Ligand Substitution in $[Fe_2(CO)_6(NO)(\mu\text{-}PPh_2)]$ and the Isomerism of $[Fe_2(CO)_4(PMe_3)_2(NO)(\mu\text{-}PPh_2)]$†

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Treatment of $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ with $NO^+BF_4^-$ provided $[Fe_2(CO)_6(NO)(\mu\text{-}PPh_2)]$ **1**. Several phosphide-bridged diiron complexes, $[Fe_2(CO)_5(PR_3)(NO)(\mu\text{-}PPh_2)]$ (R = Me **2**, OMe **3** or Ph **4**), $[Fe_2(CO)_4L_2(NO)(\mu\text{-}PPh_2)]$ [L = PMe_3 **5**, PEt_3 **6**, PPh_3 **7**, $P(C_6H_4OMe\text{-}p)_3$ **8**, $P(OMe)_3$ **9**, $P(OEt)_3$ **10**, $P(OPh)_3$ **11**, $\frac{1}{2}Ph_2PCH_2PPh_2$ **12**, $\frac{1}{2}Ph_2PP(CH_2)_3PPh_2$ **13** or $\frac{1}{2}(\eta^5\text{-}C_5H_4PPh_2)_2Fe$ **14**] and $[Fe_2(CO)_3\{P(OMe)_3\}_3(NO)(\mu\text{-}PPh_2)]$ **15**, have been derived from ligand substitution in **1**. These complexes exhibit structural versatility. Interconversion between two isomers of **5**, **5b** and **5c**, has been established by variable-temperature $^{31}P\text{-}\{H\}$ NMR, two-dimensional exchange spectroscopy and single-crystal structure determination.

Dinuclear transition-metal complexes are simple models employed to investigate the co-operative effect between adjacent metals and are of great interest in organometallic chemistry.[1] Among these, phosphide-bridged dinuclear complexes have been extensively studied due to the generally enhanced stability of the dimers.[2] In the past quite a few phosphide-bridged diiron complexes were synthesized and their chemical reactivities examined.[3] An interesting report by Baker *et al.*[3e] described the structural versatility in tertiary phosphorus derivatives of $Fe_2(CO)_7(\mu\text{-}PPh_2)$, $Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)^-$ and $FeCo(CO)_7(\mu\text{-}PPh_2)$. They also reported the possible interconversion of some of the isomers, however the fluxional behaviour was described as ill defined. We speculated that the fluxional behaviour might be better understood through a suitable modification of the aforementioned diiron complexes. Replacement of a CO by a NO ligand might be appropriate since transition metals form nitrosyl complexes which are isoelectronic and isostructural with carbonyl derivatives.[4] In this paper we describe the synthesis and reactivity of $[Fe_2(CO)_6(NO)(\mu\text{-}PPh_2)]$ **1** as well as the isomerization of several of its derivatives.

Experimental

All reactions and manipulations were carried out under N_2 with the use of standard inert-atmosphere and Schlenk techniques. Solvents were dried by standard procedures. All column chromatography was performed under N_2 with silica gel (230–400 mesh ASTM, Merck) as the stationary phase in a column 35 cm in length and 2.5 cm in diameter. The salt $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ was prepared by published procedures.[3d] Infrared measurements were made on a Perkin-Elmer 880 spectrometer, NMR on Bruker AMX500 (^1H, ^{31}P), AC200 (^1H) and AC300 (^1H, ^{31}P) spectrometers. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyser.

Preparations.—$[Fe_2(CO)_6(NO)(\mu\text{-}PPh_2)]$ **1**. One equivalent of solid $NO^+BF_4^-$ (188 mg, 1.61 mmol) was added all at once *via* a Schlenk tube into a vigorously stirring CH_2Cl_2 solution of $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ (1.00 g, 1.61 mmol) prechilled to −60 °C. After 6 h at −60 °C and 3 h at 0 °C the solvent was removed at 0 °C to give a deep red residue. Recrystallization of this from hexane at 0 °C provided dark red powdery compound **1** (558 mg, 70%) (Found: C, 43.75; H, 2.00; N, 2.70. $C_{18}H_{10}Fe_2NO_7P$ requires C, 43.70; H, 2.00; N, 2.85%).

$[Fe_2(CO)_5L(NO)(\mu\text{-}PPh_2)]$ [L = PMe_3 **2**, $P(OMe)_3$ **3** or PPh_3 **4**]. Compounds **2**–**4** were prepared by essentially the same procedure and only that of **2** will be described in detail. Trimethylamine oxide (67 mg, 0.89 mmol) in MeCN (20 cm^3) was added dropwise to a MeCN solution of **1** (400 mg, 0.81 mmol) prechilled to −30 °C. After 3 h at −30 °C the solution was treated with 1.1 equivalent of PMe_3 and the reaction was continued for 1 h. The solution was warmed gradually to room temperature and the solvent removed *in vacuo*. The crude reaction mixture was dissolved in CH_2Cl_2 and soaked with silica (2 g) and pumped dry. It was then carefully placed on the top of a column packed with silica–hexane and chromatographed under nitrogen. Elution with CH_2Cl_2–hexane (1:16) gave first a yellow band in trace amount (not characterized) and then a red band. Complex **2** was isolated from the red band in 26% yield (114 mg) (Found: C, 43.90; H, 3.45; N, 2.55. $C_{20}H_{19}Fe_2NO_6P_2$ requires C, 44.25; H, 3.55; N, 2.60%).

