Preparation of Methyl and Acetyl Complexes of Iron(II)

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The complexes [Fe(CO)$_2$(PMe$_3$)$_2$(Me)X], where X = Br, Cl, CN, NCS, CNO, OMe, or Me, have been synthesized and the structure assigned on the basis of i.r. and n.m.r. evidence. The complexes react readily and reversibly with CO to give the acetyl derivatives with the acetyl group in the *cis* position relative to X. When X = I, Br, or Cl the *cis* isomer rearranges slowly to the *trans* isomer until an equilibrium is obtained. The results are interpreted in terms of the σ- and π-accepting capabilities of the ligands.

THE insertion reaction of CO into metal–alkyl or –aryl bonds has been widely studied for the octahedral complexes [Mn(CO)$_5$R] [1] and [Fe(η^5-C$_5$H$_5$)(CO)$_2$R].[2] Only recently has such a study been extended to square-planar complexes.[3] Knowledge of the insertion reaction mechanism is important to a better understanding of many homogeneous catalytic reactions: hydroformylation, carbonylation, homologation, *etc.*[4] We have therefore undertaken a study of the CO insertion reaction for the complexes [Fe(CO)$_2$(PMe$_3$)$_2$(Me)X], the mechanism of which is not yet clear.[5] We compare our results with those obtained for [Fe(η^5-C$_5$H$_5$)(CO)$_2$R], and determine the effect of the halogen, since it was observed for square-planar complexes that different halogens can activate different reaction mechanisms.[6]

Since only the complex where X = I has been described,[7] we report the preparation of [Fe(CO)$_2$(PMe$_3$)$_2$(Me)X] where X = Br, Cl, CN, NCS, CNO, or OMe and the acetyl derivatives obtained by carbonylation. The structures of the complexes are also discussed.

EXPERIMENTAL

Instrumentation.—Infrared spectra were recorded on a Perkin-Elmer 521 grating spectrophotometer, ^{1}H n.m.r. spectra on a JEOL CHL-60 spectrometer equipped with a variable-temperature device and using SiMe$_4$ as reference.

Preparation of Complexes.—All preparative work was carried out at room temperature under an atmosphere of dry nitrogen unless otherwise stated. Tetrahydrofuran (thf) was purified according to the method described in ref. 8 and freshly distilled before use. Analytical, i.r., and n.m.r. data are shown in Tables 1, 2, and 3 respectively.

[Fe(CO)$_3$(PMe$_3$)$_2$Me][BPh$_4$] (2). Solutions of [Fe(CO)$_2$(PMe$_3$)$_2$(COMe)I] (1t) † (2.4 g) in methanol and of NaBPh$_4$ (2 g) in methanol were mixed. The formation of a white precipitate was observed. After 24 h the precipitate was filtered off and washed with methanol (yield 87%).

[Fe(CO)$_2$(PMe$_3$)$_2$(Me)X] [X = Cl (3), Br (4), NCS (5), CN (6), *or* CNO (7)]. A suspension of (2) and MX in thf (molar ratio 1 : 1.5) was vigorously stirred. A rapid reaction was observed and a yellow solution was formed. After 4 h the solvent was removed under reduced pressure; the product was extracted with benzene, the solution filtered and evaporated to dryness. The solid residue was crystallized from n-hexane (yield *ca.* 60%).

For X = CNO or CN, the reaction was slower (24 and 48 h respectively), while for X = NCS the reaction failed to go to completion even after 1 week and more solvent had to be added to the unreacted solid.

[Fe(CO)$_2$(PMe$_3$)$_2$Me$_2$] (8). A low-yield (1%) preparation of this complex has already been reported.[9] A new procedure allowed us to prepare it with a higher yield. To a stirred suspension of (2) in thf at −20 °C an equivalent quantity of LiCH$_3$ (Fluka) in an ethereal solution was added. The reaction went to completion immediately, with the formation of (8), [Fe(CO)$_2$(PMe$_3$)$_2$(COMe)Me], and [Fe(CO)$_2$(PMe$_3$)$_2$(COMe)$_2$]. The solution was rapidly evaporated to dryness at −20 °C, during which process the acetyl complexes were transformed into (8). The residue was sublimed under vacuum (yield 30%).

