Reactions of Methyl Complexes of Iron(II) with Lewis Bases

Gianfranco Bellachioma, Giuseppe Cardaci, and Gustavo Reichenbach
Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy

The ionic complex $[Fe(CO)_3(PMe_3)_2Me][BPh_4]$ reacts with Lewis bases (L) to give $[Fe(CO)_2(PMe_3)_2L(COMe)][BPh_4]$. Two reaction paths are observed: one involving carbon monoxide insertion followed by attack of the L ligand, and a second in which ligand exchange is followed by an insertion reaction. The relative importance of the two paths depends on the nature and the concentration of L. The neutral complexes $[Fe(CO)_2(PMe_3)_2(Me)X]$ also react with Lewis bases to give $[Fe(CO)(PMe_3)_2L(COMe)X]$. When X = I the acetyl complex is readily transformed into the corresponding ionic methyl complex $[Fe(CO)_2(PMe_3)_2L(Me)]I$. The neutral complexes react faster than the ionic ones. The structure of the ionic and neutral complexes has been assigned on the basis of i.r. and n.m.r. evidence.

The reaction of alkyl carbonyl complexes with Lewis bases is the easiest way to achieve carbon monoxide insertion. This reaction has been studied extensively both for preparative purposes and for its kinetic importance,[1] *e.g.* with the complexes $[Mn(CO)_5R]$ [2] and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Me]$.[3] Despite the breadth of the studies carried out,[4] some aspects of this reaction remain obscure, and further effort is necessary, since this reaction is also important in homogeneous catalysis (hydroformylation, homologation, the Fischer–Tropsch reaction, *etc.*).[5]

In the present work we report a study of the reactivity of octahedral complexes of iron (d^6) such as $[Fe(CO)_2(PMe_3)_2(Me)X]$ and $[Fe(CO)_3(PMe_3)_2Me][BPh_4]$ with a wide range of Lewis bases. The results obtained allow us to determine the stereochemistry of the products, and in some cases the reaction mechanism, and to compare them with those of the analogous ruthenium complexes.

Experimental

All reactions were carried out at room temperature under an atmosphere of dry nitrogen. All solvents were carefully dried following methods in the literature.[6] The complex $[Fe(CO)_3(PMe_3)_2Me][BPh_4]$ was prepared as described previously,[7] as were $[Fe(CO)_2(PMe_3)_2(Me)X]$.[7,8] Trimethylphosphine was prepared according to the method of Wolfsberger and Schmidbaur.[9] All the other compounds were commercial products, used without further purification.

Elemental analyses were carried out on a Carlo Erba 1106 elemental analyser. Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer, ^1H n.m.r. spectra on a JEOL CHL-60 spectrometer, and ^{13}C n.m.r. spectra on a Bruker WP-80 spectrometer. Chemical shifts are reported in p.p.m. with respect to $SiMe_4$. Analytical, i.r., and n.m.r. data are shown in Tables 1—5.

Conductivity Measurements.—Conductivity measurements were carried at 25 °C with an Amel conductometer using a cell with platinized-platinum electrodes and constant of 0.94 cm. For the tetraphenylborate complexes at *ca.* 3×10^{-3} mol dm^{-3} in CH_2Cl_2 the molar conductivity Λ was about 40 ohm^{-1} cm^2 mol^{-1}. For the iodide complexes at *ca.* 5×10^{-3} mol dm^{-3} in CH_2Cl_2, Λ was about 15 ohm^{-1} cm^2 mol^{-1}.

Carbonylation of $[Fe(CO)_3(PMe_3)_2Me][BPh_4]$ (1) *with Carbon Monoxide.*—Complex (1) (0.5 g) was dissolved in CH_2Cl_2 (50 cm^3) in an atmosphere of CO. The reaction was followed by monitoring the i.r. spectrum of the solution. After 20 h it had reached equilibrium and a new complex was formed, whose i.r. and n.m.r. spectra corresponded to $[Fe(CO)_3(PMe_3)_2(COMe)][BPh_4]$ (3) (Tables 2 and 5). The concentration ratio of (3) and (1), as determined by n.m.r. spectroscopy, was 0.53 : 1. Complex (3) could not be isolated. The reaction is reversible, passage of nitrogen giving (1) once again.