Complex **3** was obtained in 20% yield (Found: C, 40.45; H, 3.25; N, 2.20. $C_{20}H_{19}Fe_2NO_9P_2$ requires C, 40.65; H, 3.25; N, 2.35%) and **4** in 26% yield (Found: C, 57.15; H, 3.40; N, 1.85. $C_{35}H_{25}Fe_2NO_6P_2$ requires C, 57.65; H, 3.45; N, 1.90%).

$[Fe_2(CO)_4L_2(NO)(\mu\text{-}PPh_2)]$ [L = PMe_3 **5**, PEt_3 **6**, PPh_3 **7**, $P(C_6H_4OMe\text{-}p)_3$ **8**, $P(OMe)_3$ **9**, $P(OEt)_3$ **10**, $P(OPh)_3$ **11**, $\frac{1}{2}Ph_2PCH_2PPh_2$ (dppm) **12**, $\frac{1}{2}Ph_2P(CH_2)_3PPh_2$ (dppp) **13** or $\frac{1}{2}(\eta^5\text{-}C_5H_4PPh_2)_2Fe$ (dppf) **14**]. Complexes **5**–**14** were prepared by the same procedure used for **2**, except that 2 equivalents of both Me_3NO and L were used and a more polar solvent [CH_2Cl_2–hexane = (1:5–1:2)] as eluent in column chromatography. A yellow first band (not characterized) and the red second band, $[Fe_2(CO)_5L(NO)(\mu\text{-}PPh_2)]$, were obtained in only small quantities and discarded. Suffixes **b**–**d** are used to describe geometrical isomers found in $[Fe_2(CO)_4L_2(NO)(\mu\text{-}PPh_2)]$ (see below).

Complex **5a** was isolated from the red third band (10%) (Found: C, 44.50; H, 4.45; N, 2.20. $C_{22}H_{28}Fe_2NO_5P_3$ requires

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† *Supplementary data available* (No. SUP 57083, 5 pp.); two-dimensional ^{31}P–^1H homonuclear correlation NMR spectra. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: cal = 4.184 J.

C, 44.70; H, 4.75; N, 2.35%), **5b** and **5c** as a mixture from the red fourth band (12%) (Found: C, 44.15; H, 4.40; N, 2.35%); **6b** and **6c** were isolated as a mixture from the red third band (23%) (Found: C, 49.75; H, 5.95; N, 2.00. $C_{28}H_{40}Fe_2NO_5P_3$ requires C, 49.80; H, 5.95; N, 2.05%); **7b** was isolated from the red third band (13%) (Found: C, 64.45; H, 4.20; N, 1.35. $C_{52}H_{40}Fe_2NO_5P_3$ requires C, 64.80; H, 4.15; N, 1.45%); **8b** and **8c** were isolated as a mixture from the red third band (10%) (Found: C, 60.25; H, 4.75; N, 1.30. $C_{58}H_{52}Fe_2NO_{11}P_3$ requires C, 60.60; H, 5.10; N, 1.20%); **9a** was isolated from the red third band (14%) (Found: C, 38.15; H, 3.90; N, 2.05. $C_{22}H_{28}Fe_2NO_{11}P_3$ requires C, 38.45; H, 4.10; N, 2.05%), **9b** from the red fourth band (17%) (Found: C, 38.10; H, 3.90; N, 1.95%); **10a** was isolated from the red third band (15%) (Found: C, 43.45; H, 4.95; N, 1.75. $C_{28}H_{40}Fe_2NO_{11}P_3$ requires C, 43.60; H, 5.20; N, 1.80%), **10b** from the red fourth band (17%) (Found: C, 43.45; H, 4.95; N, 1.75%); **11b** and **11d** were isolated as a mixture from the red third band (23%) (Found: C, 58.45; H, 3.75; N, 1.30. $C_{52}H_{40}Fe_2NO_{11}P_3$ requires C, 58.95; H, 3.80; N, 1.30%); **12a** was isolated from the red third band (44%) (Found: C, 59.50; H, 3.90; N, 1.70. $C_{41}H_{32}Fe_2NO_5P_3$ requires C, 59.80; H, 3.90; N, 1.70%); **13a** was isolated from the red third band (10%) (Found: C, 60.25; H, 4.30; N, 1.50. $C_{43}H_{36}Fe_2NO_5P_3$ requires C, 60.65; H, 4.25; N, 1.65%), **13c** from the red third band (10%) (Found: C, 60.25; H, 4.10; N, 1.50%); **14c** was isolated from the red third band (20%) (Found: C, 60.05; H, 3.75; N, 1.35. $C_{50}H_{38}Fe_3NO_5P_3$ requires C, 60.45; H, 3.85; N, 1.40%).

$[Fe_2(CO)_3\{P(OMe)_3\}_3(NO)(\mu\text{-}PPh_2)]$ **15**. Complex **1** (500 mg, 1.01 mmol) and $P(OMe)_3$ (0.357 cm^3, 3.03 mol) in toluene (30 cm^3) was heated at 110 °C for 10 h and the solvent was removed under vacuum. The residue was then chromatographed and eluted with CH_2Cl_2. The yellow first band was not characterized. Complex **15** was isolated from the red second band (125 mg, 18%) (Found: C, 41.60; H, 5.25; N, 2.00. $C_{24}H_{37}Fe_2NO_7P_4$ requires C, 41.95; H, 5.40; N, 2.05%).