TABLE 1

Analytical data

			Analysis (%)					
			Found			Calculated		
Complex	Colour	M.p. (θ_c/°C)	C	H	N	C	H	N
(2) [Fe(CO)$_3$(PMe$_3$)$_2$Me][BPh$_4$]	White	Decomp.	65.2	6.80		65.8	7.10	
(3) [Fe(CO)$_2$(PMe$_3$)$_2$(Me)Cl]	Yellow	115—116	33.8	6.50		34.35	6.75	
(3c) + (3t) [Fe(CO)$_2$(PMe$_3$)$_2$(COMe)Cl]	Orange		33.0	6.25		32.7	6.40	
(4) [Fe(CO)$_2$(PMe$_3$)$_2$(Me)Br]	Red-orange	113—115	31.0	5.70		30.1	5.90	
(4c) + (4t) [Fe(CO)$_2$(PMe$_3$)$_2$(COMe)Br]	Red		28.55	5.90		28.8	5.65	
(5) [Fe(CO)$_2$(PMe$_3$)$_2$Me(NCS)]	Yellow	113—115	36.0	6.70	4.10	35.6	6.30	4.15
(5c) [Fe(CO)$_2$(PMe$_3$)$_2$(COMe)(NCS)]	Orange		33.9	6.10	4.00	34.0	6.00	3.95
(6) [Fe(CO)$_2$(PMe$_3$)$_2$Me(CN)]	White	132—137	40.05	7.10	4.80	39.35	6.95	4.60
(6c) [Fe(CO)$_2$(PMe$_3$)$_2$(COMe)(CN)]	White		37.6	6.20	4.25	37.4	6.60	4.35
(7) [Fe(CO)$_2$(PMe$_3$)$_2$Me(CNO)]	Red	118—120	38.1	6.95	4.00	37.4	6.60	4.35
(7c) [Fe(CO)$_2$(PMe$_3$)$_2$(COMe)(CNO)]	Red		35.5	6.55	4.30	35.65	6.30	4.15

[Fe(CO)$_2$(PMe$_3$)$_2$(COMe)X] [X = Cl (3c) *and* (3t), Br (4c) *and* (4t), NCS (5c), CN (6c), *or* CNO (7c)]. A solution of [Fe(CO)$_2$(PMe$_3$)$_2$(Me)X] in CH$_2$Cl$_2$ (*ca.* 5 × 10^{-2} mol dm^{-3})

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† The acetyl derivatives are numbered according to their methyl precursors plus either the letter c (if *cis*) or t (if *trans*).

