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Dynamic Properties of the Trinuclear Carbonyl Cluster $FeCo_2(CO)_9S$ and Its Derivatives

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^{13}C-n.m.r. spectra show that the replacement of CO by a group V ligand in $FeCo_2(CO)_9S$ is at one cobalt atom in the monosubstituted derivative, at the two cobalt atoms in the bisubstituted derivative and at the two cobalt and at the iron atom in the trisubstituted derivative. The substitution is at an equatorial position in each case. Multistage exchange of the carbonyls is a common feature of these complexes. The activation energies for the localised scrambling at the unique iron atom have been evaluated and shown to be influenced by the nature and the number of the substituents at the cobalt atoms. Localised scrambling of the CO of any $M(CO)_2L$ moiety is not observed to take place prior of internuclear scrambling.

Introduction

Recently it has been shown by dynamic ^{13}C-n.m.r. that stereochemical non rigidity is a common feature in metal carbonyls [1]. With some exceptions it is possible within the experimental range of temperature to follow the changes from the spectrum corresponding to the frozen structure to the spectrum in which fast CO exchange is taking place. Thus, the mechanistic details have been determined for a number of metal carbonyls, showing that in polynuclear metal carbonyls multistage CO exchange occurs often. However, if the formula of the molecule is a multiple of equal and geometrically equivalent $M(CO)_nL$ (L = any ligand) moieties, is not possible to obtain complete information on the mechanism involved, since no distinction is possible between scrambling localised on each moiety and intermetal CO scrambling. Secondly, the studies that have appeared so far have mainly investigated the gross features of the CO exchange process, but little attention has been devoted to the study of finer details within a homologous series. As a continuation of our studies on the dynamic properties of metal carbonyls, we have undertaken a variable temperature ^{13}C-n.m.r. investigation of $FeCo_2(CO)_9S$ and its derivatives $FeCo_2(CO)_{9-x}SL_x$ (L = phosphine, phosphite, diphosphine). These compounds are capable of giving information on the importance of steric and electronic effects in determining the rate of the carbonyl exchange. Moreover ^{13}C-n.m.r. is a powerful tool to establish their stereochemistry in solution since it should be possible to determine the position at which substitution of CO occurs.

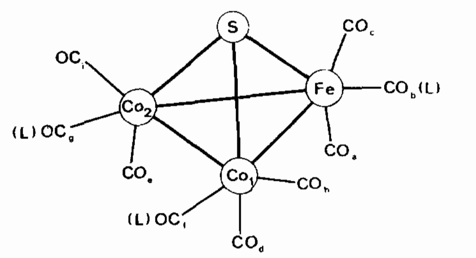
Results and Discussion

The ^{13}C chemical shifts for the lowest temperature spectrum obtained for each complex are reported in Table I. The labelling of the CO is referred to the drawing which represents $FeCo_2(CO)_9S$ and its monodentate derivatives assuming that the substitution of CO with L is at Co_1 in the mono-substituted derivative and at Co_1 and Co_2 in the bisubstituted derivative

TABLE I. ^{13}C Chemical Shifts of the Carbonyls in $FeCo_2(CO)_9S$ and Its Derivatives.

Compound	CO_a	CO_b	CO_c	CO_d	CO_e	CO_f	CO_g	CO_h	CO_i
$FeCo_2(CO)_9S$	215.1	209.8	209.8	198.5	198.5	198.5	198.5	198.5	198.5
$FeCo_2(CO)_8S\ P(OC_6H_5)_3$	217.0	210.6^a	211.8^a	206.1	199.9	–	199.9	200.8	199.9
$FeCo_2(CO)_8S\ P(n\text{-}C_4H_9)_3$	217.2	210.2^a	214.8^a	211.6	200.1	–	200.1	202.8	200.1
$FeCo_2(CO)_7S[P(n\text{-}C_4H_9)_3]_2$	219.9	215.6	215.6	213.5	213.5	–	–	206.7	206.7
$FeCo_2(CO)_6S[P(n\text{-}C_4H_9)_3]_3$	224.6	–	219.1	214.9^a	219.1^a	–	–	211.3^a	214.9^a
$FeCo_2(CO)_7S(diphos)$	221.7	212.2	212.2	210.9	210.9	–	–	200.6	200.6

