Carbon-13 Nuclear Magnetic Resonance Study of Dinuclear Iron Carbonyl Xanthate Complexes: Dynamic Behaviour and Local Scrambling of the Carbonyls at one Iron Atom

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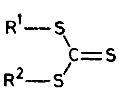
A series of compounds of general formula [$Fe_2(CO)_5L$(*S*-alkyl dithiocarbonate)], where L = CO or $P(OMe)_3$, have been studied by ^{13}C n.m.r. to observe their behaviour in solution. Over the temperature range −100 to 50 °C one of the $Fe(CO)_3$ groups was found to be static while the other was fluxional. The site of local scrambling has been identified and the relevant mechanisms discussed.

We have previously described the syntheses and properties of several new sulphur-containing ligands, *viz. S*-alkyl dithiocarbonates (xanthates), trithiocarbonates, and dithioesters.[1,2] Thus, for example, they can be desulphurised by [$Co_2(CO)_8$] to afford alkoxy- or alkyl-alkylidyne tricobalt nonacarbonyl cluster complexes;[3,4] in contrast, they react with di-iron nonacarbonyl to yield novel binuclear complexes the structures of which have been determined by *X*-ray crystallography.[5,6] From the unsymmetrical trithiocarbonates, (1), two complexes (2) or (3) are obtainable depending on which carbon–sulphur bond is broken; however, from xanthates, (4), the sole product (5) results from C–S fission, and the C–O bond is retained.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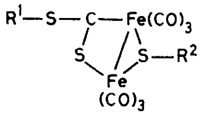
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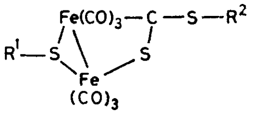
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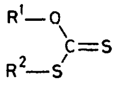
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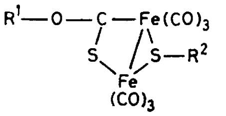
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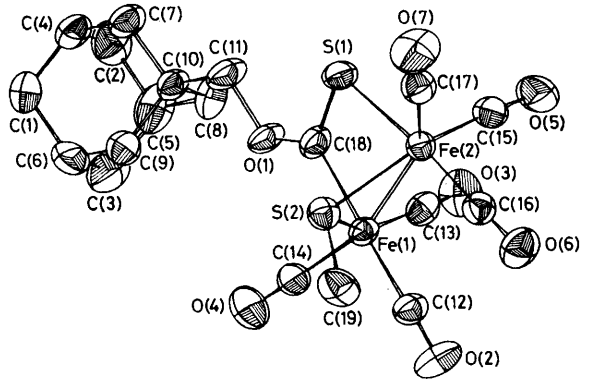


FIGURE 1 Structure of complex (5a)

An example of structure (5) (R^1 = adamantylmethyl, R^2 = methyl) is shown in Figure 1, and a series of variously substituted derivatives of (2), (3), and (5) have been prepared. They have a common structural feature in that the $Fe_2(CO)_6$ moiety is linked by a di-atomic bridge and also by a second *S*-alkyl bridge; furthermore, the plane containing O(1)–C(18)–S(1)–Fe(1)–Fe(2) makes a dihedral angle of 91° with the S(2)–Fe(1)–Fe(2) plane. Comparison of bond lengths in the complexes with those of the free ligands reveals a shortening of the C(18)–O(1) bond and a lengthening of the C(18)–S(1) bond suggesting electron delocalisation over these atoms; it is noteworthy that the C(18)–Fe(1) bond length (1.95 Å) is in the range of iron–carbene stabilised bonds. The low-field ^{13}C n.m.r. signal of C(18), at 293 p.p.m., is also in accord with the carbenic character of this bond. These studies have also revealed an unusual dynamic behaviour of the carbonyls and this we now describe.

RESULTS AND DISCUSSION

The carbonyl region of the ^{13}C n.m.r. spectrum of complex (5a) (R^1 = adamantylmethyl, R^2 = methyl) is temperature-dependent, as shown in Figure 2. The limiting spectrum (at −97 °C) shows all six carbonyl resonances, but three of these gradually coalesce so that at 38 °C the spectrum appears as four signals with intensities 1 : 3 : 1 : 1. Increasing the temperature above 38 °C does not change the spectrum but the maximum useful temperature was 70 °C, since above this limit the complex underwent thermal decomposition. It is apparent that, while one $Fe(CO)_3$ moiety is immutable, the other three carbonyl groups are exchangeable. The same situation is found for other complexes where R^1 is α- or β-cholestanyl, cholesteryl, ergosteryl, or menthyl, and R^2 is methyl, benzyl, or isopropyl; the limiting spectra and coalescences are, of course, obtained at different temperatures for the different complexes. At no time in any of these processes are signals observed in the 250 p.p.m. region where bridging carbonyls are usually observed.