TABLE 2

Infrared spectral data (cm^{-1}) for the methyl and acetyl complexes

Complex		$\nu(CO)$	$\nu(COCH_3)$	Other significant bands	Solvent
	$[Fe(CO)_3(PMe_3)_2Me][OCH_3]$	2 086w, 2 020vs			thf
(2)		2 082w, 2 018vs			CH_2Cl_2
(3)		2 004s, 1 943s			n-Hexane
(3c)		2 016s, 1 959s	1 600m		n-Hexane
(3t)		2 051w, 1 963vs	1 605m		n-Hexane
(4)		2 002s, 1 940s			n-Hexane
(4c)		2 016s, 1 960s	1 599m		n-Hexane
(4t)		2 050w, 1 966vs	1 600m		n-Hexane
(1)	$[Fe(CO)_2(PMe_3)_2(Me)I]$	2 002s, 1 943s			n-Hexane
(1c)	$[Fe(CO)_2(PMe_3)_2(COMe)I]$	2 018s, 1 965s	1 600m		n-Hexane
(1t)	$[Fe(CO)_2(PMe_3)_2(COMe)I]$	2 044w, 1 967vs	1 609m		n-Hexane
(5)		2 010s, 1 952s		$\nu(NCS)$ 2 089, 810	n-Hexane
(5c)		2 024s, 1 972s	1 609m	$\nu(NCS)$ 2 092	n-Hexane
(6)		2 004s, 1 953s		$\nu(CN)$ 2 113	n-Hexane
(6c)		2 021s, 1 972s	1 611m	$\nu(CN)$ 2 111	n-Hexane
(7)		2 003s, 1 944s		$\nu(CNO)$ 2 221	n-Hexane
(7c)		2 022s, 1 964s	1 605m	$\nu(CNO)$ 2 219	CH_2Cl_2
(8)	$[Fe(CO)_2(PMe_3)_2Me_2]$ *	1 976.5s, 1 912.5s			n-Hexane
	$[Fe(CO)_2(PMe_3)_2Me(OMe)]$	1 982s, 1 918s			thf
(9c)	$[Fe(CO)_2(PMe_3)_2(COMe)(OMe)]$	1 993s, 1 936s	1 625m		n-Hexane

* Ref. 9.

was saturated with CO and stirred. Carbonylation was complete in 1—3 h and a precipitate was obtained by adding n-hexane at −20 °C. When X = Br or Cl a mixture of *cis* and *trans* isomers was obtained.

$[Fe(CO)_2(PMe_3)_2(COMe)(OMe)]$ (9c). A suspension of (2) and NaOMe in thf was stirred at −20 °C. Dissolution of (2) and a rapid reaction were observed. The i.r. spectrum showed the presence in solution of the ion $[Fe(CO)_3(PMe_3)_2Me]^+$ which suggests that exchange of the anion BPh_4^- for OMe^- has occurred. After 30 min the reaction was almost complete. On increasing the temperature to 20 °C the salt $[Fe(CO)_3(PMe_3)_2Me][OMe]$ was formed indicating the presence of a dissociative equilibrium of complex (9c). The stream of nitrogen was unable to drive the decarbonylation equilibrium towards the methyl complex, unlike the case for the other derivatives (see below). Therefore, it was not possible to isolate this complex.

TABLE 3

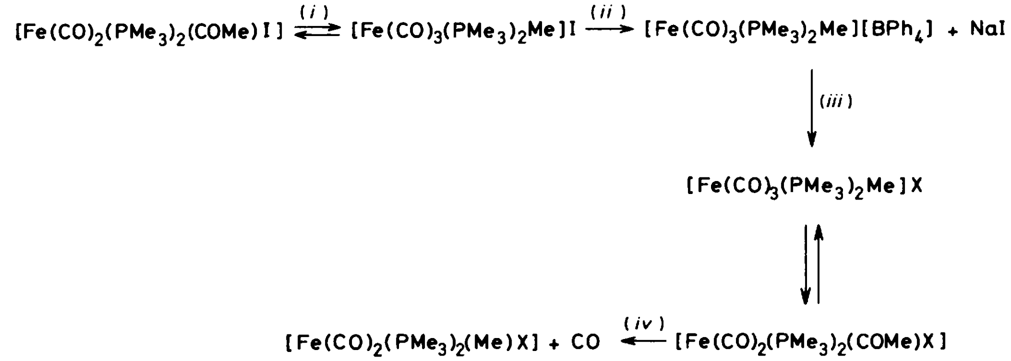
Proton n.m.r. spectra of the methyl and acetyl complexes in CD_2Cl_2