$[Fe_2(CO)_4(PBu^n{}_3)_2(NO)(\mu\text{-}PPh_2)]$ **16**. Complex **16** was prepared by essentially the same procedure used for **5**. Only impure **16** could be obtained and in very small quantities. $\delta_P[(CD_3)_2CO]$ **16b**, 188 (1 P, dd, μ-P), 60.5 [1 P, d, *J*(PP) 18.0, $PBu^n{}_3$] and 46.2 [1 P, d, *J*(PP) 65.4, $PBu^n{}_3$]; **16c**, 154 (1 P, dd, μ-P), 65.5 [1 P, d, *J*(PP) 52.6, $PBu^n{}_3$] and 55.0 [1 P, d, *J*(PP) 23.2 Hz, $PBu^n{}_3$].

Crystallographic Studies.—Crystals of complex **5c** were grown by cooling a concentrated solution of it in tetrahydrofuran (thf)–hexane (1:4) at −5 °C for several days; those of **1** and **5b** were grown by cooling a concentrated solution of the relevant compound in CH_2Cl_2–hexane (1:5) at −5 °C for several days. The crystals were mounted in thin-walled glass capillaries. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å) with the θ–2θ scan mode. Unit cells were determined by centring 25 reflections in a suitable 2θ range. Other relevant experimental details are listed in Table 1. Absorption corrections (semiempirical, from Ψ scans of three reflections) were applied for complexes **1** and **5c**. No absorption corrections were made for **5b** due to the poor quality of the crystal. All data processing was carried out on a DEC, AXP 3400 computer using the NRCVAX program.[5] The structures were solved by a combination of direct methods (SOLVERS)[6] and Fourier techniques. The structures were refined by minimizing $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F_o)^2$ was calculated from the counting statistics. Atomic scattering factors and anomalous dispersion terms f' and f'' were taken from ref. 7. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the structure-factor calculations in idealized positions with d_{C-H} = 0.98 Å. The final positional parameters are listed in Table 2, selected interatomic distances and angles in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

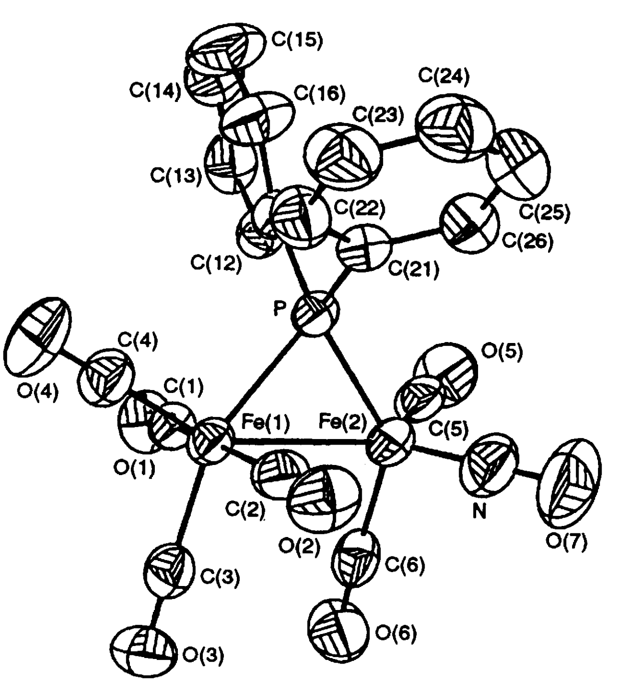


Fig. 1 An ORTEP drawing of $[Fe_2(CO)_6(NO)(\mu\text{-}PPh_2)]$ **1**. Thermal ellipsoids are drawn with 30% probabilities

Results and Discussion

Treatment of carbonyl metalates with $NO^+BF_4^-$ was found to be an effective pathway for incorporation of a NO ligand in several dinuclear Group VI metal complexes.[8] Reaction of $[NEt_4][Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}PPh_2)]$ with 1 equivalent of $NO^+BF_4^-$ in CH_2Cl_2 at −60 °C proceeds similarly to provide $[Fe_2(CO)_6(NO)(\mu\text{-}PPh_2)]$ **1** in good yield. Substitution of phosphine or phosphite for CO in **1** results in the formation of complexes $[Fe_2(CO)_5L(NO)(\mu\text{-}PPh_2)]$ [L = PMe_3 **2**, $P(OMe)_3$ **3** or PPh_3 **4**], $[Fe_2(CO)_4L_2(NO)(\mu\text{-}PPh_2)]$ [L = PMe_3 **5a–5c**, PEt_3 **6b**, **6c**, PPh_3 **7b**, $P(C_6H_4OMe\text{-}p)_3$ **8b**, **8c**, $P(OMe)_3$ **9a**, **9b**, $P(OEt)_3$ **10a**, **10b**, $P(OPh)_3$ **11b**, **11d**, $\frac{1}{2}$ dppm **12a**, $\frac{1}{2}Ph_2P(CH_2)_3PPh_2$ **13a**, **13c**, $\frac{1}{2}(\eta^5\text{-}C_5H_4PPh_2)_2Fe$ **14c**] and $[Fe_2(CO)_3\{P(OMe)_3\}_3(NO)(\mu\text{-}PPh_2)]$ **15**.