This difference in behaviour of the two $Fe(CO)_3$ moieties must be related to their local environment; one iron is bonded to the carbene and to the *S*-methyl bridge, while the other is linked to S(1) and to S(2). The difference between the two iron environments is also readily detectable by Mössbauer spectroscopy which shows isomer shifts at —0.03 and 0.06 mm s^{-1}.

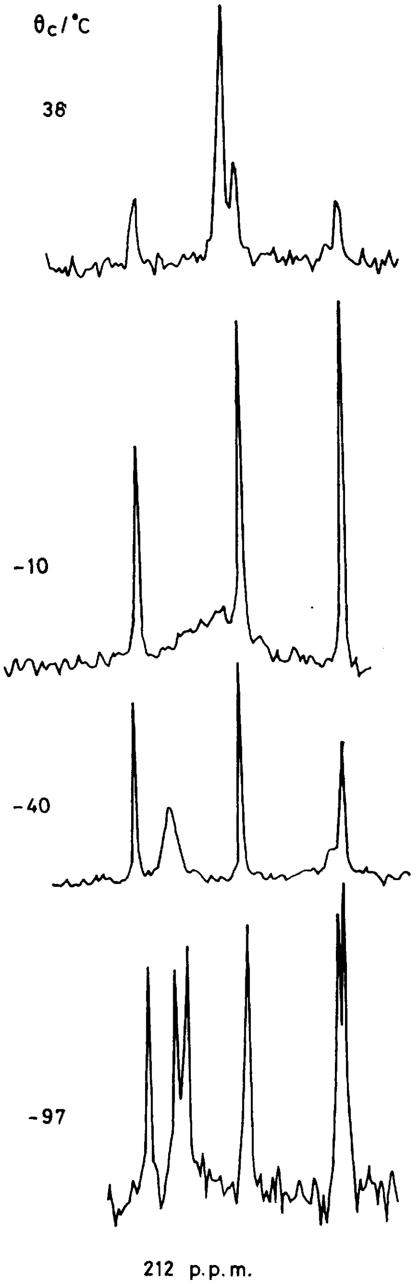


FIGURE 2 Temperature-dependent ^{13}C n.m.r. spectra of complex (5) (R^1 = adamantylmethyl, R^2 = methyl)

In order to distinguish to which iron atom the dynamic process can be associated, we have substituted a carbonyl group by trimethyl phosphite in complex (5); the temperature-dependent spectra of this phosphite complex, (6), are shown in Figure 3. It is clear that the extra bulkiness of the phosphite ligand raises the activation energy of the carbonyl exchange process since coalescence is now observed around room temperature and the limiting spectrum is obtained at 0 °C. Owing to the relative thermal instability of the phosphite derivative, it was not possible to observe a sharp signal indicating the equivalence of the exchanging carbonyls. We can deduce from the data in Figure 3 that the phosphite has replaced a carbonyl on the iron atom at which there was no scrambling, and further that this was Fe(1), the carbene-bonded iron atom.