Complex	τ(Me) *	J(Me–P)/Hz	τ(PMe_3)	J(Me–P)/Hz
(1)	9.64 (t)	9.1	8.38 (t)	4.1
(1c)	7.26 (s)	0	8.35 (t)	
(1t)	7.64 (s)	0	8.31 (t)	4.0
(3)	9.66 (t)	9.6	8.53 (t)	4.3
(3c)	7.57 (s)	0	8.47 (t)	4.8
(3t)	7.80 (s)	0	8.41 (t)	4.1
(4)	9.64 (t)	9.6	8.44 (t)	4.3
(4c)	7.44 (s)	0	8.42	
(4t)	7.74 (s)	0	8.36 (t)	4.1
(5)	9.80 (t)	8.3	8.51 (t)	4.1
(5c)	7.63 (s)	0	8.47 (t)	4.2
(6)	10.25 (t)	9.0	8.50 (t)	4.1
(6c)	7.51 (s)	0	8.49 (t)	4.1
(7)	9.90 (t)	9.2	8.55	
(7c)	7.73 (s)	0	8.60	
(2)	9.97 (t)	6.0	7.31 (t)	4.7

* Resonance due to the acetyl or to the methyl bonded to iron.

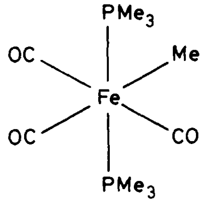
RESULTS AND DISCUSSION

Preparation and Structure of Methyl Complexes.—The mechanism of formation of the methyl complexes from the acetyl complexes is shown in the Scheme. Reaction is due to both the ionization equilibrium, which allows exchange between the anions $[BPh_4]^-$ and X^- and to the decarboxylation of the acetyl complex by a stream of nitrogen. The ionization reaction also has the effect of increasing the solubility of the ionic complex, which is very low when the anion is $[BPh_4]^-$. This effect has been clearly observed when X = I, Br, Cl, or OMe. The



SCHEME (*i*) MeOH, (*ii*) $NaBPh_4$, (*iii*) MX (M = Li, Na, or K; X = Cl, Br, CNS, CN, CNO, Me, or OMe), (*iv*) N_2 stream anion probably forms ion pairs, but does not appreciably influence the CO stretching frequency of the cation $[Fe(CO)_3(PMe_3)_2Me]^+$.

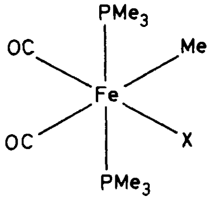
The ionization equilibrium $[Fe(CO)_2(PMe_3)_2(COMe)X] \rightleftharpoons [Fe(CO)_3(PMe_3)_2Me]X$ can be observed in polar solvents (MeOH, EtOH, MeCN, or Me_2CO) when



(A)

X = I, Br, or Cl; when X = OMe the reaction can also be observed in thf, and the equilibrium moves to the right with an increase in temperature. Quantitative data for this reaction will be presented in a future paper.

The ionic complex $[Fe(CO)_3(PMe_3)_2Me]^+$ has been attributed the structure (A). This is supported by n.m.r. and i.r. evidence. The coupling constant and the multiplicity of the methyl group bound to the iron atom are typical of a methyl group *cis* to two equivalent phosphine groups,[10] and the multiplicities of the methyl protons in the PMe_3 ligands are typical of two mutually *trans* phosphines.[11] The i.r. spectrum shows two CO stretching bands, one of low intensity at high frequency, and the other of high intensity at a lower frequency. This is consistent with structure (A) and C_{2v} symmetry, on the basis of which three i.r.-active bands are expected ($2A_1$ and $1B_1$).[12] The very weak band at 2 082 cm^{-1} is readily assigned to the A_1 mode, while the other band is due to the second A_1 and to the B_1 modes, both having high transition moments and high intensity.