Molecular Structure of Complexes **1–15**.—Molecular structures of complexes **1**, **2**, **5b**, **5c**, **6b**, **9a**, **11d**, **14c** and **15** were determined by single-crystal X-ray diffraction. The ORTEP[9] drawings of **1**, **5b** and **5c** are shown in Figs. 1, 2 and 3, respectively. Important interatomic distances and angles are listed in Table 3. The other structures will be published elsewhere

The structural data suggest the presence of a Fe–Fe metal bond in these complexes: the Fe–Fe bond distances, 2.699(1) in **1**, 2.684(4) in **5b** and **5c**, 2.812(1) Å in **5c** lie within the range previously noted for a single bond (2.43–2.88 Å);[3a] the acute Fe(1)–(μ-P)–Fe(2) angles, 74.62(4)°, 74.2(2) and 79.37(5)°, respectively, are much smaller than those [118.7(1), 118.6(1)°] in the similar complexes $[Fe_2(CO)_8(\mu\text{-}PPh_2)]$ and $[Fe_2(CO)_6(PPh_3)_2(\mu\text{-}PPh_2)]^-$[3e] which do not have a metal–metal bond. Including the metal–metal bond, the co-ordination geometries of these complexes are distorted octahedral and trigonal bipyramidal about the six- [Fe(1)] and five-co-ordinate [Fe(2)] metal centres, with the NO ligand bonded to the five-co-ordinate iron atom. The location of the NO ligand was distinguished from that of the CO ligand by conspicuous discrepancies in the thermal parameters for the N and C atoms

Table 1 Crystal data for compounds **1**, **5b** and **5c**[a]

Compound	**1**	**5b**	**5c**
Formula	$C_{18}H_{10}Fe_2NO_7P$	$C_{22}H_{28}Fe_2NO_5P_3$	$C_{22}H_{28}Fe_2NO_5P_3$
M	494.94	591.08	591.08
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/a$	$P2_1/a$
a/Å	8.776(1)	15.509(5)	12.299(1)
b/Å	9.1907(7)	9.781(2)	15.649(2)
c/Å	13.095(1)	19.159(8)	14.681(1)
α/°	84.356(7)		
β/°	105.65(1)	109.46(3)	95.106(6)
γ/°	95.63(1)		
U/Å^3	1009.3(2)	2740(2)	2814.4(5)
Z	2	4	4
D_c/g cm^{-3}	1.629	1.433	1.395
F(000)	496	1216	1216
Crystal size/mm	0.44 × 0.19 × 0.25	0.25 × 0.19 × 0.19	0.31 × 0.25 × 0.25
μ/cm^{-1}	8.6	12.6	12.3
Transmission (maximum, minimum)	1.00, 0.84		1.00, 0.92
2θ Range/°	2.0–45	2.0–50	2.0–50
Data collection (h, k, l)	±9, 9, ±14	±18, 11, 22	±14, 18, 17
Unique data	2625	4819	4959
Observed data ($I > n\sigma$)	2117 (n = 2)	1919 (n = 2.5)	2490 (n = 2.5)
Maximum Δ/σ ratio	0.001	0.066	0.009
R, R'[b]	0.035, 0.042	0.106, 0.113	0.037, 0.038
Goodness of fit	1.92	3.09	1.33
$\Delta\rho$/e Å^{-3}	0.49	1.43	0.44

[a] T = 295 K. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

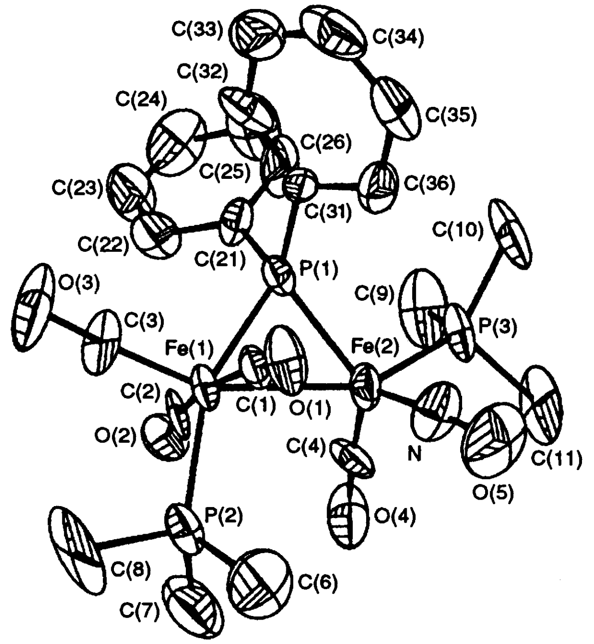


Fig. 2 An ORTEP drawing of $[Fe_2(CO)_4(PMe_3)_2(NO)(\mu\text{-}PPh_2)]$ **5b**. Thermal ellipsoids as in Fig. 1

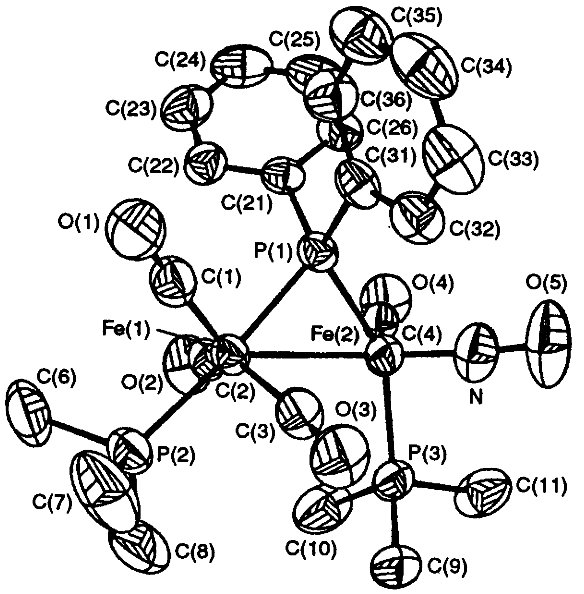
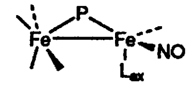
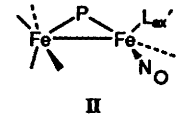