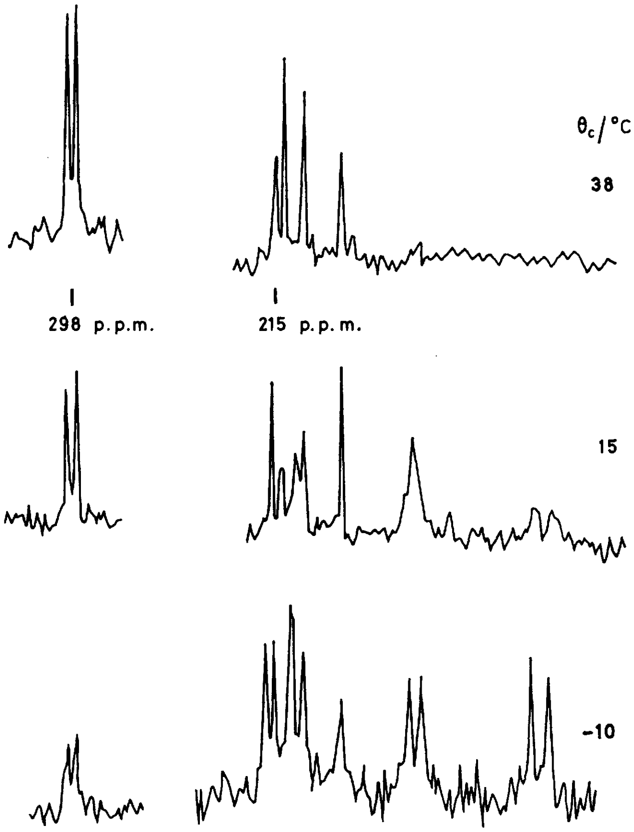


FIGURE 3 Temperature-dependent ^{13}C n.m.r. spectra of complex (6), $[Fe_2(CO)_5(SR^2)\{COR^1(S)\}\{P(OMe)_3\}]$ (R^1 = β-cholestanyl, R^2 = methyl)

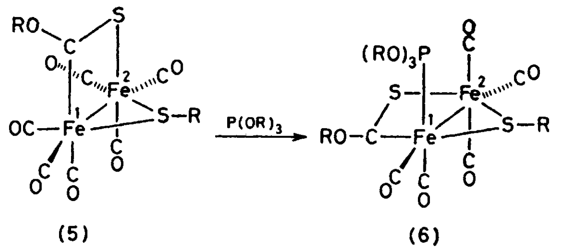
By running these spectra at different field strengths one can with some confidence assign the J_{CP} values listed in the Table. It is readily apparent that only two immutable carbonyl groups remain and these show $^2J_{CP}$ values of 20 and 4.5 Hz. The carbene carbon maintains an unchanging $^2J_{CP}$ value of 6 Hz over the temperature range studied and this is characteristic of coupling between *cis* disposed nuclei.[7] Typically, in $[Mo(CO)_5\{P(OEt)_3\}]$ the values of $^2J_{(C-P)}$ are 18.9 and 6.7 Hz for *trans* and *cis* respectively.[8] It is, therefore, unreasonable to assume that the phosphorus is mutually *cis* to the carbene carbon and to the remaining two carbonyls on Fe(1) since the $^2J_{CP}$ values for these carbonyls are 20 and 4.5 Hz. Indeed, it seems mandatory to orient the substituents around Fe(1) such that the phosphite is *cis* to the carbene and to one carbonyl and *trans* to the

Carbon-13 n.m.r. data for complexes $[Fe_2(CO)_4(SR^2)\{COR^1(S)\}L^1L^2]$ [a]

R^1	R^2	L^1	L^2	θ_c/°C	δ(C–S)	δ(CO)					
Adamantylmethyl	Me	CO	CO	38	295.9	212.3	210.2 (3)	209.9		207.3	
				−10	295.3	212.3		209.8		207.3	
				−40	294.8	212.4	211.6	209.8		207.3	
				−97 [b]	293.4	211.9	211.3	210.9	209.4	207.2	207.0
β-Cholestanyl	Me	CO	CO	36	294.5	212.5	210.3 (3)	209.7			207.2
				−58	293.6	212.5	211.6	209.6	209.4	207.4	207.2
α-Cholestanyl	Pr^i	CO	CO	−30	293.4	212.6	211.8	209.9	207.6	207.2	206.8
β-Cholesteryl	Me	CO	CO	36	294.2	212.1	209.9 (3)	209.5			206.9
β-Cholesteryl	Pr^i	CO	CO	−30	294.9	212.4	211.7	211.5	209.8	207.5	207.2
α-Cholesteryl	Pr^i	CO	CO	35	294.8	212.6	210.8 (3)	210.1			206.9
Menthyl	Bz [c]	CO	CO	15	293.6	212.5	210.7 (3)	210.3			207.2
β-Ergosteryl	Me	CO	CO	36	294.6	212.1	209.9 (3)	209.5			206.8
β-Cholestanyl	Me	$P(OMe)_3$	CO	−16	297.4	215.7	215.1	214.2	211.7	208.1	
					$^2J = 5.9$	$^2J = 4.6$	$^3J < 1$	$^2J = 21.3$	$^3J = 6.1$	$^3J = 10.7$	
				38	298.0	215.6		214.3			
					$^2J = 6.1$	$^2J = 4.7$		$^2J = 21.5$			
α-Cholestanyl	Bz	$P(OMe)_3$	CO	40	296.9	215.5		214.5			
					$^2J = 6.1$	$^2J = 4.6$		$^2J = 21.2$			
β-Cholesteryl	Pr^i	$P(OMe)_3$	CO	38	298.2	215.8	215.1	214.6	211.7	208.3	
					$^2J = 4.6$	$^2J = 4.6$	$^3J < 1$	$^2J = 20.5$	$^3J = 4.5$	$^3J = 10.5$	
β-Ergosteryl	Bz	$P(OMe)_3$	CO	−10	297.7	215.7	214.9	214.7	211.8	207.8	
					$^2J = 4.8$	$^2J = 6.6$	$^3J < 1$	$^2J = 21.5$	$^3J = 5$	$^3J = 11.4$	

