm^3) of water and filtered. After addition of ethanol (10 cm^3) and concentration in vacuum yellow crystals of VIII were obtained (yield 0.14 g, 42%).

Acknowledgements

We thank the Spanish M.E.C. for a Scholarship (J.R.) and CAICYT for financial support (Project No. PB85-0402).

References

1 E. Singleton and H.E. Oosthuizen, Adv. Organomet. Chem., 22 (1984) 209.
2 P.M. Treichel and J.P. Stenson, Inorg. Chem., 8 (1969) 2563.
3 P.M. Treichel and J.P. Stenson, Chem. Commun., (1969) 423.
4 J. Chatt, A.J.L. Pombeiro, R.L. Richards, J. Chem. Soc., Dalton Trans., (1980) 492.
5 A.J.L. Pombeiro, M.F.N.N. Carvalho, P.B. Hitchcock and R.L. Richards, J. Chem. Soc., Dalton Trans., (1981) 1629.
6 F.A. Cotton and C.M. Lukehart, Prog. Inorg. Chem., 16 (1972) 4877.
7 V. Riera, J. Ruiz and F. Mayor, J. Organomet. Chem., 276 (1984) 47.
8 V. Riera, J. Ruiz, A. Tiripicchio and M. Tiripicchio Camellini, J. Organomet. Chem., 327 (1987) C5.
9 J. Miller, A.L. Balch and J.H. Enemark, J. Am. Chem. Soc., 93 (1971) 4613.
10 T. Sawai and R.J. Angelici, J. Organomet. Chem., 80 (1974) 91.
11 A.L. Balch and J. Miller, J. Am. Chem. Soc., 94 (1972) 417.
12 A.L. Steinmetz and B.V. Johnson, Organometallics, 2 (1983) 705.

13 D.J. Doonan and A.L. Balch, J. Am. Chem. Soc., 95 (1973) 4769.
14 D.J. Doonan and A.L. Balch, Inorg. Chem., 13 (1974) 921.
15 B.V. Johnson, D.P. Sturtzel and Joyce E. Shade, J. Organomet. Chem., 154 (1978) 89.
16 R.J. Angelici and L.M. Charley, J. Organomet. Chem., 24 (1970) 205.
17 A.L. Balch and J. Miller, J. Organomet. Chem., 32 (1971) 263.
18 W.J. Knebel and P.M. Treichel, J. Chem. Soc., Chem. Commun., (1971) 516.
19 P.M. Treichel and W.J. Knebel, Inorg. Chem., 11 (1972) 1285.