Fig. 3 An ORTEP drawing of $[Fe_2(CO)_4(PMe_3)_2(NO)(\mu\text{-}PPh_2)]$ **5c**. Thermal ellipsoids as in Fig. 1



I



II

when incorrectly assigned.[10] Two different structures, **I** (*e.g.* **1** and **5c**) and **II** (*e.g.* **5b**) are found in these dimers if the difference between CO and phosphine ligands is overlooked. In **I** the μ-PPh_2 and the ligand L_{ax} occupy the axial positions of the trigonal bipyramid, whereas the Fe–Fe bond and the ligand L_{ax}' constitute the axial portion of the trigonal bipyramid in **II**. Significant deviation of the five-co-ordinate iron from an ideal trigonal bipyramid is evident from the angle spanned by the two axial ligands [P–Fe(2)–C(6) 135.8(2)° in **1**, P(1)–Fe(2)–P(3) 153.32(6)° in **5c**, Fe(1)–Fe(2)–P(3) 151.2(2)° in **5b**]. The structure of the monosubstituted complex **2** is similar to that of **1**, except that the C(3)O(3) ligand in **1** is replaced by PMe_3 in **2**; *i.e.* the PMe_3 ligand is co-ordinated to Fe(1) and *trans* to μ-PPh_2. Other monosubstituted complexes such as **3** and **4** should have very similar structures to that of **2** on the basis of the infrared and the ^{31}P NMR spectra (see below). In comparison, both *cis* and *trans* isomers were observed for $[L(OC)_3Ru(\mu\text{-}PPh_2)Co(CO)_3]$.[11] The structures **I** and **II** could be further divided into four distinct geometrical isomers, **a**–**d**, for the disubstituted complexes $[Fe_2(CO)_4L_2(NO)(\mu\text{-}PPh_2)]$ **5**–**14**.