[a] δ Values in p.p.m., J in Hz; relative intensities are given in parentheses. [b] Solvent mixture was $CDCl_3$–CS_2. [c] Bz = Benzyl.

other carbonyl. This places the *S*-methyl bridge now *trans* to the thiocarbonyl bridge rather than *cis* as in (5) itself. Such a rearrangement would require the loss of the carbonyl originally *trans* to the carbene–iron bond, but such a process is not unreasonable in view of the short length (and presumably high bond strength) of the latter interaction; this would have the effect of labilising the ligand *trans* to it. The three interchangeable carbonyl groups in (6) show different $^3J_{CP}$ values in the slow exchange limit and are presumably a function of the dihedral angles involved. While the $^3J_{HH}$ coupling in methylene chains is moderately well understood,[9] we are loath to speculate on the dihedral angle dependence of $^3J_{CP}$ values transmitted *via* two iron atoms and prefer to await reliable structural data on (6).



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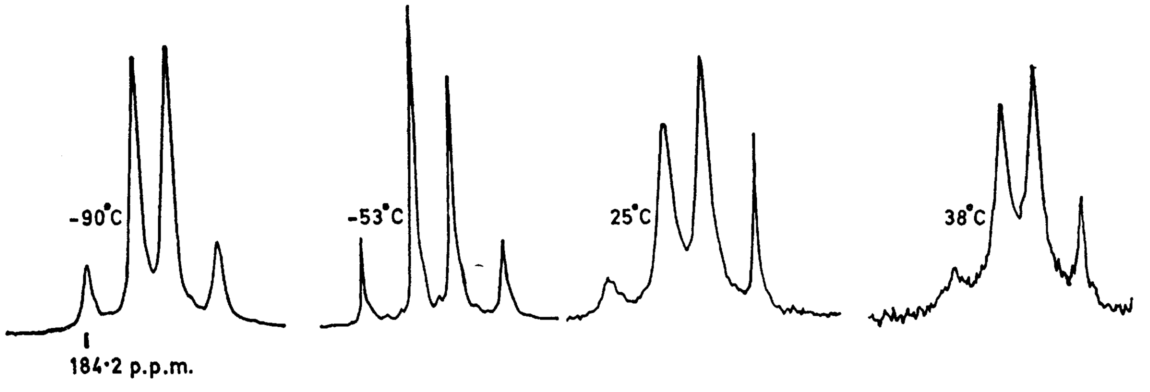
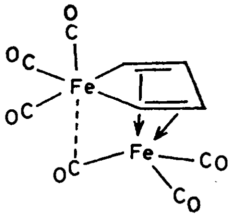


FIGURE 4 Temperature-dependent ^{31}P n.m.r. spectra of $[Fe_2(CO)_4(SR^2)\{COR^1(S)\}\{P(OMe)_3\}_2]$ (R^1 = β-cholestanyl, R^2 = methyl)

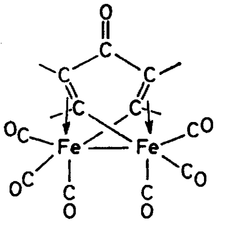
The ^{31}P n.m.r. spectrum of the monophosphite complex was recorded over the temperature range −90 to 25 °C and showed a sharp singlet at 177 p.p.m. When a second phosphite ligand was introduced, the spectrum (see Figure 4) showed an AB quartet at −90 °C. Upon raising the temperature, the spectrum was progressively perturbed suggesting that the relative orientations of the phosphites were changing; this is consistent with the incorporation of the second phosphite ligand at Fe(2).