Isotopic Exchange of Complex (1) *with Labelled Carbon Monoxide.*—A solution of complex (1) (0.1 g) in CH_2Cl_2 (5 cm^3) was injected into a reactor (20 cm^3) containing ^{13}CO. The reaction was followed by monitoring the i.r. spectrum in the 2 100—1 550 cm^{-1} range. It reached equilibrium after 1.5 h and scrambling was complete on repeating the exchange procedure four times (Table 2). The i.r. band at 1 600 cm^{-1}, characteristic of the acetyl complex (3), was always absent.

Preparations.—$[Fe(CO)_2(PMe_3)_2L(COMe)][BPh_4]$ [L = PMe_3 (4a), $P(OMe)_3$ (4b), *or* $P(OPr^i)_3$ (4c)]. To a solution of complex (1) in CH_2Cl_2 an equivalent quantity of L was added. The reaction was very fast; the products were precipitated by adding n-hexane, and then filtered off (yield 90%). In the case of $P(OPr^i)_3$ an excess of ligand (4 : 1) had to be added; the reaction was complete only after 30 min.

$[Fe(CO)_2(PMe_3)_2L(Me)][BPh_4]$ [L = PMe_3 (2a), $P(OMe)_3$ (2b), *or* $P(OPr^i)_3$ (2c)]. A solution of complex (4) was left in a nitrogen stream. After 8 h the decarbonylation was complete and the methyl complex was precipitated with n-hexane (yield 90%).

$[Fe(CO)_2(PMe_3)_2L(Me)][BPh_4]$ [L = PEt_3 (2d) *or* 4-*aminopyridine* (2e)]. To a solution of complex (1) a 3 : 1 excess of L was added. The reaction was very slow, and an equilibrium mixture of (1), the methyl complex, and the corresponding acetyl complex was obtained. A nitrogen stream drove the equilibrium towards the methyl complex (2d,e). After 8 h the decarbonylation was complete, and the complex was precipitated by adding n-hexane. In the case of 4-aminopyridine the precipitate was repeatedly washed with diethyl ether to eliminate the ligand, and crystallized from a solution of CH_2Cl_2–n-hexane (yield 70%).

$[Fe(CO)_2(PMe_3)_2L(Me)][BPh_4]$ [L = MeCN (2f) or $CH_2{=}CHCN$ (2g)]. Complex (1) was dissolved in L; the reaction was similar to the preceding one. After 3 h the solvent was removed under reduced pressure and the solid residue crystallized from a solution of CH_2Cl_2–diethyl ether at −20 °C (yield 35%).

$[Fe(CO)(PMe_3)_2\{P(OMe)_3\}(COMe)(CN)]$ (5b). To a solution of $[Fe(CO)_2(PMe_3)_2Me(CN)]$ in CH_2Cl_2 a 5 : 1 excess of $P(OMe)_3$ was added. After 24 h the reaction was complete and the solution evaporated under reduced pressure to eliminate