Table 2 Atomic coordinates for complexes **1**, **5b** and **5c**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Complex **1**							
Fe(1)	0.739 83(7)	0.221 94(6)	0.904 29(5)	C(5)	0.422 6(6)	0.524 9(6)	0.794 5(4)
Fe(2)	0.463 23(8)	0.340 10(7)	0.806 23(5)	C(6)	0.419 6(6)	0.297 2(5)	0.932 9(4)
P	0.677 00(14)	0.359 73(12)	0.748 21(9)	C(11)	0.799 1(5)	0.529 5(5)	0.733 2(4)
N	0.325 6(5)	0.235 3(5)	0.722 7(4)	C(12)	0.798 7(6)	0.646 4(5)	0.791 3(4)
O(1)	0.833 7(4)	0.481 9(4)	1.029 3(3)	C(13)	0.896 5(7)	0.773 4(5)	0.781 0(4)
O(2)	0.575 8(5)	−0.031 8(4)	0.787 0(3)	C(14)	0.989 7(8)	0.783 5(6)	0.712 9(5)
O(3)	0.688 8(5)	0.061 6(4)	1.100 1(3)	C(15)	0.990 3(8)	0.670 0(8)	0.654 8(6)
O(4)	1.059 7(5)	0.153 4(5)	0.908 6(4)	C(16)	0.896 0(7)	0.541 6(6)	0.663 8(5)
O(5)	0.383 2(5)	0.642 0(4)	0.782 2(3)	C(21)	0.670 0(5)	0.265 5(4)	0.630 2(3)
O(6)	0.387 1(5)	0.267 5(5)	1.010 7(3)	C(22)	0.785 8(6)	0.175 7(6)	0.627 0(4)
O(7)	0.216 6(5)	0.177 2(5)	0.665 1(4)	C(23)	0.777 6(7)	0.107 9(6)	0.536 1(4)
C(1)	0.795 6(5)	0.385 5(5)	0.977 8(4)	C(24)	0.655 0(8)	0.128 1(6)	0.447 9(4)
C(2)	0.635 9(6)	0.068 7(5)	0.830 3(4)	C(25)	0.538 0(7)	0.215 3(7)	0.450 1(4)
C(3)	0.708 5(6)	0.123 6(5)	1.025 1(4)	C(26)	0.544 5(6)	0.284 7(5)	0.541 3(4)
C(4)	0.936 6(6)	0.182 1(5)	0.907 2(4)				
Complex **5b**							
Fe(1)	0.660 02(22)	0.687 84(28)	0.714 08(17)	C(8)	0.500 5(21)	0.903 8(28)	0.610 2(22)
Fe(2)	0.716 31(23)	0.441 77(30)	0.684 58(19)	C(9)	0.935 8(19)	0.324 0(29)	0.729 7(18)
P(1)	0.758 2(4)	0.548 2(5)	0.793 3(3)	C(10)	0.824 2(21)	0.167 4(23)	0.789 3(17)
P(2)	0.561 6(4)	0.750 5(6)	0.604 5(4)	C(11)	0.794 8(23)	0.161 9(24)	0.630 5(19)
P(3)	0.816 8(5)	0.275 4(5)	0.709 8(4)	C(21)	0.866 2(15)	0.609 4(23)	0.843 9(12)
N	0.623 3(13)	0.338 7(21)	0.660 6(12)	C(22)	0.896 4(17)	0.749 5(27)	0.844 9(14)
O(1)	0.507 8(12)	0.541 5(15)	0.736 2(9)	C(23)	0.980 7(23)	0.789 3(28)	0.886 1(17)
O(2)	0.803 4(12)	0.794 2(16)	0.662 1(9)	C(24)	1.049 7(21)	0.702 9(39)	0.925 3(18)
O(3)	0.655 3(17)	0.918 2(18)	0.808 2(12)	C(25)	1.026 2(22)	0.562 0(34)	0.925 9(18)
O(4)	0.769 5(13)	0.512 6(17)	0.560 2(11)	C(26)	0.937 5(19)	0.524 3(24)	0.885 1(16)
O(5)	0.563 1(15)	0.261 6(22)	0.634 4(12)	C(31)	0.723 6(15)	0.485 0(21)	0.865 9(12)
C(1)	0.570 6(16)	0.594 3(20)	0.730 4(11)	C(32)	0.741 9(16)	0.546 6(24)	0.934 5(14)
C(2)	0.749 1(18)	0.754 7(20)	0.686 5(12)	C(33)	0.712 0(21)	0.505 3(32)	0.989 4(15)
C(3)	0.655 5(21)	0.829 0(24)	0.769 0(14)	C(34)	0.654 3(22)	0.392 0(34)	0.976 8(17)
C(4)	0.751 8(21)	0.486 6(23)	0.616 8(14)	C(35)	0.634 0(21)	0.321 4(26)	0.910 6(18)
C(6)	0.463 1(19)	0.640 8(29)	0.561 7(16)	C(36)	0.663 8(16)	0.366 0(23)	0.852 8(13)
C(7)	0.605 3(23)	0.773 8(29)	0.526 5(16)				
Complex **5c**							
Fe(1)	0.219 13(6)	0.054 80(5)	0.167 69(5)	C(8)	0.363 7(7)	0.225 4(5)	0.088 1(5)
Fe(2)	0.246 01(6)	0.055 52(5)	0.359 90(5)	C(9)	0.500 0(4)	0.148 6(4)	0.348 7(4)
P(1)	0.130 97(11)	−0.017 36(9)	0.268 65(9)	C(10)	0.327 6(5)	0.268 7(4)	0.357 3(5)
P(2)	0.288 01(12)	0.130 25(10)	0.058 73(10)	C(11)	0.401 9(5)	0.171 2(5)	0.512 8(4)
P(3)	0.367 72(11)	0.161 10(10)	0.391 44(10)	C(21)	−0.015 2(4)	0.001 5(3)	0.271 5(3)
N	0.313 9(4)	−0.018 7(3)	0.422 6(3)	C(22)	−0.078 7(4)	0.037 6(3)	0.199 5(3)
O(1)	0.114 1(4)	−0.061 6(3)	0.033 3(3)	C(23)	−0.189 9(5)	0.050 4(4)	0.205 4(4)
O(2)	0.105 2(3)	0.214 1(3)	0.204 1(3)	C(24)	−0.236 8(5)	0.027 7(4)	0.282 7(6)
O(3)	0.436 4(3)	−0.018 3(3)	0.211 8(3)	C(25)	−0.174 6(5)	−0.007 4(4)	0.354 9(5)
O(4)	0.086 3(3)	0.144 9(3)	0.455 1(3)	C(26)	−0.063 6(4)	−0.021 0(3)	0.350 5(4)
O(5)	0.347 7(4)	−0.065 0(4)	0.480 4(3)	C(31)	0.136 1(4)	−0.134 1(3)	0.261 7(3)
C(1)	0.154 8(5)	−0.013 9(4)	0.085 1(4)	C(32)	0.233 3(4)	−0.176 6(4)	0.284 7(4)
C(2)	0.149 4(4)	0.150 3(4)	0.193 3(3)	C(33)	0.236 6(6)	−0.265 9(4)	0.278 3(4)
C(3)	0.349 9(5)	0.010 2(4)	0.200 2(4)	C(34)	0.146 5(7)	−0.310 7(4)	0.247 4(4)
C(4)	0.147 5(4)	0.111 0(3)	0.412 3(3)	C(35)	0.050 5(6)	−0.268 8(4)	0.223 8(4)
C(6)	0.187 4(5)	0.167 8(5)	−0.028 1(4)	C(36)	0.045 8(5)	−0.181 3(4)	0.230 8(4)
C(7)	0.378 8(6)	0.072 3(5)	−0.008 1(5)				

The trisubstituted complex **15** has a structure similar to that of **9a** except that L_{ax}' (structural type **II**) is $P(OMe)_3$ instead of CO.

Ligand Substitution of Complex **1**.—Removal of one or two CO ligands from complex **1** was readily achieved at −30 °C with the use of Me_3NO. Subsequent addition of tertiary phosphorus ligands results in the formation of complexes **2**–**14**. Complex **15** could be obtained only through heating **1** and $P(OMe)_3$ at $\geqslant 90$ °C. The yields for **2**–**15** were not optimized. The generally low yields are due to the thermal instability of $[Fe_2(CO)_{6-n}L_n(NO)(\mu\text{-}PPh_2)]$ ($n = 1$ or 2; L = MeCN or NMe_3) generated *in situ* from complex **1** and Me_3NO, and to the unavoidable decomposition of $[Fe_2(CO)_{6-n}(PR_3)_n(NO)(\mu\text{-}PPh_2)]$ during column chromatography.

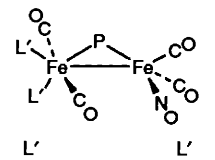
Monosubstitued complexes. That the first ligand substitution in complex **1** occurs only at the six-co-ordinate iron [Fe(1)] is different from what we observed for several dinuclear hydride-bridged Group VI metal nitrosyl carbonyls, where ligand substitution always occurred at the metal centre bearing the NO ligand.[12] Site preference in the first ligand substitution in **1** could be attributable to electronic effects: results of Fenske–Hall calculation on **1**[13] indicate that C(3) on Fe(1) has the lowest Mulliken atomic charge and suggest that C(3)O(3) is the most activated CO ligand.

