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XIII *. ALKYLATION OF η^2-CS_2 DERIVATIVES AND REACTION WITH $NaBH_4$. EVIDENCE FOR A η^2-CH(S)SR LIGAND

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Summary

The cationic complexes **2** $[Nb(\eta\text{-}C_5H_5)_2(Bu)[\eta^2\text{-}C(S)SR]]X$ are formed from $[Nb(\eta\text{-}C_5H_5)_2(Bu)[\eta^2\text{-}CS_2]]$ (**1**) and RX (R = Me, Et, i-Pr, CH_2COOEt; X = I. R = $CH_2C_6H_5$, $CH_2CH_2CH_2Cl$, $CH_2\text{-}CH{=}CH_2$; X = Br). They react with $NaBH_4$ in THF giving complexes **4**. These decompose in solution and give, after column chromatography, neutral complexes **3** of the type $[Nb(\eta\text{-}C_5H_5)_2(Bu)[\eta^2\text{-}CH(S)SR]]$. The conversion of **2** into **3**, which corresponds to nucleophilic attack by the hydride ion on the CS_2 carbon atom, seems to proceed via formation of intermediate derivatives **4** containing a niobium-coordinated BH_4 group. Reaction of **1** with diiodomethane as alkylating reagent results in the formation of a dimeric niobium compound containing the $\overline{\text{Nb–C(S}}\text{)–S–CH}_2\text{–S–(}\overline{\text{S)C–Nb}}$ unit, which reacts further with $NaBH_4$.

Introduction

Since the preparation of the first transition metal CS_2 derivatives in 1967 [2], there has been gradually increasing activity in the chemistry of transition metal-carbon

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* For part XII see ref. 1.

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disulphide complexes. It is now clear that carbon disulphide is a versatile ligand which can bond to metals in a wide range of coordination modes [3].

Most the reactions of η^2-CS_2 complexes that have been reported involve the nucleophilic character of the uncoordinated sulphur atom. For example, the $[ML_n(\eta^2\text{-}CS_2)]$ complexes have been shown to act as monodentate two-electron ligands through their uncoordinated sulphur atom, giving the dinuclear complexes $[L_nM(\mu\text{-}CS_2)M'(CO)_nL'_n]$ [4]. These complexes are also well-known to be alkylated at the sulphur atom by some alkyl halides, giving $[ML_n[\eta^2\text{-}C(S)SR]]^+$ [5].

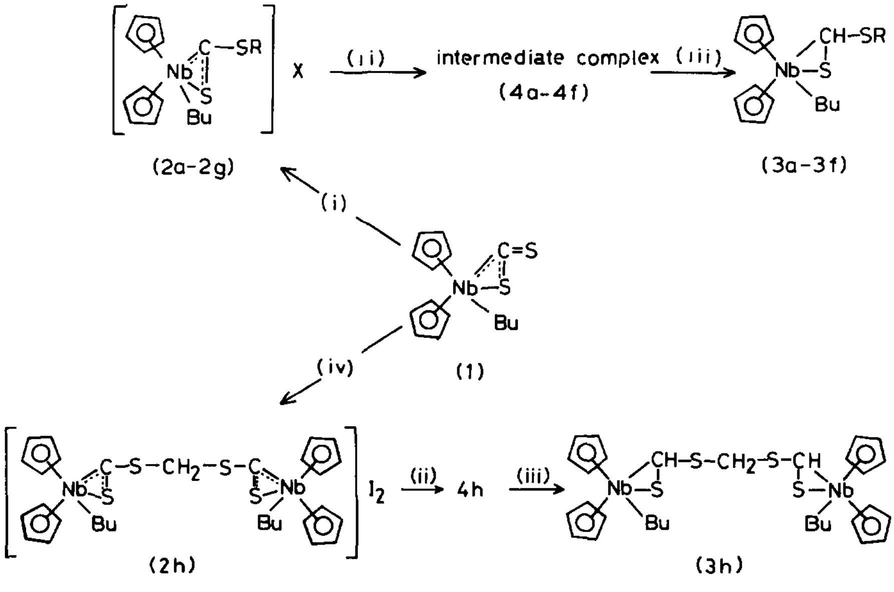
Previous work in this and other laboratories [4h,6] has shown the ability of niobium to form 18-electron η^2-CS_2 derivatives **1** of formula $[Nb(\eta\text{-}C_5H_5)_2(R)[\eta^2\text{-}CS_2]]$ ($R = CH_3$, C_4H_9, C_3H_5). In a recent paper [4h] we were able to show the ability of compounds **1** to act as monodentate ligands, and we gave three examples of their alkylation with alkyl halides RX.

