Reactions of a Terminal Phosphido-group in an Organoiron Complex. Part III.† Complexes containing Two Metal Atoms with a Single Phosphido-bridge

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The phosphido-complex $[Fe(cp)(CO)_2\{P(CF_3)_2\}]$ (L) (cp = η-cyclopentadienyl) acts as a Lewis base towards metal carbonyls and nitrosyls, forming the monosubstituted complexes $[Ni(CO)_3L]$, $[Co(CO)_2(NO)L]$, $[Fe(CO)(NO)_2L]$, $[Fe(CO)_4L]$, $[Mn(CO)_3(NO)L]$, and *trans*-$[Mn(CO)_4(H)L]$. With $[Co_2(CO)_8]$, (L) forms the tetranuclear complex $[Co_2(CO)_6L_2]$. I.r. studies suggest that the donor–acceptor ability of (L) is intermediate between that of triarylphosphines and trialkyl phosphites. In the i.r. spectra, $[Co(CO)_2(NO)L]$ and $[Mn(CO)_3(NO)L]$ show more than one ν(NO) band and additional ν(CO) bands compared to the other complexes, the presence of which is attributed to rotational isomerism about the P–Co and P–Mn bond respectively.

THE preparation of $[Fe(cp)(CO)_2\{P(CF_3)_2\}]$ (L; cp = η-cyclopentadienyl) from $[Fe_2(cp)_2(CO)_4]$ and $(F_3C)_2P{\cdot}P(CF_3)_2$ made available a complex with a lone pair of electrons on phosphorus which can be regarded as a tertiary phosphine, one substituent being the $Fe(cp)(CO)_2$ group.[1] Earlier papers [1,2] have reported the ease of oxidation at phosphorus in complex (L). We now report an investigation of the Lewis-base properties of (L) towards low-oxidation-state metals including an assessment of its donor–acceptor character. Related work concerns the reaction of $[Fe(cp)(CO)_2(PPh_2)]$ with $[Fe_2(CO)_9]$ to give $[(cp)Fe(CO)_2(PPh_2)Fe(CO)_4]$,[3] and the preparation of other bridged PR_2 complexes by the displacement of halide from a metal [4] or from free [5] or co-ordinated [3,6] halogenophosphines.

RESULTS AND DISCUSSION

The phosphido-complex $[Fe(cp)(CO)_2\{P(CF_3)_2\}]$ reacted at room temperature with $[Ni(CO)_4]$, $[Co(CO)_3(NO)]$, $[Fe(CO)_2(NO)_2]$, $[Mn(CO)_4(NO)]$, and $[Mn(CO)_5H]$ to give monosubstituted products. Reaction with $[Fe_2(CO)_9]$ gave $[Fe(CO)_4L]$ and with $[Co_2(CO)_8]$ the complex $[Co_2(CO)_6L_2]$ was formed. When compared with known reactions of fluorocarbon phosphines the results are interesting in several ways. First, while CF_3 phosphines replace one or two carbonyl groups in $[Co(CO)_3(NO)]$ and $[Fe(CO)_2(NO)_2]$ and form complexes of $[Fe(CO)_4]$ with $[Fe_2(CO)_9]$,[7] polysubstitution at $[Ni(CO)_4]$ is found without exception.[7b,8] The absence of further substitution at nickel is attributed partly to steric effects,[9] and partly to electronic effects as the ligand is a stronger donor but weaker acceptor than other fluorocarbon phosphines (see later). Secondly, no evidence is found for Fe–P bond fission analogous to X–P fission in reactions of $P(CF_3)_2X$ (X = H or halogen) with the above carbonyls or nitrosyls.[7d,e,10] This suggests that the Fe–P bond is relatively strong. Finally, the substitution reactions of (L) are more rapid by a factor of at least 10 than those of other $(F_3C)P$ ligands under comparable conditions. Thus the Lewis basicity of the ligand is increased when $[Fe(cp)(CO)_2]$ is a substituent at phosphorus.