Table 1. Analytical data

		Analysis (%)					
		Calculated			Found		
	Complex	C	H	N	C	H	N
(2a)	$[Fe(CO)_2(PMe_3)_3Me][BPh_4]$	64.1	7.45		64.3	7.65	
(6a)	$[Fe(CO)_2(PMe_3)_3Me]I$	29.9	6.25		29.65	6.30	
(2b)	$[Fe(CO)_2(PMe_3)_2\{P(OMe)_3\}Me][BPh_4]$	59.85	6.95		60.25	7.10	
(6b)	$[Fe(CO)_2(PMe_3)_2\{P(OMe)_3\}Me]I$	27.2	5.70		27.55	5.95	
(2d)	$[Fe(CO)_2(PMe_3)_2(PEt_3)Me][BPh_4]$	65.4	7.90		65.65	7.80	
(2c)	$[Fe(CO)_2(PMe_3)_2\{P(OPr^i)_3\}Me][BPh_4]$	62.5	7.75		62.55	7.50	
(2e)	$[Fe(CO)_2(PMe_3)_2(4NH_2\text{-}C_5H_4N)Me][BPh_4]$	65.9	6.85	4.05	65.7	6.85	3.85
(2f)	$[Fe(CO)_2(PMe_3)_2(MeCN)Me][BPh_4]$	65.75	6.95	2.20	65.9	7.00	2.05
(4a)	$[Fe(CO)_2(PMe_3)_3(COMe)][BPh_4]$	63.25	7.15		63.3	7.25	
(4b)	$[Fe(CO)_2(PMe_3)_2\{P(OMe)_3\}(COMe)][BPh_4]$	59.2	6.70		59.2	6.80	
(4c)	$[Fe(CO)_2(PMe_3)_2\{P(OPr^i)_3\}(COMe)][BPh_4]$	61.85	7.50		62.1	7.25	
(5b)	$[Fe(CO)(PMe_3)_2\{P(OMe)_3\}(COMe)(CN)]$	36.4	7.05	3.25	36.15	7.15	3.10

Table 2. Infrared data (cm^{-1}) for the ionic complexes $[Fe(CO)_2(PMe_3)_2L(Me)][BPh_4]$ and $[Fe(CO)_2(PMe_3)_2L(COMe)][BPh_4]$ in CH_2Cl_2

Complex	ν_{CO} [a]	ν_{COMe} and other bands
$[Fe(CO)_3(PMe_3)_2Me][BPh_4]$ (1)	2 085w, 2 022s	
$[Fe(^{13}CO)_3(PMe_3)_2Me][BPh_4]$	2 034w, 1 972.5s	
(2a)	2 018s, 1 962s	
(2b)	2 026s, 1 972s	
(2c)	2 018s, 1 959s	
(2d)	2 019s, 1 962s	
(2e)	2 009s, 1 950s	1 631m [ν(C=N)]
(2f)	2 022s, 1 972s	
$[Fe(CO)_3(PMe_3)_2(COMe)][BPh_4]$ (3)	2 097w, 2 036s	1 640m
(4a)	2 022s, 1 972s	1 620m
(4b)	2 036s, 1 988s	1 624m
(4c)	2 029s, 1 980s	1 619m
$[Fe(CO)_2(PMe_3)_2(MeCN)(COMe)][BPh_4]$ [b] (4f)	2 038s, 1 990s	1 628m
$[Fe(CO)_2(PMe_3)_2(CH_2{=}CHCN)(COMe)][BPh_4]$ [c] (4g)	2 035s, 1 985s	1 605m [$\nu(CH_2{=}CH)$]

[a] w = Weak, s = strong, and m = medium. [b] Solvent CH_3CN. [c] Solvent $CH_2{=}CHCN$.

the solvent and the excess of $P(OMe)_3$. The complex (yield 90%) cannot be kept for a long time (even at −15 °C) or crystallized since it gives the starting complex once again. In the case of L = PMe_3 an equilibrium was reached even with a 5 : 1 excess. The complex $[Fe(CO)(PMe_3)_3(COMe)(CN)]$ (5a) could not be separated and was characterized spectroscopically (Table 3).