In order to have available a range of compounds with a variety of substituents we thought it of interest to explore more widely the reactions of alkyl halides with **1**. The cationic structure of the alkylated derivatives seemed to be especially appropriate for investigating their reactivity towards some nucleophilic reagents, and so we decided to investigate their reaction with the hydride ion from $NaBH_4$.

Results and discussion

1. Alkylation studies

The general procedure was to treat a benzene solution of $[Nb(\eta\text{-}C_5H_5)_2(Bu)(\eta^2\text{-}CS_2)]$ (**1**) with either an equimolar quantity or an excess of alkyl halide RX ($R = CH_3$, C_2H_5, i-C_3H_7, $CH_2COOC_2H_5$; $X = I$. $R = CH_2C_6H_5$, $CH_2CH_2CH_2Cl$, $CH_2\text{-}CH{=}CH_2$; $X = Br$). This treatment results in the precipitation in almost quantitative yield of yellow complexes **2** (see Scheme 1). These compounds are



SCHEME 1. Synthesis of complexes **2**–**4**. (i) Excess of RX in benzene (X = I, ca. 20–40°C; X = Br, ca. 70°C); yield almost quantitative (ii) Excess $NaBH_4$ in THF, 12 h, room temp. (iii) Alumina column chromatography of THF solutions of **4**; yield ca. 70% from **2**. (iv) Excess CH_2I_2 in benzene, ca. 70°C.

sparingly soluble in organic solvents. The 1 : 1 ionic nature is supported by their molar conductivities. The analytical and spectroscopic data are consistent with the formulation of **2** as 18-electron cationic complexes in which the dithioalkylester group behaves in a bidentate fashion with the carbon and sulphur atoms acting as donors (observed ν(CS) values: 1110–1145 cm^{-1}, as expected for a bidentate dithioalkyl group; monodentate coordination via the central carbon atom causes a significant shift to a ν(CS) of about 1000 cm^{-1} [4h,7]).

The ease of the alkylation reaction depends on the nature of the alkylating reagent RX: alkyl iodides reacted at 20–40°C and bromides at 60–70°C, while no reaction was observed with chlorides at reflux. For a given halide, the rate of the reaction is increased by an electron-withdrawing group in the radical R.

It is noteworthy that the presence of an excess of the alkyl halide during the preparation of the alkylated complexes from **1** did not significantly affect their formation and did not afford dithiocarbene derivatives [8].

2. *Reaction with $NaBH_4$*

The reaction of the cation $[Os[\eta^2\text{-}CS_2Me](CO)_2(PPh_3)_2]^+$ with $NaBH_4$ has been reported recently and the formation of the neutral complex $[OsH[\eta^1\text{-}C(S)SMe](CO)_2(PPh_3)_2]$, which contains mutually *cis* hydride and η^1-dithiomethylester ligands, was observed [9]. A solution of this hydride, when heated, eliminates methanethiol (MeSH) and gives the thiocarbonyl-complex $[Os(CS)(CO)_2(PPh_3)_2]$. In order to elucidate further the chemistry of niobium η^2-CS_2 derivatives, we have now carried out a study of similar reactions between the complexes **2** and the hydride ion from $NaBH_4$. These reactions were performed in THF at room temperature and complexes **2** were smoothly converted into new derivatives **4** (see below). Column chromatography experiments on the THF solutions of these products resulted in immediate decomposition, with gas evolution, at the top of the alumina column. However, elution with benzene gave new complexes **3**. Compounds **3** are all white air-stable crystalline solids, soluble in usual organic solvents. All have been characterized by analysis, NMR and IR spectroscopy. The presence of a Nb–S–CH–SR unit in **3** was clearly deduced from ^1H and ^{13}C NMR spectra. For complex **3a**, for instance, a peak of relative intensity 1 was observed at δ 4.21 ppm in the ^1H NMR spectrum while the ^{13}C NMR spectrum reveals that the signal corresponding to the CS_2 carbon atom appears as a doublet from coupling with a proton (δ 55.4 ppm; $^1J(C/H)$ 169 Hz).