Studies of the fluxional nature of transition-metal carbonyls continue to attract attention[10,11] and, over the last few years, a number of examples have appeared in which carbonyl scrambling involved a doubly bridged $Fe_2(CO)_6$ moiety. However, there are very few reports of independent behaviour for the two $Fe(CO)_3$ units in the same molecule. In (7),[12] the non-participation of $(OC)_3Fe(1)$ in any exchange process has been ascribed to the presence of the two iron–carbon σ bonds of the ferradiene ring, whereas the semi-bridging carbonyl[13] may facilitate exchange in $(OC)_3Fe(2)$ by internal scrambling. In complexes (8) [12] and (9) [14] the averaging process in each $Fe(CO)_3$ unit occurs at a different rate although in both cases the low-temperature limiting spectrum shows degenerate resonances for the two carbonyls. Finally, we note that Cotton and Hunter [15] explained the dynamic behaviour of (10) by invoking a twitching mechanism associated with σ–π rearrangement within the ligand.



(7)

Apart from these examples, local interchange among the carbonyls in $Fe_2(CO)_6$ systems seems not to have been convincingly explained. In the present case, it is necessary to rationalise not only why the carbonyls at Fe(2) exchange but also why the $(OC)_3Fe(1)$ moiety is immutable on the n.m.r. time scale. The simplest explanation is to invoke an intermediate which contains a six-co-ordinate Fe and a five-co-ordinate Fe; this could readily be generated by cleavage of an Fe(2)–S bond thus allowing the five groups around Fe(2) to interchange *via* a Berry pseudorotation [16] or a turnstile mechanism.[17]



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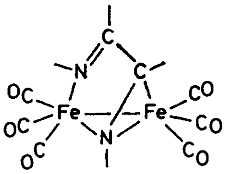

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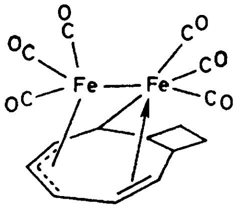

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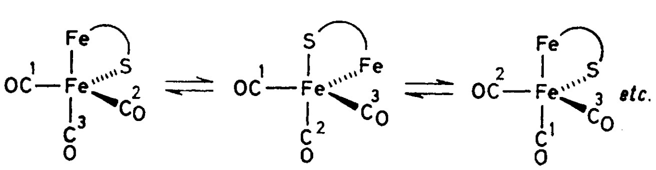
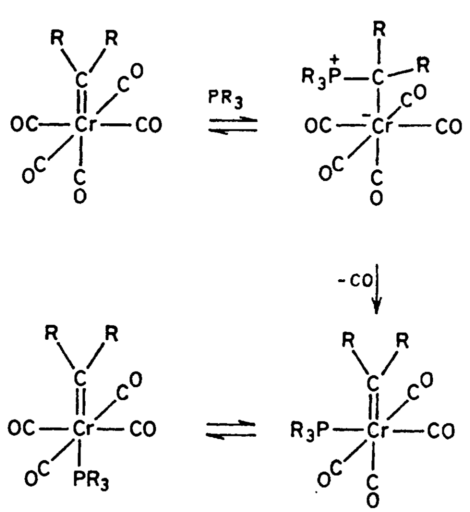
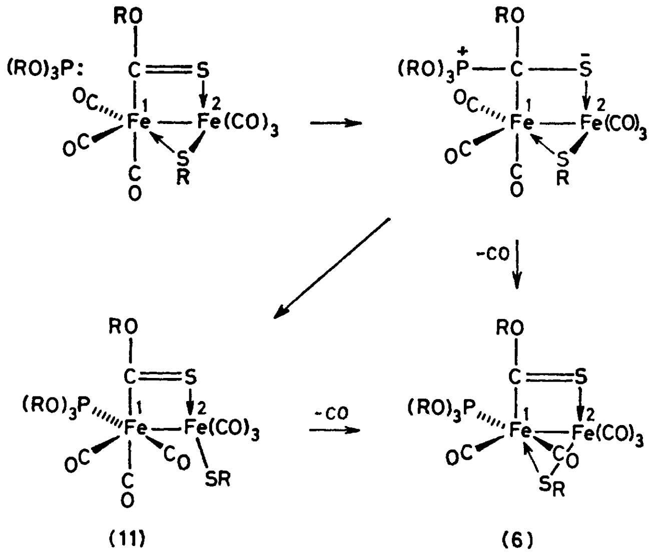