$[Fe(CO)_2(PMe_3)_3Me]I$ (6a). To a solution of $[Fe(CO)_2(PMe_3)_2(Me)I]$ in diethyl ether was added a solution of PMe_3 also in ether (molar ratio 1 : 5). A rapid reaction was observed and a yellow precipitate formed. The solution showed two stretching bands at 1 939 cm^{-1} (ν_{CO}) and 1 576 cm^{-1} (ν_{COMe}) attributed to the acetyl complex $[Fe(CO)(PMe_3)_3(COMe)I]$ (7a). The precipitate showed three CO stretching bands at 2 020, 1 960, and 1 940 cm^{-1} and no bands in the region of 1 600 cm^{-1} in the solid state (Nujol mull); when dissolved in CH_2Cl_2 it showed two bands at 2 020 and 1 960 cm^{-1}. The solid, whose elemental analysis corresponds to (6a), reacts under vacuum to give the starting complex once again. For all these reasons we think that the solid is a mixture of two ionic isomers having two CO in *cis* or *trans* positions: to the first we attribute the bands at 2 020 and 1 960 cm^{-1}, to the second that at 1 940 cm^{-1}.

$[Fe(CO)_2(PMe_3)_2L(Me)]I$ [L = $P(OMe)_3$ (6b), $P(OPr^i)_3$ (6c), *or 4-aminopyridine* (6e)]. To a solution of $[Fe(CO)_2(PMe_3)_2(Me)I]$ in CH_2Cl_2 a 5 : 1 excess of L was added. The final product (yield 90%) was precipitated by adding n-hexane. When the reaction was performed in an n-hexane solution, a precipitate of $[Fe(CO)(PMe_3)_2L(COMe)I]$ and $[Fe(CO)_2(PMe_3)_2L(Me)]I$ was obtained.

Reaction between $[Fe(CO)_2(PMe_3)_2(Me)I]$ *and* MeCN.—When $[Fe(CO)_2(PMe_3)_2(Me)I]$ was dissolved in MeCN an equilibrium was readily reached according to equation (i). If

$$[Fe(CO)_2(PMe_3)_2(Me)I] + MeCN \rightleftharpoons [Fe(CO)_2(PMe_3)_2(MeCN)Me]^+ + I^- \quad (i)$$

c_i is the concentration of $[Fe(CO)_2(PMe_3)_2(MeCN)Me]^+$ and c_n that of $[Fe(CO)_2(PMe_3)_2(Me)I]$ at equilibrium, the equilibrium constant is proportional to c_i^2/c_n and therefore to D_i^2/D_n where D_i and D_n are the absorbances of one of the CO stretching bands of $[Fe(CO)_2(PMe_3)_2(MeCN)Me]^+$ (ν_{CO} at 2 022 and 1 966 cm^{-1}) and $[Fe(CO)_2(PMe_3)_2(Me)I]$ (ν_{CO} at 1 997 and 1 936 cm^{-1}) respectively. A plot of log (D_i^2/D_n) *vs.* $1/T$ was linear and the ΔH value was calculated from the slope.

Results and Discussion

Reaction of the Ionic Complex $[Fe(CO)_3(PMe_3)_2Me][BPh_4]$ *with Lewis Bases.*—The reaction of the salt with nucleophiles [L = PMe_3, PEt_3, $P(OMe)_3$, $P(OPr^i)_3$, 4-aminopyridine, MeCN, CO, or $CH_2{=}CHCN$] is shown in the Scheme. With L = CO the complexes (1) and (3) reach an equilibrium and when P_{CO} = 1 atm (101 325 Pa), K[CO] = [(3)]/[(1)] = 0.53 in CH_2Cl_2. With other ligands [L = PEt_3, $P(OPr^i)_3$, and 4-aminopyridine] there is also an equilibrium, but in such cases this can be driven towards complex (2) by a nitrogen stream.