Further evidence of a $[Nb[\eta^2\text{-}CH(S)SR]]$ unit was given by deuteration experiments. Reaction of complex **2a** with $NaBD_4$ gave, after further work-up, a complex **3a**′, the ^1H NMR spectrum of which was similar to that of **3a**, except for the peak at δ 4.21 ppm, which did not appear. For all the complexes **3**, the NMR data also show the presence of a $[Nb(\eta\text{-}C_5H_5)_2(Bu)]$ moiety.

Therefore the overall reaction between **2** and $NaBH_4$ may be written as:

$$\{[Nb][\eta^2\text{-}C(S)SR]\}^+ + H^- \rightarrow \{[Nb][\eta^2\text{-}CH(S)SR]\} \qquad (1)$$

with $[Nb] = [Nb(\eta\text{-}C_5H_5)_2(Bu)]$.

Reaction 1 corresponds to nucleophilic attack by the hydride ion from $NaBH_4$ on the CS_2 carbon atom of the ligand without any change of the metal oxidation number. It differs from the reaction of BH_4^- with the osmium cation $[Os[\eta^2$-

(Continued on p. 58)

TABLE 1. ANALYTICAL AND SPECTROSCOPIC RESULTS

Compound	Analysis [a] (%)					Λ [b]	^1H and ^{13}C NMR data [c]	Selected IR data ν(CS) [d] (cm^{-1})
	C	H	S	Nb	X			
2 {*Nb(η-Cp)$_2$(Bu)[η^2-C(S)SR]*} *X*								
2a R = Me, X = I [e]	42.0	4.7	11.0	17.6	24.0 [f]	87	^1H: 6.00, s(10), Cp; 3.43. s(3), SCH_3	1130s,1145m
	(42.5)	(4.7)	(11.9)	(17.3)	(23.6)			
2b R = Et, X = I [e]	43.0	5.0	11.2		22.9 [f]	94	^1H: 5.97, s(10), Cp; 3.72, q(2,^3J(HH) = 7), CH_2; 1.50, t(3,^3J(HH = 7), CH_3	1130s.1148m
	(43.5)	(4.9)	(11.6)		(23.0)			
2c R = i-Pr, X = I	40.7	4.9	12.1		24.4 [f]	89	^1H: 5.92, s(10), Cp; 4.20, sept(1, ^3J(HH) = 7), CH; 1.57, d (6,^3J(HH) = 7), CH_3	1130s(br)
	(41.0)	(4.9)	(12.1)		(24.1)			
2d R = CH_2COOEt, X = I	40.6	4.2	11.0		22.5 [f]	87	^1H: 6.00, s(10), Cp; 4.70, s(2) SCH_2; 4.20, q(2, ^3J(HH) = 7) CH_2(Et); 1.30, t(3, ^3J(HH) = 7), CH_3(Et).	1120s,1140m
	(40.0)	(4.6)	(11.2)		(22.3)			
2e R = $CH_2C_6H_5$, X = Br	50.1	4.6	11.4		15.4 [g]	84		1120s(br)
	(50.1)	(4.9)	(12.1)		(15.1)			
2f R = $CH_2CH_2CH_2Cl$, X = Br	41.1	4.9	11.6		17.0 [g]	78	^1H: 5.97, s(10), Cp; 4.00, t(2, ^3J(HH) = 7), CH_2; 3.60, t(2, ^3J(HH) = 7) CH_2; 2.40, q(2, ^3J(HH) = 7), CH_2	1110s,1130m
	(42.0)	(4.8)	(12.4)		(15.5)			
2g R = CH_2–CH=CH_2, X = Br	45.2	5.0	13.1	18.8	17.2 [g]	79	^1H: 5.97, s(10), Cp; 5.50, c(3), CH=CH_2; 4.40, δ(2, ^3J(H,H) = 7), SCH_2	1120s,1145m
	(45.3)	(5.0)	(13.4)	(19.5)	(16.8)			
2h R = 1/2 CH_2, X = I	38.0	4.0	12.4	18.9		127		1120s,1150m
	(37.9)	(4.0)	(13.0)	(18.9)				
3 {*Nb(η-Cp)$_2$(Bu)[η^2-CH(S)SR]*}								
3a R = Me	51.0	6.2	16.3	24.8 [h]			^1H [i]: 5.43, s(5), Cp; 5.38, s(5), Cp; 4.21, s(1), CH; 2.50, s(3) SCH_3. ^{13}C: 104.3, s, Cp; 103.2, s, Cp; 55.4, d(^1J(CH) = 169), NbCH; 38.0, t(^1J(CH) = 123), $C^{\gamma}H_2$; 29.0, t (^1J(CH) = 127), $C^{\beta}H_2$; 25.2, t(^1J(CH) = 133), $C^{\alpha}H_2$; 24.8, t(^1J(CH) = 138), SCH_3; 14.1, q(^1J(CH) = 129), CH_3(Bu).	1135s
	(51.6)	(6.2)	(17.2)	(25.0)				