^{a}Tentative assignment.



and at the two Co and at Fe in the trisubstituted derivative. The solid state structure of $FeCo_2(CO)_9S$ (I) has shown that it is composed of an equilateral triangle with three $M(CO)_3$ groups at the corners and an apical triply bridging sulfur atom [2]. Accordingly five CO resonances are expected in the spectrum corresponding to the frozen structure. The dynamic properties of I have been recently investigated: in particular it has been stated that poor solubility prevented the observation of a ^{13}CO enriched sample at temperature below −80 °C and that at such temperature two resonances are observed in the ratio 1:2 for the iron and cobalt bound carbonyls respectively [3]. However our results are not entirely consistent with the above observations, as shown in Fig. 1. Actually we were able to obtain spectra as low as −115 °C, temperature at which three signals are observed with integrated intensities 1:2:6. The upfield signal is slightly broad as a result either of incipient freezing of the CO exchange process or of the cobalt electric quadrupole [4] or for both reasons.

As the temperature is raised to −100 °C the linewidth of the two downfield signals is unchanged, whereas the upfield resonance sharpens: thus slowing of the CO's exchange process accounts for the broadening of the upfield resonance in the −115 °C spectrum. A further increase in the temperature causes the broadening of the three resonances, but only two merge in a single peak at −72 °C. The broadening of the upfield resonance up to this stage is therefore due to the progressively inefficient cobalt relaxation, but not to chemical exchange. These observations are consistent with there being a two stage exchange process in I: the first step is CO scrambling at the cobalt atoms and the second is CO scrambling at the iron atom. In the first step the CO scrambling may be either localised or delocalised. A third step in the CO exchange of I is noticeable at higher temperature: the carbonyls are rapidly exchanging between the three metal atoms *via* bridged intermediate since in the room temperature spectrum one resonance only is observed, its chemical shift being in good accord with the weighted average of the −115 °C spectrum.

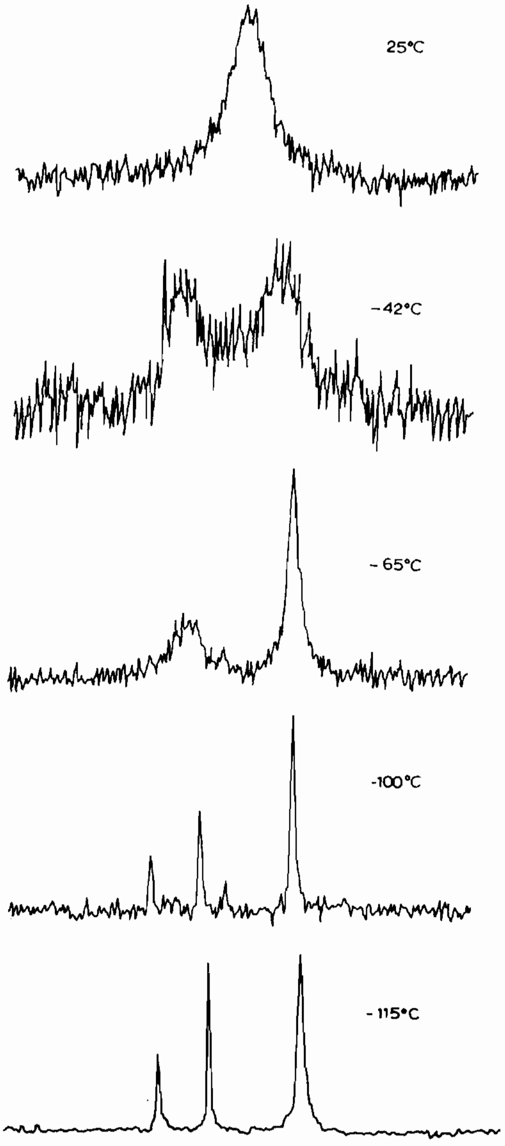


Figure 1. Variable temperature ^{13}C-n.m.r. spectra of $FeCo_2(CO)_9S$ (I).