The ionic nature of complexes (2)—(4) is demonstrated by conductivity measurements. Their stereochemistry follows

Table 3. Infrared data (cm^{-1}) for the complexes [$Fe(CO)(PMe_3)_2L(COMe)X$] in diethyl ether

Complex	X	L	ν_{CO}	ν_{COMe}	Other bands
(5b)	CN	$P(OMe)_3$ [a]	1 960	1 590	2 099 [$\nu(C{=}N)$]
(5a)	CN	PMe_3	1 937	1 594	2 100 [$\nu(C{=}N)$]
(7b)	I	$P(OMe)_3$ [b]	1 972	1 600	
(7a)	I	PMe_3	1 939	1 576	

[a] Proton n.m.r. in CD_2Cl_2: τ 8.63 [t, J(Me–P) = 3.8, PMe_3], 7.51 (s, COMe), and 6.30 [d, J 9.7 Hz, $P(OMe)_3$]. ^{13}C N.m.r. in CD_2Cl_2: δ 19.4 {dt, J[Me–$P(OMe)_3$] = 3.4, J(Me–P) = 15.5, PMe_3}, 49.2 [d, J(Me–P) = 10.3, $P(OMe)_3$], and 49.1 {d, J[Me–$P(OMe)_3$] = 29.3 Hz, COMe}. [b] Solvent CH_2Cl_2.

Table 4. Proton n.m.r. spectra of [$Fe(CO)_2(PMe_3)_2L(Me)$]X complexes in CH_2Cl_2

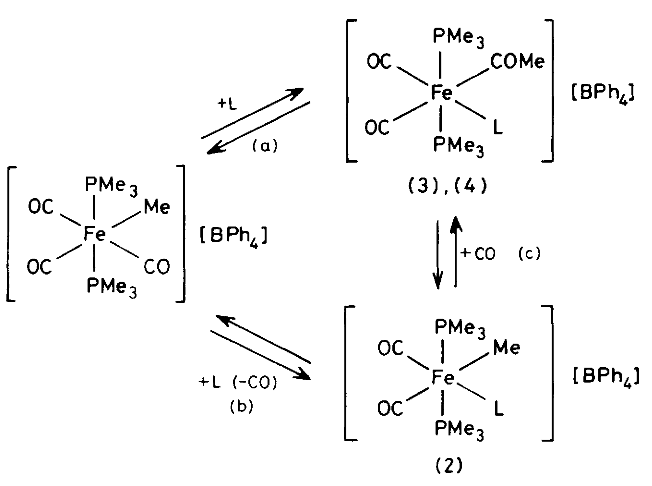
Complex	X	L	τ_L	J_L/Hz	$\tau(PMe_3)$	J(MeP)/ Hz	τ_{Me}	J(MeP)/ Hz	J(MeP$_L$)/ Hz
(2b)	BPh_4	$P(OMe)_3$	6.23 (d, 9)	10.2	8.45 (t, 18)	4.2	10.10 (dt, 3)	8.4	9.0
(6b)	I	$P(OMe)_3$	6.12 (d, 9)	10.2	8.45 (t, 18)	4.3	10.10 (dt, 3)	8.0	9.3
(2a)	BPh_4	PMe_3	8.74 (d, 9)	7.8	8.61 (t, 18)	3.8	10.10 (dt, 3)	8.3	9.8
(2f)	BPh_4	MeCN	8.05 (s, 3)		8.52 (t, 18)	4.5	9.77 (t, 3)	7.9	
(2d)	BPh_4	PEt_3	8.59 (m)		8.51 (t)	3.6	10.20 (dt, 3)	9.5	9.7
(2c)	BPh_4	$P(OPr^i)_3$	τ_H = 5.2 (dsept, 3) τ_{Me} = 8.55 (d, 18)	J(HP) = 10.0 J(HMe) = 6.0	8.45 (t, 18)	4.5	9.97 (dt, 3)	9.0	10.2
(2e)	BPh_4	$4NH_2$-C_5H_4N	τ_{NH_2} = 3.82 (s, 2)		8.66 (t, 18)	3.9	9.52 (t, 3)	8.1	
(1)	BPh_4	CO			8.45 (t, 18)	4.5	9.89	7.3	

s = Singlet, d = doublet, t = triplet, dt = doublet of triplets, dsept = doublet of septets, and m = multiplet. Number in parentheses are relative intensities. P$_L$ refers to the phosphorus of ligand L.