3b R = Et	53.0 (52.8)	6.6 (6.5)	16.4 (16.6)		^1H: 5.34, s(5), Cp; 5.26, s(5) Cp; 4.22, s(1), CH; 2.90, q(2, $^3J(HH) = 7$), CH_2; 1.40, t(3, $^3J(HH) = 7$), CH_3	1130s
3c R = i-Pr	54.2 (54.0)	6.7 (6.8)	16.2 (16.0)		$^1H^j$: 5.38, s(5), Cp; 5.28, s(5), Cp; 4.21, s(1), CH; 3.16, sept(1, $^3J(HH) = 7$) CH(i-Pr); 1.42, d(6, $^3J(HH) = 7$), CH_3(i-Pr) ^{13}C: 104.4 s, Cp; 103.3, s, Cp; 49.7, s, NbCH; 43.2, s, CH(i-Pr); 38.1, s, $C^{\gamma}H_2$; 29.3, s, $C^{\beta}H_2$; 25.5, s, $C^{\alpha}H_2$, 23.4, s, CH_3(i-Pr); 14.7, s, CH_3(Bu).	1135s
3d R = CH_2COOEt					^1H: 5.38, s(5), Cp; 5.28, s (5), Cp; 4.37, s(1), CH; 4.25, q(2, $^3J(HH) = 7$), CH_2(Et); 3.62, s(2), SCH_2; 1.32, t(3, $^3J(HH) = 7$), CH_3(Et)	
3e R = $CH_2C_6H_5$					^1H: 7.2, c(5), C_6H_5; 5.37, s(5), Cp; 5.22, s(5), Cp; 4.1, s(1), CH; 1.25, s(2), CH_2.	
3f R = $CH_2CH_2CH_2Cl$					^1H = 5.32, s(5), Cp; 5.25, s(5), Cp; 4.10, s(1), CH; 3.68, t(2, $^3J(HH) = 7$), CH_2Cl; 2.97, t(2, $^3J(HH) = 7$) SCH_2; 2.23, c(2), CH_2	
3h R = 1/2 CH_2	52.1 (51.1)	6.0 (5.8)	16.9 (17.5)		^1H: 5.58, s(10), Cp; 5.30, s(10), Cp; 4.56, s(2), CH; 2.5, s(2), CH_2.	
4 {*Nb(η-Cp)$_2$(Bu)[η^1-CH(SH)SR](HBH$_3$)*}						
4a R = CH_3 [e]	53.1 (53.2)	6.8 (7.3)	14.1 (15.0)	23.3 [k] (21.9)	$^1H^l$: 5.37, s(5), Cp; 5.32, s(5) Cp; 3.67, s(1)CH; 2.55, s(3), SCH_3	1090s [m]