The free ligand (L) has strong bands in the i.r. spectrum at 2 046 and 2 000 cm^{-1} shifted to higher wavenumber (2 062 and 2 008 cm^{-1}) in the complexes of quinquevalent phosphorus, $[Fe(cp)(CO)_2\{P(CF_3)_2E\}]$ (E = O, S, or Se).[2] Co-ordination of phosphorus to a metal will also shift ν(CO) to higher frequency since the positive charge on phosphorus following donation of the lone pair will be partially compensated by back donation from both metal atoms. Thus the bands of nearly equal intensity in the spectrum of each of the complexes (I)—(VII) at *ca.* 2 055 and 2 020 cm^{-1} represent the ν(CO) vibrations of the co-ordinated ligand (L). In the case of the manganese hydride the necessary use of a more polar solvent, acetone, gave absorptions at slightly lower wavenumber. Discounting the ligand carbonyl vibrations, there remain two and four bands for the complexes $[Ni(CO)_3L]$ and $[Fe(CO)_4L]$ respectively, as expected for C_{3v} and C_{2v} local symmetry about Ni and Fe. Other workers [3,6] have assigned an axial structure to the complexes $[(cp)Fe(CO)_2(PR_2)Fe(CO)_4]$ (R = Me or Ph), assuming that the four i.r. bands of the $Fe(CO)_4$ unit include an *E* symmetry class mode split by the ligand asymmetry. However, this explanation need not apply to (IV). The complex $[Ni(CO)_3L]$, with a high-frequency A_1 mode at 2 079 cm^{-1}, must have an *E* mode close to 2 000 cm^{-1} by comparison with other tricarbonylphosphinenickel complexes.[11] A strong feature in the spectrum at 1 996 cm^{-1}

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† Part II is ref. 2.

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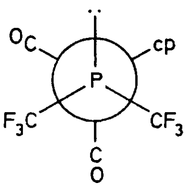
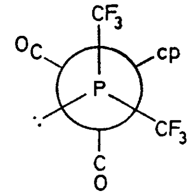
is clearly the unperturbed *E* mode. The absence of splitting by ligand asymmetry in [$Ni(CO)_3L$] makes a reasonable case for assigning the four strong, sharp, well spaced bands arising from the $Fe(CO)_4$ unit in (IV) to a molecule of C_{2v} local symmetry where ligand–ligand repulsions involving the bulky group L are minimised. In [$Fe(CO)(NO)_2L$], accidental degeneracy produces only two carbonyl bands as well as the expected two nitrosyl bands. The complex [$Mn(CO)_4(H)L$] has two absorptions in the range 2 100—1 950 cm^{-1} in addition to the two ligand carbonyl bands, implying a *trans* structure. The ^{19}F n.m.r. spectrum showed one doublet, consistent with the presence of one isomer, and the ^1H n.m.r. spectrum had a metal hydride resonance showing the H–P coupling typical of *trans* ligands. (For the complexes *trans*-[$Mn(CO)_4H\{P(CF_3)_2X\}$] the values of $^2J(HP)$ are 72, 62, and 57 Hz respectively when X = F, CF_3, and Me, whereas the *cis* isomers of the same complexes have $^2J(HP) < 10$ Hz.[10b]

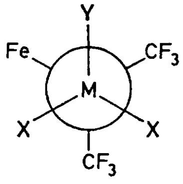
The complexes [$Co(CO)_2(NO)(L)$] and [$Mn(CO)_3(NO)(L)$] give more complicated i.r. spectra which do not change on resublimation or recrystallisation and are only marginally affected by change of solvent. Neither complex showed changes in the ^{19}F n.m.r. spectrum when cooled to −60 °C. The extra i.r. bands in the five-co-ordinate manganese complex could arise from positional isomerism. However, the tetrahedral cobalt complex cannot have structural isomers and the additional bands in both complexes may result from rotational isomerism. The *X*-ray crystal structure of (L) [12] shows a staggered asymmetric conformation [(A) rather than (B)] in the solid state and this is maintained in solution.[13] The absence of additional ν(CO) bands in the region expected for the vibrations of the co-ordinated ligand suggests that the locked conformation (A) persists in complexes (I)—(VI) and that the additional i.r. bands in (II) and (V) arise from restricted rotation about the P–Co or P–Mn bond. For the complex [$(cp)(OC)_2Fe\{P(CF_3)_2\}MX_2Y$] two rotamers [(C) and (D)] are possible. Variable-temperature i.r. experiments (20 to −40 °C) showed slight but reproducible and reversible changes in the relative intensities of the bands of [$Co(CO)_2(NO)L$] at 2 036, 1 976, and 1 782 cm^{-1} compared to the stronger features at 2 059, 2 046, 2 016, 1 998, and 1 752 cm^{-1}, consistent with rotational isomerism. Rotamers are also possible for [$Fe(CO)(NO)_2L$], (III), but only one was observed in the spectrum, suggesting that two NO groups enhance the stability of one conformation. When X and Y are identical, as in [$Ni(CO)_3L$], the rotamers are indistinguishable and this is also true for *trans*-[$Mn(CO)_4(H)L$]. Equatorially substituted [$Fe(CO)_4L$] has only one non-eclipsed conformation. However, for the complex [$Mn(CO)_3(NO)L$], different staggered conformations are possible whether (L) is axial or equatorial, provided the nitrosyl ligand is equatorial. Ehrl and Vahrenkamp [14] proposed a similar explanation for additional carbonyl bands in the spectra of complexes containing an $AsMe_2$ bridging group, although isomers arise from restricted rotation about the As–M(cp)$(CO)_3$ bond (M = Mo or W). The difference between the two types of complex is attributed to the much greater bulk of the $P(CF_3)_2$ compared to the $AsMe_2$ bridging ligand.