Table 5. Proton n.m.r. spectra of [$Fe(CO)_2(PMe_3)_2L(COMe)$][BPh_4] complexes in CH_2Cl_2

Complex	L	τ_L	J_L/Hz	$\tau(PMe_3)$	J(Me–P)/Hz	τ(COMe)
(3)	CO			8.33 (t, 18)	4.5	7.44 (s, 3)
(4b)	$P(OMe)_3$	6.12 (d, 9)	10.1	8.37 (t, 18)	4.3	7.50 (s, 3)
(4a)	PMe_3	8.55 (d, 9)	8.4	8.44 (t, 18)	3.9	7.46 (s, 3)
(4c) *	$P(OPr^i)_3$			8.35 (t, 18)	4.5	7.54 (s, 3)

* The spectrum was recorded in the presence of an excess of the ligand L.



Scheme.

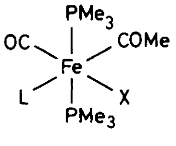
from the observation of two CO stretching bands of similar intensity due to two mutually *cis* carbonyl ligands (see Table 2),[10] and from observation of the triplet n.m.r. signal of the methyl in PMe_3 due to two mutually *trans* phosphine ligands (see Tables 4 and 5).[11,12] Furthermore, the methyl group bound to the iron atom shows a coupling constant and a multiplicity (triplet) typical of a methyl group *cis* to two equivalent PMe_3 groups; in the case of L = PR_3 a double triplet is obtained, the coupling constant of which corresponds to a structure in which the methyl is *cis* to all the phosphine ligands.

As far as the mechanism is concerned, when L = ^{13}CO the direct exchange is ten times faster than the acetylation, and isotopic exchange proceeds *via* a CO dissociation, in accordance with the positive charge which labilizes the Fe–CO bond.[13]

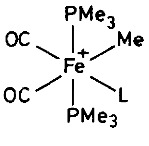
The reaction of complex (1) with PMe_3 and $P(OMe)_3$ is very fast, and gives the acetyl complexes (4a) and (4b). The reaction between the complex (2a) and CO slowly (reaction time >15 h) gives a mixture of (1) and (4a), showing that substitution by PMe_3 [path (b)] and CO insertion [path (c)] occur simultaneously. The slowness of this reaction tells us that the reaction between (1) and PMe_3 takes place predominantly *via* CO insertion [path (a)], since the other path [(b) + (c)] contains a very slow step (c).

In conclusion, complex (1) reacts with Lewis bases according to both the dissociative path (b) and the direct insertion path (a); the relative importance of the two paths depends on the nature and the concentration of L. Similar results were obtained by Mawby and co-workers[14] with non-ionic ruthenium complexes.

The reaction in the Scheme is not observed for L = PPh_3, $P(C_6H_{11})_3$, or $Ph_2PCH_2CH_2PPh_2$ due to the steric hindrance of the ligands.[15] The importance of steric requirements has recently been pointed out by Jablonski and Wang[16] in the carbonyl-insertion reaction of the cation *fac*-tricarbonylmethyl[*o*-phenylenebis(dimethylarsine)]iron. The reaction is not observed for NEt_3 either, so we suppose that the 4-aminopyridine ligand is bound to the iron atom through the aromatic nitrogen and that the softness of the ligand is im-



(5), (7)



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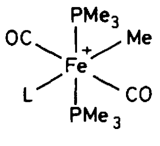
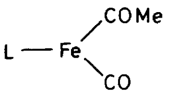


(8)

portant in the stability of the complexes.[17] The ligands MeCN and CH_2=CHCN are bound to the iron atom through the nitrogen lone pairs; in the case of acrylonitrile the double bond is not involved, as shown by the fact that no shift in its stretching frequency is observed.[18]