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[a] Calculated values are given in parentheses. [b] Molar conductivity in Ω^{-1} cm^2 mol^{-1} (10^{-3} *M*, CH_3NO_2, 20°C). [c] Given as: chemical shift (δ), multiplicity (relative intensity, *J* in Hz), assignment. Solvent $CDCl_3$, unless otherwise stated. Carbon atoms of the butyl group given as Nb–$C^{\alpha}H_2$–$C^{\beta}H_2$–$C^{\gamma}H_2$–CH_3. ^1H NMR butyl resonances appear as a poorly resolved signal at δ 0.5–2.5 ppm and are not reported. [d] Nujol mulls. [e] With 0.5 C_6H_6. [f] X = I. [g] X = Br. [h] Mass spectrum shows parent ion P^+ at $m/e = 372$ (weak peak) and a strong peak at 314.9603 (P^+ –Bu: calcd. 314.9600). [i] In C_6D_6: 4.35, s(5), Cp; 4.04, s(5), Cp; 3.63, s(1), CH; 1.90, s(3), SCH_3. For the deuterated analog (**3'a**) [Nb(η-Cp)$_2$(Bu)(η^2-CD(S)SMe)] in $CDCl_3$: 5.31, s(5), Cp; 5.22, s(5), Cp; 2.45, s(3), CH_3. [j] In C_6D_6: 4.46, s(5), Cp; 4.15, s(5), Cp; 3.80, s(1), CH; 2.80, sept(1), CH(i-Pr); 1.00, d(6), CH_3(i-Pr). [k] Other analytical data, B: 3.3(2.6). [l] In C_6D_6: 4.40, s(5), Cp; 4.20, s(5), Cp; 3.25, s(1), CH; 1.90, s(3), SCH_3. The ^{11}B NMR spectrum exhibits an unresolved multiplet at δ −43.6 ppm relative to H_3BO_3 in H_2O–D_2O. The ^1H BH_4 resonances appear with the butyl signals. [m] ν(BH): 2280sh, 2350sh, 2380s. ν(BH) values commonly observed for mononuclear MBH_4 configurations: BH_4 monodentate 2300–2450, BH_4 bidentate 2400–2600, BH_4 tridentate 2450–2600 [11].

C(S)SMe](CO)$_2$(PPh$_3$)$_2$]$^+$ which gave an hydrido-osmium complex (see above and ref. 9).

However, reaction 1 may be compared with the reaction [(triphos)Cu(BH$_4$)] + CS$_2$ → [(triphos)Cu–SCHS] recently reported by Bianchini et al. [10].

In an effort to gain further insight into the mechanism of reaction 1, we have studied the intermediate complexes **4** but attempts fully to characterize these products were unfortunately foiled by (i) partial and rapid decomposition in organic solvents and (ii) difficulties of removing benzene in the solid state. However, careful examination of the analytical and spectroscopic data for complex **4** in the most favorable case (**4a**, R = Me) suggests that reaction 1 proceeds via the formation of an intermediate derivative containing a niobium-coordinated BH$_4$ group. Coordination of the BH$_4$ unit to niobium was deduced from the solubility of **4a** in nonpolar solvents and from conductivity measurements. The three possible ligation modes conceivable for the BH$_4$ ligand in a mononuclear complex may be distinguished by IR spectroscopy [11]. The observed ν(BH) values for **4a** (Table 1) would be in agreement with a monodentate BH$_4$ group linked to the metal by a bridging hydrogen atom as recently shown for [Cu(triphos)(BH$_4$)] by an X-ray study [12].

Since single crystals suitable for an X-ray study could not be obtained, we cannot be sure about the exact nature of complexes **4** but their identity as [Nb(η-C$_5$H$_5$)$_2$(Bu)[η^1-CH(SH)SR](HBH$_3$)] is suggested by the above evidence.

3. *Formation of dimeric niobium complexes*

It is noteworthy that the reaction of **2** with diiodomethane as the alkylating reagent (12 h, 70°C) results in the formation of a dimeric compound **2h** with a Nb–C(S)–S–CH$_2$–S(S)C–Nb unit. Further reaction of **2h** with NaBH$_4$ gives complex **3h** with a Nb–CH(S)–S–CH$_2$–S–(S)CH–Nb moiety (see Scheme 1).

4. *Spectroscopic studies*

NMR and IR data for the reported complexes show the following three interesting features:

(i) A strong solvent influence of the ^{1}H NMR chemical shifts was found for complexes **3** and **4**. The resonances in C$_6$D$_6$ solutions are shielded relative to those in CDCl$_3$ solutions. The differences in the chemical shifts are in the ranges 0.92–1.34 ppm for the cyclopentadienyl protons and 0.36–0.65 ppm for the dithio-ligand protons. Such benzene-induced solvent dependence of proton resonances has previously been interpreted as resulting from the formation of a 1 : 1 benzene-solute transient collision complex at each electron-deficient site in the solute molecule [13].

(ii) The ^{1}H NMR resonances appear at higher field in complexes **3** than the corresponding resonances in **2**. In agreement with the cationic nature of complexes **2**, the strong shielding which is observed for the Cp protons (**2**: δ 5.90–6.00 ppm; **3**: δ 5.38–5.43 ppm) and for the Nb–C(S)–S-C*H* proton (for example **2a**: δ 3.43 ppm; **3a**: δ 2.50 ppm) is indicative of an increase in electron density from **2** to **3**.