Six resonances are present in the −123 °C spectrum of $FeCo_2(CO)_8S\ P(OC_6H_5)_3$ (II) with integrated intensities 1:1:1:1:1:3. Comparison with the chemical shifts of I allows assignment of the three downfield resonances to the iron bonded carbonyls and the remaining three signals to the cobalt bonded ones. The three upfield resonances are slightly broad (W ½ *ca.* 15 Hz) confirming their attribution to the carbonyls bonded to the cobalt atoms. The quadrupolar broadening prevents the observation of the two bond coupling with phosphorus expected for CO_d and CO_h.

Neither is coupling with phosphorus observed for CO_a, CO_b and CO_c as their signals are sharp singlets. These results are consistent only with the replacement by the phosphite of one CO bonded to cobalt confirming that the substitution occurs at cobalt as suggested by a Mössbauer study of $FeCo_2(CO)_8S\ P(C_6H_5)_3$ [5]. An increase in the temperature causes coalescence of the three resonances of the iron bound

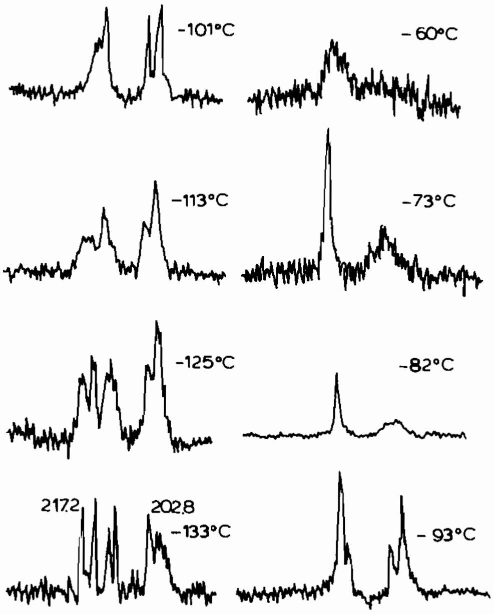


Figure 2. Variable temperature ^{13}C-n.m.r. spectra of the CO region of $FeCo_2(CO)_8SP(n\text{-}C_4H_9)_3$ (III).

carbonyls at –73 °C; the corresponding average peak does not sharpen completely and above –55 °C it begins to broaden again. In this range of temperature the resonances of the cobalt bound carbonyls progressively broaden, but no average peak is observed. We feel that this broadening is due only to the cobalt quadrupole and not to an exchange process. However we cannot completely exclude the possibility that the cobalt bonded carbonyls are engaged in a scrambling process among themselves. Above –55 °C broadening of all the resonances is observed; at –36 °C they collapse.

At higher temperature an average peak is observed indicating that also in II the final stage is internuclear CO scrambling. The variable temperature spectra of $FeCo_2(CO)_8SP(n\text{-}C_4H_9)_3$ (III) are shown in Fig. 2. The dynamic behaviour of III is quite complex since four independent steps are present in the CO exchange. The first stage is noticeable in the –133 °C––125 °C interval. The sharpening of the upfield resonances in this range suggests that at –133 °C the localised CO scrambling at the unsubstituted cobalt is almost frozen. In the second step (–133 °C––93 °C) the CO scrambling is localised at the iron. In the range –93 °C––73 °C the lowfield resonance keeps sharp, whereas the remaining ones broaden and merge in a new peak. Therefore the third step is represented by internuclear CO scrambling only between the cobalt atoms. Eventually as the temperature is further raised the final step is total CO scrambling as in I and in II (T_c = –41 °C).

A further molecule of phosphine replaces a carbonyl at the unsubstituted cobalt as indicated by the