Disubstituted complexes. Substitution of phosphine for the second CO ligand in complex **1** appears to be non-selective: it could be co-ordinated to Fe(1) (type **a**) or to Fe(2) (types **b**–**d**) with almost equal probability. The phosphine $P(C_6H_{11})_3$ (cone angle = 170°) appears to be too bulky to form disubstituted

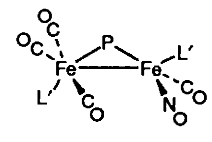
Table 3 Selected bond lengths (Å) and angles (°) for complexes **1**, **5**^{b} and **5c**

	1	**5b**	**5c**
Fe(1)–Fe(2)	2.699(1)	2.684(4)	2.812(1)
Fe(1)–P(1)	2.260(1)	2.225(6)	2.221(2)
Fe(1)–P(2)		2.231(7)	2.216(2)
Fe(2)–P(1)	2.192(1)	2.224(7)	2.182(2)
Fe(2)–P(3)		2.193(7)	2.250(2)
Fe(1)–C(1)	1.819(5)	1.78(2)	1.756(6)
Fe(1)–C(2)	1.814(5)	1.76(3)	1.780(6)
Fe(1)–C(3)	1.816(5)	1.75(2)	1.779(6)
Fe(1)–C(4)	1.790(5)		
Fe(2)–C(4)		1.63(3)	1.725(6)
Fe(2)–C(5)	1.753(5)		
Fe(2)–C(6)	1.799(6)		
Fe(2)–N	1.688(5)	1.69(2)	1.660(5)
C(1)–O(1)	1.135(6)	1.14(3)	1.148(8)
C(2)–O(2)	1.140(6)	1.16(3)	1.154(7)
C(3)–O(3)	1.132(6)	1.15(3)	1.153(7)
C(4)–O(4)	1.132(7)	1.23(3)	1.152(7)
C(5)–O(5)	1.146(6)		
C(6)–O(6)	1.132(7)		
N–O(5)		1.17(3)	1.164(7)
N–O(7)	1.166(6)		
Fe(1)–P(1)–Fe(2)	74.62(4)	74.2(2)	79.37(5)
P(1)–Fe(1)–C(1)	91.2(1)	87.7(7)	86.2(2)
P(1)–Fe(1)–C(2)	86.5(1)	90.3(7)	90.7(2)
P(1)–Fe(1)–C(3)	157.0(2)	103(1)	96.0(2)
P(1)–Fe(1)–C(4)	99.9(2)		
P(1)–Fe(1)–P(2)		155.4(3)	173.27(6)
P(2)–Fe(1)–C(1)		88.7(7)	90.3(2)
P(2)–Fe(1)–C(2)		88.6(8)	85.8(2)
P(2)–Fe(1)–C(3)		101(1)	90.5(2)
C(1)–Fe(1)–C(2)	166.1(2)	169.1(9)	117.6(2)
C(1)–Fe(1)–C(3)	87.8(2)	96(1)	106.6(3)
C(1)–Fe(1)–C(4)	96.8(2)		
C(2)–Fe(1)–C(3)	89.0(2)	94(1)	135.6(2)
C(2)–Fe(1)–C(4)	97.1(2)		
C(3)–Fe(1)–C(4)	103.0(2)		
P(1)–Fe(2)–C(4)		123(1)	95.4(2)
P(1)–Fe(2)–C(5)	100.2(2)		
P(1)–Fe(2)–C(6)	135.8(2)		
P(1)–Fe(2)–N	106.5(2)	119.3(7)	104.0(2)
P(1)–Fe(2)–P(3)		100.2(3)	153.32(6)
P(3)–Fe(2)–C(4)		88.3(8)	91.1(2)
P(3)–Fe(2)–N		95.5(7)	96.2(2)
C(3)–Fe(2)–C(4)	103.0(2)		
C(4)–Fe(2)–N		115(1)	116.3(2)
C(5)–Fe(2)–C(6)	95.7(2)		
C(5)–Fe(2)–N	113.8(2)		
C(6)–Fe(2)–N	104.2(2)		
Fe(1)–Fe(2)–C(4)		98.4(8)	115.1(2)
Fe(1)–Fe(2)–C(5)	127.7(2)		
Fe(1)–Fe(2)–C(6)	84.1(2)		
Fe(1)–Fe(2)–N	116.9(2)	106.5(7)	124.2(2)
Fe(1)–Fe(2)–P(3)		151.2(2)	103.07(5)
Fe(2)–Fe(1)–C(1)	87.3(1)	84.4(6)	134.5(2)
Fe(2)–Fe(1)–C(2)	80.4(2)	85.8(6)	78.5(2)
Fe(2)–Fe(1)–C(3)	105.5(2)	156(1)	73.1(2)
Fe(2)–Fe(1)–C(4)	151.3(2)		
Fe(2)–Fe(1)–P(2)		102.5(2)	134.74(5)
Fe(1)–C(1)–O(1)	175.7(4)	174(2)	177.2(5)
Fe(1)–C(2)–O(2)	176.7(4)	174(2)	175.4(5)
Fe(1)–C(3)–O(3)	179.6(4)	176(3)	172.9(5)
Fe(1)–C(4)–O(4)	178.3(4)		
Fe(2)–C(4)–O(4)		172(3)	173.4(4)
Fe(2)–C(5)–O(5)	174.2(5)		
Fe(2)–C(6)–O(6)	177.4(5)		
Fe(2)–N–O(5)		169(2)	165.7(5)
Fe(2)–N–O(7)	170.7(4)		