(iii) The IR band near 1210 cm^{-1} in complexes **3** does not appear for the deuterated complex **3'a**, while a new band is observed at 915 cm^{-1}. This value shows that this absorption is not assignable to a CS$_2$ vibration but must be attributed to a carbon–hydrogen vibration involving the CS$_2$ carbon atom ($\bar{\nu}$(CH)/$\bar{\nu}$(CD) ca. 1.4).

Conclusions

All the reactions and structures of the new complexes are shown in Scheme 1. It seems of interest that η^2-CS_2 derivatives may, after alkylation of the sulphur atom, undergo reaction with $NaBH_4$ giving new complexes by attack of the hydride ion on the CS_2 carbon atom. The reactivity of complexes **2** towards other nucleophilic reagents is currently under investigation.

Experimental

All reactions were performed in Schlenk tubes in a dry oxygen-free dinitrogen atmosphere. All solvents were distilled by standard techniques and thoroughly deoxygenated before use. All elemental analyses were performed by the "Service Central de Microanalyse du C.N.R.S.". IR spectra were recorded on a Perkin-Elmer 557 Spectrometer. ^1H and ^{13}C NMR spectra were obtained on a JEOL FX 100 spectrometer operating in the F.T. model ($SiMe_4$ as internal standard). Mass spectra were obtained with a Varian MAT 311 spectrophotometer ("Centre de Mesures Physiques", Rennes, France). The conductance measurements were performed at 22°C with a Tacussel CD7-N conductivity bridge on approximately 10^{-3} *M* solutions (solvent: nitromethane, dried over molecular sieves and deoxygenated before use).

Complex **1**, $[Nb(\eta\text{-}Cp)_2(Bu)(\eta^2\text{-}CS_2)]$, was prepared as in the literature [4h].

Preparation of complexes 2 $[Nb(\eta\text{-}Cp)_2(Bu)[\eta^2\text{-}C(S)SR]]X$

The general procedure was to treat a benzene solution of **1** $[Nb(\eta\text{-}Cp)_2(Bu)(\eta^2\text{-}CS_2)]$ with a benzene solution containing an excess of the alkyl halide. The mixtures were heated when necessary (temperature 20–40°C for alkyl iodides, except for diiodomethane (70°C), and 60–70°C for alkyl bromides). Complexes **2** precipitated as yellow products, which were filtered off, washed twice with benzene and dried in vacuo. The yield was almost quantitative.

*Preparation of complexes **4a** and **3a** by reaction of **2a** with sodium borohydride*

An excess of sodium borohydride was added to a THF solution of **2a** and the suspension was stirred at room temperature for ca. 12 h. The solvent was removed under reduced pressure and the residue stirred with pentane in order to extract small amounts of complex **3a**. After filtration, the residue was stirred with benzene. The mixture was filtered and the filtrate was concentrated under reduced pressure to give the crude product. This was washed with pentane and dried in vacuo to give complex **4a**. Attempts to grow single crystals of **4a** were unsuccessful.

A THF solution of **4a** (or the starting THF solution described above) was chromatographed on an alumina column made up with petroleum ether. After elution with benzene, the eluate was stripped dry to give compound **3a**.

Compounds **3b**–**3f** were prepared analogously to **3a**, while **3h** was eluted with THF. The yield of complexes **3** was ca. 70%, from **2**.

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References

1 J. Sala-Pala, J.L. Migot, J.E. Guerchais, L. Le Gall and F. Grosjean, J. Organomet. Chem., 248 (1983) 299.

2 (a) M.C. Baird and G. Wilkinson, J. Chem. Soc. (A), (1967) 865; (b) M.C. Baird, G. Hartwell Jr. and G. Wilkinson, J. Chem. Soc. (A), (1967) 2037.

3 See for instance: (a) I.S. Butler and A.E. Fenster, J. Organomet. Chem., 66 (1974) 161; (b) N.I. Kirillova, A.I. Gusev, A.A. Pasynskii and Yu.T. Struchkov, Zh. Strukt. Khim., 15 (1974) 288; (c) P.V. Yaneff, Coord. Chem. Rev., 23 (1977) 183; (d) M. Cowie and S.K. Dwight, J. Organomet. Chem., 214 (1981) 233; (e) J.A. Ibers, Chem. Soc. Rev., 11 (1982) 57; (f) J.J. Maj, A.D. Rae and L.F. Dahl, J. Am. Chem. Soc., 104 (1982) 4279; (g) P.V. Broadhurst, B.F.G. Johnson, J. Lewis and P.R. Raithby, J. Chem. Soc., Chem. Commun., (1982) 140; (h) G. Gervasio, R. Rossetti, P.L. Stanghellini and G. Bor, Inorg. Chem., 21 (1982) 3781; (i) M.G. Mason, P.N. Swepston and J.A. Ibers, Inorg. Chem., 22 (1983) 411; (j) H. Stolzenberg and W.P. Fehlhammer, J. Organomet. Chem., 235 (1982) C7.