Reaction of Neutral $[Fe(CO)_2(PMe_3)_2(Me)X]$ *Complexes with Lewis Bases*.—With X = CN and L = PMe_3 or $P(OMe)_3$ an equilibrium was reached between the starting material and the product $[Fe(CO)(PMe_3)_2L(COMe)(CN)]$ (5). Only an excess of ligand drove the reaction to completion. Attempts at decarbonylating (5) to obtain the complex $[Fe(CO)(PMe_3)_2L(Me)(CN)]$ were not fruitful, and only the starting complex was obtained.

With X = I and L = PMe_3 the acyl complex $[Fe(CO)(PMe_3)_3(COMe)I]$ (7a) is formed, from which the iodo-ligand is readily displaced by methyl migration to iron to give the ionic methyl complex $[Fe(CO)_2(PMe_3)_3Me]I$ (6a). This complex exists in two forms, *cis* and *trans*, the second of which is unstable and is transformed into the other. In a non-polar solvent the two isomers (6) and (8) precipitate, and the isomerization does not occur (see Experimental section). The presence of the two isomers suggests that the displacement of the iodine atom produces a trigonal-bipyramidal intermediate (I) from which both isomers can be formed. With L = $P(OMe)_3$ or $P(OPr^i)_3$ the behaviour is quite similar, but only the *cis* isomer (6) is observed. With other phosphines the reaction does not occur, so we deduce that the steric effect is more important than in the ionic complexes discussed in the previous paragraph. With MeCN the equilibrium (i) is reached. This equilibrium is driven to the left upon increasing the temperature ($\Delta H = -20.0$ kJ mol^{-1}).



(I)

The structure of the acyl complex $[Fe(CO)(PMe_3)_2\{P(OMe)_3\}(COMe)(CN)]$ (5b) can be assigned on the basis of n.m.r. spectra. The triplet exhibited by PMe_3 in the ^1H n.m.r. spectrum shows that the two phosphines are *trans* to each other, and a ^{13}C n.m.r. spectrum clearly shows a doublet for the acyl methyl (49.1 p.p.m.), which is therefore *trans* to the phosphite as in similar complexes[14,16] (see Table 3).

Conclusions

Both ionic complexes $[Fe(CO)_3(PMe_3)_2Me]^+$ and neutral complexes $[Fe(CO)_2(PMe_3)_2(Me)X]$ react with Lewis bases. In both cases the reaction goes through insertion of carbon monoxide, followed by attack of the Lewis basis. The insertion of CO is faster in the neutral complexes than in the cationic ones. This may be due to the fact that migration of the methyl group is inhibited by a positive charge on the central metal. The decarbonylation, on the contrary, is favoured by a positive charge, and the rate follows the trend $[Fe(CO)_2(PMe_3)_2L(COMe)]^+ > [Fe(CO)_2(PMe_3)_2(COMe)X] > [Fe(CO)_2(PMe_3)_2(COMe)(CN)]$ (X = Cl, Br, or I). This is consistent with the smaller extent of back donation from the formally positive iron to CO, which labilizes the Fe–CO bond.[13]

In a similar way the cationic complex *fac*-$[Fe(CO)_3(pdma)(COMe)]^+$ is decarbonylated very easily while the analogous neutral complex $[Fe(CO)_2(pdma)(COMe)I]$ does not decarbonylate [pdma = *o*-phenylenebis(dimethylarsine)].[16,19]

Some interesting conclusions can be drawn on comparing the reactivity of iron complexes and of the isoelectronic and isostructural ruthenium complexes $[Ru(CO)_2L_2(Me)X]$ with Lewis bases, reactions that have recently been studied by Mawby and co-workers.[14] The iron complexes (5) and (7) have only one structure, while the corresponding ruthenium complexes present two isomeric structures in equilibrium. This may be due to the greater covalent radius of Ru, which lowers the importance of the steric hindrance of the ligands.