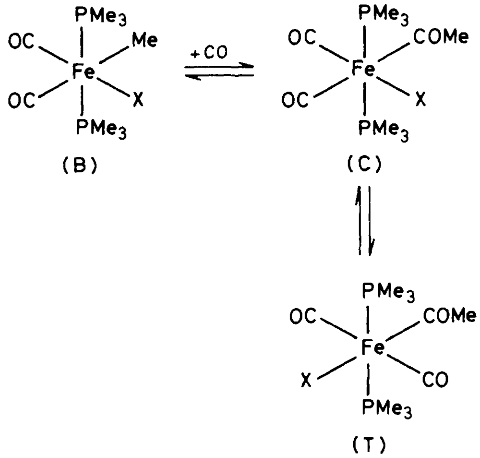


(B)

The methyl complexes have been ascribed the structure (B) with two mutually *cis* carbonyl groups and two mutually *trans* phosphines. The n.m.r. data agree with this structure [see the discussion for (A)]. The i.r. spectra, showing two CO stretching bands of similar intensity, indicate an angle of *ca.* 90° between the two carbonyl groups.[12] Structure (B) implies that the X ligands have a lower π-accepting capability than the CO groups, and so the latter lie in a mutually *cis* position to compete to a lesser extent for the same *d* orbital.[13]

Complex (5; X = NCS) shows a CS stretching band at 810 cm^{-1}, typical of M–NCS compounds,[14] whereas, on the basis of the i.r. spectra, the nature of the bond between iron and the CNO ligand in complex (6) is not clear.

Carbonylation of the Methyl Complexes.—$[Fe(CO)_2(PMe_3)_2(Me)X]$ (X = NCS, CN, CNO, *or* OMe). Carbonylation with carbon monoxide at room temperature is very rapid and the reaction goes to completion in a few minutes, with the exception of the complex with X = CN for which reaction is complete in 3 h. The products $[Fe(CO)_2(PMe_3)_2(COMe)X]$ have structure (C) with two CO ligands in the *cis* positions and the PMe_3 ligands in the *trans* positions, as evidenced by n.m.r. and i.r. spectra.



$[Fe(CO)_2(PMe_3)_2(Me)X]$ (X = Cl, Br, *or* I). The carbonylation of complexes (1), (3), and (4) occurs according to the scheme shown above. When X = I, the equilibrium at room temperature is shifted towards the (T) isomer. The concentration of the (C) isomer increases on going from X = I to Br or Cl.

The formation of complex (C) from (B) is again very rapid. The kinetics are followed by monitoring the n.m.r. spectra of a benzene solution containing complexes (B), (C), and (T). In the n.m.r. spectrum of the complex with X = Cl the triplet at τ 9.66 is attributed to complex (B), a singlet at τ 7.57 to complex (C), and a singlet at τ 7.80 to (T). Up to 0 °C no appreciable variation in the spectrum is observed; but at higher temperatures a broadening of the singlet at τ 7.57 and a shift of this band to higher field occur. In the same temperature range, a broadening of the triplet and a shift to lower field are observed. At 35 °C, the triplet collapses into a broad singlet. At higher temperatures there is further broadening. This trend is typical of the fast interconversion of the methyl complex (B) into the acetyl complex (C). In the same temperature range the singlet at τ 7.80 undergoes no appreciable change which indicates that the isomerization to (T) is slower than the carbonylation of (B).

The τ values for the COMe group of complexes (C) are lower than those of (T) since the CO group in the *trans* position is more deshielding than a halogen group.

The τ values of the methyl groups bonded either to the phosphorus or to the metal, or in the acetyl group (both *cis* and *trans*), follow the same trend in relation to X with Cl $\geqslant$ CN $\approx$ NCS > Br > I. A similar trend has been found in the halogen derivatives of ruthenium complexes.[13] However, this contrasts with the results found by Jenkins and Shaw [15] on some octahedral complexes of iridium, and cannot be interpreted on the basis of σ and π effects of the halogens. The only conclusion which can be drawn, at present, is that the X substituent exerts its effect predominantly through its π-accepting capability. This is confirmed by the marginal effect exerted on the methyl bonded to iron which does not form π bonds. The greater influence of the halogens in *cis* isomers of acetyls with respect to *trans* isomers may be interpreted on the basis of a through-space π interaction.[16]