4 M. Herberhold, M. Süss-Fink and C.G. Kreiter, Angew. Chem. Int. Ed. Engl., 16 (1977) 193; (b) M. Herberhold and M. Süss-Fink, Chem. Ber., 111 (1978) 2273; (c) H. Werner, K. Leonard and C.H. Burschka, J. Organomet. Chem., 160 (1978) 291; (d) U. Oehmichen, T.G. Southern, H. Le Bozec and P. Dixneuf, J. Organomet. Chem., 156 (1978) C29; (e) W.P. Fehlhammer, A. Mayr and H. Stolzenberg, Angew. Chem. Int. Ed. Engl., 18 (1979) 626; (f) T.G. Southern, U. Oehmichen, J.Y. Le Marouille, M. Le Bozec, D. Grandjean and P.H. Dixneuf, Inorg. Chem., 19 (1980) 2976; (g) C. Bianchini, C. Mealli, A. Meli, A. Orlandini and L. Sacconi, Inorg. Chem., 19 (1980) 2968; (h) J. Amaudrut, J. Sala-Pala, J.E. Guerchais, R. Mercier and J. Douglade, J. Organomet. Chem., 235 (1982) 301; (i) W.A. Schenk, T. Schwietzke and H. Müller, J. Organomet. Chem., 232 (1982) C41; (j) C. Moïse, J. Organomet. Chem., 247 (1983) 27.

5 (a) D.H. Farrar, R.O. Harris and A. Walker, J. Organomet. Chem., 124 (1977) 125; (b) D. Touchard, H. Le Bozec and P. Dixneuf, J. Organomet. Chem., 170 (1979) C34; (c) P. Conway, S.M. Grant and A.R. Manning, J. Chem. Soc. Dalton Trans., (1979) 1920. (d) H. Le Bozec, P.H. Dixneuf, A.J. Carty and N.J. Taylor, Inorg. Chem., 17 (1978) 2568. (e) D. Touchard, H. Le Bozec, P.H. Dixneuf, A.J. Carty and N.J. Taylor, Inorg. Chem., 20 (1981) 1811. (f) H. Stolzenberg, W.P. Fehlhammer and P. Dixneuf, J. Organomet. Chem., 246 (1983) 105. (g) G. Fachinetti, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Chem. Soc. Dalton Trans., (1979) 1612.

6 (a) G.W.A. Fowles, L.S. Pu and D.A. Rice, J. Organomet. Chem., 54 (1973) C17; (b) M.G.B. Drew and L.S. Pu, Acta Crystallogr. Sect. B, B33 (1977) 1207.

7 J.M. Walters and J.A. Ibers, Inorg. Chem., 16 (1977) 3273.

8 (a) K.R. Grundy, R.O. Harris and W.R. Roper, J. Organomet. Chem., 90 (1975) C34; (b) T.J. Collins, K.R. Grundy and W.R. Roper, J. Organomet. Chem., 107 (1976) C37.

9 T.J. Collins, W.R. Roper and K.G. Town, J. Organomet. Chem., 121 (1976) C41.

10 C. Bianchini, C.O. Ghilardi, A. Meli, S. Midollini and A. Orlandini, J. Organomet. Chem., 248 (1983) C13.

11 T.J. Marks and J.R. Kolb, Chem. Rev., 77 (1977) 263, and refs. therein.

12 C.A. Ghilardi, S. Midollini and A. Orlandini, Inorg. Chem., 21 (1982) 4096.

13 (a) J. Ronayne and D.H. Williams, Chem. Commun., (1966) 712; (b) M. Honda, Y. Kawasaki and T. Tanaka, Tetrahedron Lett., (1967) 3313; (c) M.M. Kubicki, R. Kergoat, J.E. Guerchais, R. Mercier and J. Douglade, J. Cryst. Mol. Struct., 11 (1981) 43.