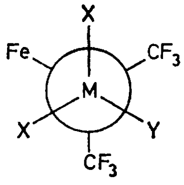
(A)



(B)



(C)



(D)

Comparison of the ν(CO) and ν(NO) band positions in the i.r. spectra of complexes (I)—(VI) with those of other phosphine complexes shows that the donor–acceptor properties of [$Fe(cp)(CO)_2\{P(CF_3)_2\}$] are different from other fluorocarbon phosphines.[7,8] For example, the C–O stretching frequencies for tricarbonylphosphinenickel complexes [8c,11] fall in the order $P(CF_3)_3 > P(CF_3)_2Me > P(OPh)_3 > P(OMe)_3 > [P(CF_3)_2\{Fe(cp)(CO)_2\}] > PPh_3 > PMe_3$. The electronic character of (L) lies between that of triarylphosphines and trialkyl phosphites in each of the complexes (I)—(VI) for which comparisons can be made. Previous experiments [2] have shown that [$Fe(cp)(CO)_2\{P(CF_3)_2\}$] is a much stronger base than other fluorocarbon phosphines towards Lewis acids, *e.g.* H^+, $SnCl_4$, and I_2. Hence the i.r. data suggest a strengthening in the donor action of the $P(CF_3)_2$ group when it is bonded to iron, probably accompanied by a weakening of its π-acceptor properties.

The reaction of [$Co_2(CO)_8$] with [$Fe(cp)(CO)_2\{P(CF_3)_2\}$] gives off 2.0 mol of CO, forming a tetranuclear complex, [$Co_2(CO)_6L_2$], analogous to the product formed under more forcing conditions by other Group 5 bases.[15] The i.r. spectrum of (VII) in the solid state showed four strong terminal ν(CO) bands and no absorptions in the bridging region, consistent with the anticipated [16] structure of D_{3d} symmetry (axial substitution) which would minimise interactions between the bulky ligands (L). Complex (VII), which is insoluble in non-polar solvents, gave an i.r. spectrum in polar solvents which changed with time. The initial spectrum, deduced by extrapolation, is

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[12] M. J. Barrow and G. A. Sim, *J.C.S. Dalton*, 1975, 291.

[13] W. A. G. Graham and E. Wood, personal communication.

[14] W. Ehrl and H. Vahrenkamp, *Chem. Ber.*, 1973, **106**, 2550, 2556.

[15] A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1135 and refs. therein.

[16] J. A. Ibers, *J. Organometallic Chem.*, 1968, **14**, 423; R. F. Bryan and A. R. Manning, *Chem. Comm.*, 1968, 1316.

similar to that in the solid state (Table 1). Although the nature of the change is not known, it does not appear to involve bridged isomers of the type reported earlier for $[Co_2(CO)_6L'_2]$ (L′ = tertiary phosphine, arsine, or stibine).[17] The n.m.r. spectrum of a solution which had stood at room temperature for some hours showed only one absorption for both ^1H and ^{19}F nuclei.

The n.m.r. spectra of the complexes prepared in this work are very similar. The resonance of the cyclopentadienyl protons (τ 4.4—4.8) appeared as a closely spaced doublet caused by H–P coupling, as found in $[Fe(cp)(CO)_2\{P(CF_3)_2\}]$ itself.[1] The ^{19}F n.m.r. spectrum also showed a simple doublet in each case, ^2J(FP) varying from 45 to 55 Hz. The range of ^{19}F shifts observed is narrow, emphasising the similar magnetic environment of the CF_3 groups, and to high field of that for the free ligand (L) as invariably found for co-ordinated trifluoromethylphosphines.[7] It should be noted, however, that the normal increase of ^2J(FP) on co-ordination was not observed. The equivalence of the CF_3 groups and the detection of only one n.m.r. signal for each complex is due to rapid rotation about metal–phosphorus bonds on the n.m.r. time scale, as found by others[18] for similar complexes. Accidental degeneracy of the ^{19}F n.m.r. signals of rotamers is very unlikely.