Ruthenium gives only neutral complexes, while iron gives ionic complexes and non-ionic intermediates. A similar behaviour has been observed in the *trans–cis* isomerization of $M(CO)_2(PR_3)_2Cl_2$ complexes. When M = Ru the isomerization goes *via* a five-co-ordinated covalent intermediate, but when M = Fe it goes *via* an ionic intermediate $[Fe(CO)_3(PR_3)_2I]I$.[20] The tendency of iron to give ionic compounds may be due to its lower π-bonding capability as compared with ruthenium(II).[21] This may also be why ruthenium has a greater effectiveness in homogeneous catalysis. In fact its lesser tendency to give ionic complexes allows reductive coupling processes, which are not possible in the case of iron.[22]

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References

1 T. H. Coffield, R. D. Claisen, and J. Kozikowski, *J. Org. Chem.*, 1957, **22**, 598; K. A. Keblys and A. M. Filbey, *J. Am. Chem. Soc.*, 1960, **82**, 4204.
2 F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, 1962, **1**, 30; R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, 1964, **86**, 3994; K. Noack and F. Calderazzo, *J. Organomet. Chem.*, 1967, **10**, 101; T. C. Flood, J. E. Jensen, and J. A. Statler, *J. Am. Chem. Soc.*, 1981, **103**, 4410.
3 J. P. Bibler and A. Wojcicki, *Inorg. Chem.*, 1966, **5**, 889.
4 F. Calderazzo, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 299; A. Wojcicki, *Adv. Organomet. Chem.*, 1973, **11**, 87.
5 D. R. Fahey, *J. Am. Chem. Soc.*, 1981, **103**, 136.
6 A. Weissberger, 'Techniques of Organic Chemistry: Organic Solvents,' 2nd edn., Interscience, New York, 1955.
7 G. Reichenbach, G. Cardaci, and G. Bellachioma, *J. Chem. Soc., Dalton Trans.*, 1982, 847.
8 M. Pankowski and M. Bigorgne, *J. Organomet. Chem.*, 1971, **30**, 227.
9 W. Wolfsberger and H. Schmidbaur, *Synth. React. Inorg. Metal-org. Chem.*, 1974, **4**, 149.
10 P. S. Bratermann, 'Metal Carbonyl Spectra,' Academic Press, London, 1975.
11 J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc., London*, 1963, 291.
12 J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. A*, 1966, 1407.
13 F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967.
14 C. F. J. Barnard, J. A. Daniels, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1979, 1331.
15 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313; H. C. Clark, *Isr. J. Chem.*, 1976—1977, **15**, 210.
16 C. R. Jablonski and Yu-Pin Wang, *Inorg. Chem.*, 1982, **21**, 4037.

17 J. Chatt and F. A. Hart, *J. Chem. Soc. A*, 1960, 1378.
18 H. W. Quinn and J. H. Tsaj, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 243.
19 C. R. Jablonski, *Inorg. Chem.*, 1981, **20**, 3940.
20 C. F. J. Barnard, J. A. Daniels, J. Jeffrey, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1976, 953; M. Pankowski and M. Bigorgne, *J. Organomet. Chem.*, 1977, **125**, 231; L. M. Wilkes, J. H. Nelson, P. Mitchener, M. W. Babich, W. C. Riley, B. J. Helland, R. A. Jacobson, M. Y. Cheng, K. Seff, and L. B. McCusker, *Inorg. Chem.*, 1982, **21**, 1376.
21 P. J. Domaille, S. D. Ittel, J. P. Jesson, and D. A. Sweigart, *J. Organomet. Chem.*, 1980, **202**, 191 and refs. therein.
22 J. R. Blackborow, R. J. Daroda, and G. Wilkinson, *Coord. Chem. Rev.*, 1982, **43**, 17.

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