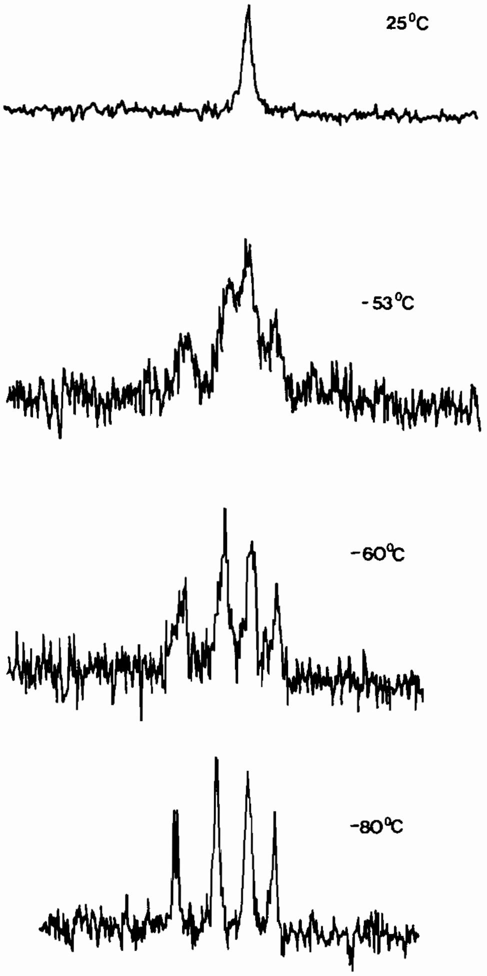


Figure 3. Variable temperature ^{13}C-n.m.r. spectra of the CO region of $FeCo_2(CO)_6S[P(n\text{-}C_4H_9)_3]_3$ (V).

–137 °C spectrum of the bisphosphine derivative $FeCo_2(CO)_7S[P(n\text{-}C_4H_9)_3]_2$ (IV): four resonances are present with integrated intensities 1:2:2:2. This suggests that the replacement of two CO ligands by phosphine takes place at each cobalt at the same position, but does not allow at this stage the distinction between substitution at the axial position or at one of the equatorial positions. The dynamic behaviour of IV is similar to that of III, except for the obvious absence of the first step present in III. Upon increasing the temperature firstly the resonances of the iron bound carbonyls merge in a new peak (T_c = –131 °C). Secondly an average peak is observed for the cobalt bound carbonyls (T_c = –112 °C). A slight increase in the temperature is sufficient to allow complete CO scrambling between iron and cobalt. In the trisubstituted derivative $FeCo_2(CO)_6S[P(n\text{-}C_4H_9)_3]_3$ (V) four resonances are observed in the –80 °C spectrum with integrated intensities 1:2:2:1 (Fig. 3), the downfield resonance of intensity 1 being a doublet J ^{13}C–^{31}P = 12 Hz). The intensity and the multiplicity of this signal suggest that the third molecule of phosphine substitutes one equatorial carbonyl at the iron atom. On this basis and on the assumption that for the rest of the molecule the stereochemistry is like IV, six resonances are expected: the observation of only four indicates that accidental superposition occurs. Upon increasing the temperature all the resonances broaden, collapse and merge in a new peak (T_c = −42 °C). The data for II–V and for VI (*vide infra*) favour the equatorial replacement by L also at the cobalt atom. Firstly this is the case for the replacement at the iron atom and then this can be extended to the cobalt case. Secondly we note that within a $Co(CO)_2L$ moiety the chemical shift difference between the carbonyls is dependent on the nature and the number of the L groups, being 5.3 ppm in II, 8.8 ppm in III, 6.8 ppm in IV and 10.3 ppm in VI. If L lies in an axial position the difference in the environment of the two equatorial carbonyls is only due to their relative position towards the $Fe(CO)_3$ unit. In this case we would hence expect $\Delta(CO_f - CO_h)$ to be almost constant in all the cases. For L lying in an equatorial position CO_d and CO_h have a different shift irrespectively of their orientation towards $Fe(CO)_3$. Changes in L are then expected to affect to a different extent the chemical shift of CO_d and CO_h and hence $\Delta(CO_d - CO_h)$.

From Table I it appears that the chemical shift of the carbonyls is progressively at higher frequency since L is better "sigma" donor and a poorer "pi" acceptor than CO and since the number of L groups increases. This trend has been explained in terms of an increase in the electron density at the metal which is reflected in an increase in the metal carbon "pi" bonding and hence in a decrease in the carbon oxygen "pi" bond order [6]. It can additionally be seen that this effect is felt not only by the carbonyls bonded to the substituted metal but also, though to a lesser extent, by the carbonyls bonded to the unsubstituted metals. These findings for a metallic cluster follow similar observations for the binuclear species $C_{10}H_{12}Fe_2(CO)_5P(C_2H_5)_3$ [7], (guaiazulene)$Mo_2(CO)_5P(C_2H_5)_3$ [8] and $C_2RR'Co_2(CO)_5L$ [9].