TABLE 1

Spectroscopic data for some phosphido-bridged complexes

Complex	τ	^3J(PH)/Hz	δ/p.p.m.	^2J(PF)/Hz	$\tilde{\nu}$(CO) and $\tilde{\nu}$(NO)/cm^{-1}
$[Fe(cp)(CO)_2\{P(CF_3)_2\}]$ (L)	4.60 [a]	2.5	45.5	54	2 048vs, 2 008vs [b]
$[Ni(CO)_3L]$ (I)	4.80 [c]	2.0	53.0	54	2 079m, 2 054vs, 2 020vs, 1 996s [b]
$[Co(CO)_2(NO)L]$ (II)	4.80 [c]	2.0	53.5	53	2 059vs, 2 046vs, 2 036(sh),m, 2 016vs, 1 998s, 1 976m, 1 782(sh),m, 1 752s [b]
$[Fe(CO)(NO)_2L]$ (III)	4.40 [a]	2.0	52.7	55	2 055vs, 2 015vs, 1 770vs, 1 720vs [d]
$[Fe(CO)_4L]$ (IV)	4.70 [c]	2.0	53.7	52	2 062s, 2 049vs, 2 021s, 1 996s, 1 970s, 1 947s [b]
$[Mn(CO)_3(NO)L]$ (V)	4.45 [a]		52.4	49	2 060vs, 2 039vs, 2 033(sh),s, 2 022vs, 1 991s, 1 969w, 1 932s, 1 921m, 1 748mw, 1 704m [b]
$[Mn(CO)_4(H)L]$ (VI)	4.40 [a,e]	2.0	53.0	45	2 062s, 2 042vs, 2 000vs, 1 970vs,br [a]
$[Co_2(CO)_6L_2]$ (VII)	4.60 [a]		53.0	48	2 054s, 2 018s, 1 980ms, 1 956vs,[f] 2 058s, 2 020s, 1 970ms [d]

[a] In Me_2CO. [b] In n-C_6H_{14}. [c] In $CDCl_3$. [d] In CH_2Cl_2. [e] H–Mn resonance, τ 17.62, ^2J(HP) 43 Hz. [f] KBr disc.

TABLE 2

Preparation and characterisation of some phosphido-bridged complexes

Starting material	Solvent	Reaction conditions t/d (θc/°C)	Product	Yield (%)	Colour	M.p. (θc/°C)	Analysis [a]/% C	H	Fe	E [b]	M [c]
$[Ni(CO)_4]$ [d]	CCl_3F [e]	1(20)	$[Ni(CO)_3L]$	81	chrome yellow	65—70	24.4 (24.6)	0.9 (1.0)			488
$[Co(CO)_3(NO)]$ [d]	CCl_3F [f]	3(20)	$[Co(CO)_2(NO)L]$	78	red	113—116	26.7 (26.9)	1.2 (1.0)	11.5 (11.4)	12.1 (12.0)	491
$[Fe(CO)_2(NO)_2]$ [d]	CCl_3F [f]	5(20)	$[Fe(CO)(NO)_2L]$	74	deep red	110—112	24.2 (24.3)	1.1 (1.0)	23.0 (22.4)		490
$[Fe_2(CO)_9]$ [g]	CH_2Cl_2 [f]	1(20)	$[Fe(CO)_4L]$	88	cherry red	118—121	30.6 (30.4)	1.0 (1.0)	21.4 (21.8)		514
$[Mn(CO)_4(NO)]$ [d]	$CHCl_3$ [e]	14(20)	$[Mn(CO)_3(NO)L]$	55	dark red	119—121	27.8 (28.0)	1.0 (1.0)			515
$[Mn(CO)_5H]$ [d]	n-C_5H_{12} [e]	2(20)	$[Mn(CO)_4(H)L]$	85	dark yellow	71—74	30.4 (30.4)	1.3 (1.2)	10.5 (10.9)	10.2 (10.7)	514
$[Co(CO)_8]$ [g]	CCl_3F [e]	5 min(20)	$[Co_2(CO)_6L_2]$	90	dark brown	170 (decomp.)	29.3 (29.4)	1.1 (1.0)	11.2 (11.5)	12.0 (12.1)	

[a] Calculated values are given in parentheses. [b] Refers to the metal other than iron. [c] Molecular weight, determined by mass spectroscopy on the major isotope. [d] Allowed to react with an excess of (L). [e] Purified by crystallisation. [f] Purified by sublimation. [g] Allowed to react with a deficit of L.

EXPERIMENTAL

Volatile compounds were handled in a Pyrex vacuum system by standard methods. The solid products of the reactions were generally stable in air for short periods but most gave solutions which were markedly air sensitive. I.r. spectra were recorded on Perkin-Elmer 457 and 257 spectrometers and mass spectra on an A.E.I. MS9 instrument operating at an ionising energy of 70 eV.* N.m.r. spectra were recorded on a Brüker Spectrospin HFX spectrometer operating at 90.00 MHz for ^1H and 84.66 MHz for ^{19}F nuclei, with $SiMe_4$ and CCl_3F as internal standard. The organophosphine complex $[Fe(cp)(CO)_2\{P(CF_3)_2\}]$ was prepared according to the literature method.[1] Details of the preparation of each new complex are given in Table 2.

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* 1 eV ≈ 1.60 × 10^{-19} J.

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