It is apparent that cleavage of the longest iron–sulphur bond, *i.e.* the thiocarbonyl–Fe(2) linkage, provides ready access to the five-co-ordinate intermediate at Fe(2) and thus facilitates a Berry-pseudorotation pathway. However, this raises the interesting question as to why the reaction of trimethyl phosphite with (5) leads to replacement of a carbonyl at Fe(1), which is always six-co-ordinate, while Fe(2) offers a 16-electron configuration apparently with a vacant co-ordination site. The answer is provided by Fischer's now classic studies in which he showed that phosphines can initially attack [18] the relatively electron-deficient carbene carbon of $CH_3O(CH_3)C{=}Cr(CO)_5$ before migrating to a *cis* position on the metal atom.[19] It has been suggested [20] that a trigonal-twist mechanism can be invoked to account for the slow conversion to the *trans* isomer. An analogous mechanism in the present system would require initial attack by the phosphite at the thiocarbonyl carbon (which has carbenic character) with subsequent loss of CO and migration of the phosphite to a *cis* position on Fe(1). It is also plausible that migration of the phosphite is concomitant with fragmentation of the Fe(1)–





(11)

(6)

S(2) bond to give (11) which subsequently loses the CO *trans* to the carbene moiety leading ultimately to (6).

EXPERIMENTAL

The complexes (5) (L = CO) and (6) [L = $P(OMe)_3$] were prepared by published procedures.[1,6] The ^{13}C and ^{31}P n.m.r. spectra were obtained on a Bruker WP80 spectrometer using $CDCl_3$ as solvent and $SiMe_4$ and H_3PO_4 as standards. Carbon-13 spectra were also recorded at 62.86 MHz (courtesy of Professor Martin, Service de RMN, Université de Nantes) to verify the J_{CP} values in (6). The chemical shifts and coupling constants are listed in the Table.

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REFERENCES

[1] H. Patin, G. Mignani, R. Dabard, and A. Benoit, *J. Organomet. Chem.*, 1979, **168**, C21.

[2] H. Patin, G. Mignani, C. Mahé, J. Y. Le Marouille, A. Benoit, and D. Grandjean, *J. Organomet. Chem.*, 1980, **193**, 93.

[3] H. Patin, G. Mignani, and R. Dabard, *J. Organomet. Chem.*, 1979, **169**, C19.

[4] H. Patin, G. Mignani, and M. T. Van Hulle, *Tetrahedron Lett.*, 1979, 2441.

[5] H. Patin, G. Mignani, C. Mahé, J. Y. Le Marouille, T. G. Southern, A. Benoit, and D. Grandjean, *J. Organomet. Chem.*, 1980, **197**, 315.

[6] H. Patin, G. Mignani, A. Benoit, J. Y. Le Marouille, and D. Grandjean, *Inorg. Chem.*, in the press.

[7] B. E. Mann, *Adv. Organomet. Chem.*, 1974, **12**, 135.

[8] P. S. Braterman, D. W. Milne, E. W. Randal, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 1973, 1027.

[9] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11; *J. Am. Chem. Soc.*, 1963, **85**, 2870.

[10] J. Evans, *Adv. Organomet. Chem.*, 1977, **16**, 319.

[11] S. Aime and L. Milone, *Prog. Nucl. Magn. Reson. Spectroscopy*, 1977, **11**, 183.

[12] S. Aime, L. Milone, and E. Sappa, *J. Chem. Soc., Dalton Trans.*, 1976, 838.

[13] F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, 1974, **96**, 1233.

[14] L. H. Staal, J. Keijsper, L. H. Polm, and K. Vrieze, *J. Organomet. Chem.*, 1981, **204**, 101.

[15] F. A. Cotton and D. L. Hunter, *J. Am. Chem. Soc.*, 1975, **97**, 5739.

[16] R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.

[17] P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 687.

[18] F. R. Kreissl, E. O. Fischer, C. G. Kreiter, and H. Fischer, *Chem. Ber.*, 1973, **106**, 1262.

[19] H. Fischer, E. O. Fischer, and F. R. Kreissl, *J. Organomet. Chem.*, 1974, **64**, 841.

[20] H. Fischer, E. O. Fischer, and H. Werner, *J. Organomet. Chem.*, 1974, **73**, 331.