Unfortunately the determination of the thermodynamic parameters for the exchange process in which cobalt bound carbonyls are engaged has been prevented by the impossibility of evaluating the contribution to the broadening of their resonances due to the cobalt electric quadrupole. For the determination of this contribution too many variables are unknown, such as the cobalt carbon spin spin coupling constant, the correlation time of the molecule and the quadrupolar coupling constant [4]. However we were able to evaluate E_a for the exchange at iron in I–IV (Table II). It appears than that substitution of a CO by a group V ligand in II and III lowers the free energy of activation of the CO scrambling at iron and that the effect is much stronger for the phosphine than for the phosphite. The trend is confirmed by the size of the decrease of E_a in the bis-derivative IV. The decrease in the activation energy of the CO exchange of $M(CO)_3$ as consequence of substitution at the neighbour metal has been reported to be *ca.* 4 Kcal mol^{-1} for $C_{10}H_{12}Fe_2(CO)_5P(C_2H_5)_3$ [7]. Doubts on the generality of this effect have been raised by the observation of the dynamic behaviour of the two isomers of (guaiazulene)$Mo_2(CO)_5P(C_2H_5)_3$ since this effect is clearly shown in one isomer, whereas in the other seems to be absent [8]. It has already been noted above that the increased electric charge at the metal when substitution occurs is spread over the cluster causing a strenghtening of all the metal carbonyl bonds. Additionally we can consider that this goes along with a weakening of the metal–metal bonds according to the qualitative LCAO–MO treatment given for the trinuclear metal–carbonyl clusters. Dahl suggested that the lower empty MO is antibonding with respect to the metal–metal bonding framework, whilst the highest filled MO is weakly antibonding, so the addition of electrons to the metal cluster will lead to a decrease in the metal–metal character of the unit [10]. It could be expected that strong electron donors like trialkylphosphine could increase the antibonding character of the filled MO and so destabilize the cluster. In this light it appears that the overall result is an increase in the facility of the rotation of the $M(CO)_3$ moieties and hence of the localised scrambling of their COs.

TABLE II. Energies of Activation for the Carbonyl Scrambling at the $Fe(CO)_3$ Unit.

Compound	E_a (Kcal/mol)
$FeCo_2(CO)_9S$ (I)	6.0 ± 0.5
$FeCo_2(CO)_8S\ P(OC_6H_5)_3$ (II)	5.8 ± 0.5
$FeCo_2(CO)_8S\ P(n\text{-}C_4H_9)_3$ (III)	4.5 ± 0.8
$FeCo_2(CO)_7S[P(n\text{-}C_4H_9)_3]_2$ (IV)	3.4 ± 0.9

The dynamic behaviour of any $M(CO)_2L$ moiety in II–V shows that upon substitution of a CO ligand localised carbonyl exchange is not detected. The stereochemical non rigidity of such carbonyls is attained only when the energy barrier for internuclear scrambling is overcome.

Since the CO replacement alters the energy barrier for the localised exchange we expect that also the energy barrier of the delocalised exchange is affected. However in these systems the presence of quadrupolar nuclei prevented the extraction of any valuable information. The problem is deferred to the study of suitable species.

Internuclear scrambling is prevented if two metal atoms are linked by a chelating ligand as in $FeCo_2(CO)_7S(C_6H_5)_2PCH_2P(C_6H_5)_2$ (VI) for which ^{13}C-n.m.r. results indicate that the ligand is binding two equatorial positions, one on each cobalt.