The order of thermodynamic stability of complex (T) with respect to (C) is as follows: I > Br > Cl $\gg$ CN, NCS, CNO, OCH_3. This trend is also observed in the $[Ru(CO)_2(PMe_2Ph)_2(COMe)X]$ complexes (X = I, Br, or Cl),[13] the behaviour of which is very similar to the complexes studied here. For the ruthenium derivatives the stability trend was attributed to steric factors. The synthesis in the present work of other (C) complexes containing different X substituents with different steric requirements suggests that this explanation is inadequate. Since only the acetyl complexes give rise to the *trans* arrangement, the acetyl ligand is obviously the most important in stabilizing this structure. This can be explained on the basis that the acetyl group competes for the *d* orbitals of iron (while the methyl group does not) and so structure (T) may be stabilized. This feature was also observed in octahedral complexes of various Group 7 metals.[17]

The *trans* effect [18] does not explain the trend in the stability of complex (T) with respect to (C) on varying X. In fact when X = CN the structure (C) is formed although (T) ought to be stabilized by the strong π *trans* effect. On the basis of our data, the stabilization of complex (C) can be attributed to the effective positive charge localized on the iron atom. The X substituent with strong σ electronegativity [19] hence stabilizes the (C) structure, since the positive charge on the metal destabilizes the two CO groups in *trans* positions in structure (T).

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REFERENCES

[1] F. Calderazzo, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 299; R. Mawby, F. Basolo, and R. Pearson, *J. Am. Chem. Soc.*, 1964, **86**, 3994; K. Noack and F. Calderazzo, *J. Organomet. Chem.*, 1967, **10**, 101.

[2] A. Wojcicki, *Adv. Organomet. Chem.*, 1973, **11**, 87; H. Brunner and H. Vogt, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 405; H. Brunner and H. Vogt, *Chem. Ber.*, 1981, **114**, 2186.

[3] G. K. Anderson and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 1980, 1434.

[4] I. Wender and P. Pino, 'Organic Syntheses *via* Metal Carbonyls,' Wiley, New York, 1977, vol. 2.

[5] H. Berke and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 7224.

[6] G. K. Anderson and R. J. Cross, *Chem. Soc. Rev.*, 1980, **9**, 185.

[7] M. Pankowski and M. Bigorgne, *J. Organomet. Chem.*, 1971, **30**, 227.

[8] K. A. Keblis and A. H. Filbey, *J. Am. Chem. Soc.*, 1960, **82**, 4204.

[9] M. Pankowski, E. Samuel, and M. Bigorgne, *J. Organomet. Chem.*, 1975, **97**, 105.

[10] Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 1873.

[11] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 291.

[12] P. S. Bratermann, 'Metal Carbonyl Spectra,' Academic Press, London, 1975; M. Pankowski and M. Bigorgne, *J. Organomet. Chem.*, 1977, **125**, 231.

[13] C. F. J. Barnard, J. A. Daniels, and R. J. Mawby, *J. Chem. Soc. Dalton Trans.*, 1976, 961; 1979, 1331.

[14] A. Turco and C. Pecile, *Nature (London)*, 1961, **191**, 66; T. J. Verzremi, J. Nagy, I. A. Buta, and Z. Zsombok, *J. Organomet. Chem.*, 1980, **185**, 323.

[15] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 1966, 1407.

[16] D. Drew, M. Y. Darensbourg, and D. J. Darensbourg, *J. Organomet. Chem.*, 1975, **85**, 73.

[17] C. S. Kraihanzel and P. K. Maples, *Inorg. Chem.*, 1968, **7**, 1806; D. W. Kuty and J. J. Alexander, *ibid.*, 1978, **17**, 1489; R. P. Stewart, jun., *ibid.*, 1979, **18**, 2083.

[18] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' W. A. Benjamin, New York, 1966.

[19] J. K. Wilmshurst, *J. Chem. Phys.*, 1958, **28**, 733; L. Vaska and J. Peone, jun., *Chem. Commun.*, 1971, 418.