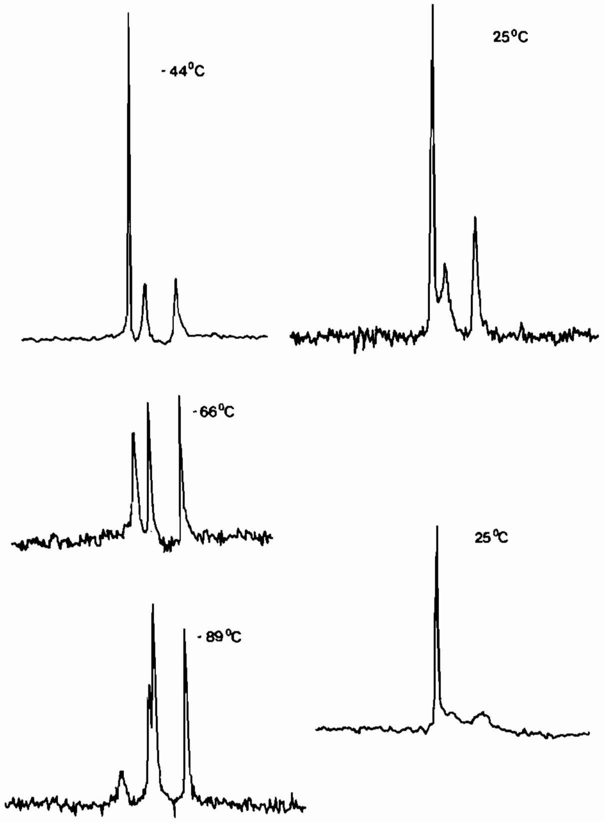
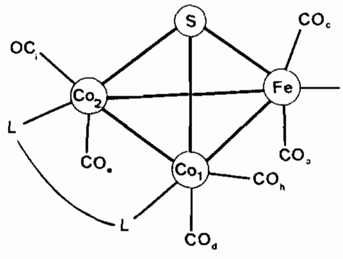


Figure 4. Variable temperature ^{13}C-n.m.r. spectra of the CO region of $FeCo_2(CO)_7S(C_6H_5)_2PCH_2P(C_6H_5)_2$ (VI) in $CDCl_3$; top right in 25/75 v/v $CDCl_3$/Nujol.



In the −89 °C spectrum four resonances are observed with integrated intensities 1:2:2:2 (Fig. 4). Changes in the spectra up to room temperature show that only the iron bonded carbonyls are participating in an exchange process since the two downfield resonances merge in a single peak (T_c = −76 °C) whereas the chemical shifts of the two other resonances remain unchanged. Actually the two upfield resonances progressively broaden as the temperature is raised, but this is due to the inefficient cobalt quadrupolar relaxation and not to chemical exchange as shown by the room temperature spectrum of VI in a viscous solution. In a mixture $CDCl_3$/Nujol (25/75, v/v) the broadening is drastically reduced.

Experimental

$Co_2FeS(CO)_9$ was prepared by reacting $Co_2(CO)_8$ and $Fe_2(CO)_6S_2$ according to the method previously reported [11]. It was enriched by stirring for one day in a sealed ampoule at 70 °C in the presence of <1 atmosphere of 90% enriched ^{13}CO (Stohler Isotope Chemicals). Sample purity after enrichment was checked by mass spectroscopy.

The labelled parent compound was used to prepare the substituted derivatives, as previously described [12]. The reaction between Co_2Fe $S(CO)_9$ and $(C_6H_5)_2PCH_2P(C_6H_5)_2$ has not yet been reported and is described below in some detail.

$Co_2FeS(CO)_9$ (0.4 g, ~0.87 mmol) and $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (1.7 g, ~4.4 mmol) were allowed to react in petroleum ether solution under CO for 2 hours at room temperature. The mixture was filtered and separated by repeated TLC (adsorbent Silicagel 9 according to Stahl, elutant petroleum ether/ethyl ether 1:1). Four compounds were collected, two of which were identified on the basis of elemental analysis, IR and NMR spectra. They are, in order of increasing R_F:

$Co_2FeS(CO)_8$ $[(C_6H_5)_2PCH_2P(C_6H_5)_2]$ (monosubstituted, mono-*hapto*): amorphous brown solid. *Anal.* Calcd. for $C_{33}H_{22}Co_2FeO_8P_2S$: C 48.68; H 2.72; CO 14.48; Fe 6.86; O 15.72; P 7.61; S 3.94. Found: C 48.9; Co 14.2; Fe 6.8; P 7.6. IR (CO stretch n-heptane sol.) 2065 (vs); 2021 (s); 2015 (s); 2000 (m); 1997 (m); 1977 (m); 1964 (m); 1926 (m).

$Co_2FeS(CO)_7[(C_6H_5)_2PCH_2P(C_6H_5)_2]$ (monosubstituted, bi-*hapto*): dark green crystals; m.p. 181 °C. *Anal.* Calcd. for $C_{32}H_{22}Co_2FeO_7P_2S$: C 48.88; H 2.82; Co 14.99; Fe 7.10; O 14.24; P 7.88; S 4.08. Found: C 48.9; Co 15.2; Fe 7.3; P 7.9. IR: 2057 (*vs*); 2023 (s); 2017 (vs); 2003 (vs); 1997 (m); 1959 (m).

IR spectra were obtained by an IR 12 Beckman Spectrophotometer. Elemental analyses were performed by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, West Germany.

^{13}C-n.m.r. spectra were recorded on a JEOL-PFT 100 spectrometer operating at 25.1 MHz in the Fourier transform mode. The chemical shifts are downfield positive with respect to internal tetramethylsilane. Accumulations of 1,000–5,000 transients were made at a spectral width of 1,000 or 5,000 Hz. The temperature was monitored by a JEOL JNM-DBT-P-5-H 100 E temperature control unit with the thermocouple *ca.* 1 cm above the sample (outside of the radiofrequency and decoupling coils). Solutions were sealed *in vacuo* in 10 mm tubes together with $SiMe_4$ as an internal standard. $Cr(acac)_3$, 5 mg, was added to each sample. The solvents were $CDCl_3$, CD_2Cl_2 and CD_2Cl_2/CF_2Cl_2 for intermediate and low temperatures. Deuterated solvents were purchased from NMR

Ltd and used immediately after drying over molecular sieves.

The energies of activation have been obtained through the K values determined by band-shape analysis using the POLY-EXCHANGE Program, obtained from Dr. R. K. Harris (University of East Anglia, Norwich, England) who is warmly acknowledged.

References

1 R. D. Adams and F. A. Cotton, "Dynamic NMR Spectroscopy", Ed. by L. M. Jackman and F. A. Cotton, Academic Press, New York (1975) Chapter 12;
M. H. Chisholm and S. Godleski, *Progr. Inorg. Chem., 20,* 299 (1975);
S. Aime and L. Milone, "Progress in NMR Spectroscopy", Ed. by J. Emsley, J. Feeney and L. Sutcliffe, Pergamon Press, London, (1977).

2 D. L. Stevenson, C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc., 93,* 6027 (1971).

3 A. Forster, B. F. G. Johnson, J. Lewis and T. W. Matheson, *J. Organomet. Chem., 104,* 225 (1976).

4 S. Aime, G. Gervasio, L. Milone and E. Rosenberg, *Trans. Met. Chem., 1,* 177 (1976).

5 K. Burger, L. Korecz and G. Bor, *J. Inorg. Nucl. Chem., 31,* 1527 (1969).

6 P. S. Braterman, D. W. Milne, E. W. Randall and E. Rosenberg, *J. Chem. Soc. Dalton,* 1027 (1973).
G. M. Bodner and L. J. Todd, *Inorg. Chem., 13,* 1335 (1974).

7 F. A. Cotton and D. L. Hunter, *J. Am. Chem. Soc., 97,* 5739 (1975).

8 F. A. Cotton, D. Lahuerta and B. R. Stults, *Inorg. Chem., 15,* 1866 (1976).

9 S. Aime, L. Milone, R. Rossetti and P. L. Stanghellini, *Inorg. Chim. Acta, 22,* 135 (1977).

10 C. E. Strouse and L. F. Dahl, *J. Am. Chem. Soc., 93,* 6032 (1971);
B. K. Teo, M. B. Hall, R. F. Fenske and L. F. Dahl, *J. Organometal. Chem., 70,* 413 (1974).

11 S. A. Khattab, L. Marko, G. Bor and B. Marko, *J. Organometal. Chem., 1,* 373 (1964).

12 R. Rossetti, G. Gervasio and P. L. Stanghellini, *J. Chem. Soc. Dalton,* submitted for publication.