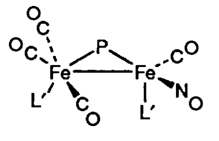
complexes. Complexes of type **a** apparently are more sterically congested and are confined to bidentate phosphine ligands (**12a**, **13a**) and less bulky monodentate phosphines. For



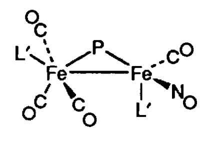
	L′		L′
5a	PMe_3	**12a**	½ dppm
9a	$P(OMe)_3$	**13a**	½ dppp
10a	$P(OEt)_3$		



	L′		L′
5b	PMe_3	**9b**	$P(OMe)_3$
6b	PEt_3	**10b**	$P(OEt)_3$
7b	PPh_3	**11b**	$P(OPh)_3$
8b	$P(C_6H_4OMe\text{-}p)_3$		



	L′		L′
5c	PMe_3	**13c**	½ dppp
6c	PEt_3	**14c**	½ dppf
8c	$P(C_6H_4OMe\text{-}p)_3$		



	L′
11d	$P(OPh)_3$

phosphorus ligands with electron-withdrawing substituents complexes of type **b** are strongly favoured. For instance, no derivatives of type **c** are found in the reactions of complex **1** with $P(OR)_3$ (R = Me, Et or Ph). For trialkylphosphine ligands, complexes of types **b** and **c**, which rapidly establish an equilibrium (see below), are obtained as a mixture. Isomer **b** seems to be more stable than **c** for $[Fe_2(CO)_4(PR_3)_2(NO)(\mu\text{-}PPh_2)]$ (R = Ph **7** or $C_6H_4OMe\text{-}p$ **8**) since we could isolate only **7b**, and the relative yield of **8c** : **8b** is 1 : 4 at best. Isomer **d** is found in $[Fe_2(CO)_4\{P(OPh)_3\}_2(NO)(\mu\text{-}PPh_2)]$ **11** only, and the reason for its formation is not yet clear. A trisubstituted derivative of complex **1** was obtained only when $P(OMe)_3$ was used, apparently due to the steric constraints.

Most of the aforementioned complexes can also be synthesized by heating a mixture of **1** in toluene with appropriate quantities of phosphines at appropriate temperatures (60–90 °C). Although the derivatives of **1** in this study still retain the metal–metal bond, heterolytic fission of the metal Fe→M bond was found to occur in the reaction of two closely related isoelectronic complexes $[(OC)_4Fe(\mu\text{-}AsMe_2)M]$ [M = $Fe(CO)_2(NO)$ or $Co(CO)_3$] with phosphorus donors L [equation (1)].[14] Apparently μ-PPh_2 is a better bridge than μ-

$$[(OC)_4\overline{Fe(\mu\text{-}AsMe_2)M}] + L \longrightarrow [(OC)_4Fe(\mu\text{-}AsMe_2)ML] \quad (1)$$

$AsMe_2$ in preventing the Fe–Fe bond from breaking during ligand substitution, or helps the Fe–Fe bond to reform after ligand substitution. Two complexes which are closely related to **1**, $[(OC)_4Fe(\mu\text{-}PPh_2)Fe(CO)_3]$ and $[(OC)_4Fe(\mu\text{-}PPh_2)Co(CO)_3]$, were reported to react with phosphorus donors (L) to provide the monosubstituted product, where L resided on the six-co-ordinate iron centre and was *trans* to the PPh_2 bridge, and two disubstituted products which had structures similar to those of **b** and **c**. No isomers of the type **a** or **d** were mentioned in the same report.

Spectroscopic Characterization of Complexes **1–15**.—Both ν(CO) and ν(NO) absorptions in the infrared spectra (Table 4) decrease in intensity as more CO ligands in complex **1** are displaced by phosphorus donors. The ν(NO) absorption is also a sensitive indicator for the location of phosphorus ligands, *e.g.* complexes of type **a** have ν(NO) values 10–20 cm^{-1} higher than those of their isomers. The $^{31}P\text{-}\{^1H\}$ NMR spectra for complexes **1–15** are consistent with their formulation. The chemical shifts of μ-P for all complexes appear in the range δ 95–207. These values are consistent with a 'closed' PPh_2 bridge,[2f,15] *i.e.* the presence of a Fe–Fe bond. The $\delta_{\mu\text{-}P}$ value is sensitive to both the Fe(1)–(μ-P)–Fe(2) angle and Fe(1)–Fe(2) distance. For instance, complex **5c** has a longer

Table 4 Infrared spectra in the ν(CO) region and ^1H and ^{31}P-{H} NMR spectra of compounds **1–15**

Complex[a]	$\tilde{\nu}$(CO), $\tilde{\nu}$(NO)[b]/cm^{-1}	δ_H[c,d] J/Hz	δ_P/[c,e] J/Hz
1 *	2089m, 2018vs, 1944m, *1729m*		194 (s, μ-PPh_2)
2 *	2036w, 1981vs, 1922m, *1702m*	1.90 [9 H, d, *J*(PH) 10.3, Me]	196 [1 P, d, *J*(PP) 24.2, μ-P], 20.8 (1 P, d, PMe_3)
3	2044w, 1991vs, 1934m, *1710m*	3.92 [9 H, d, *J*(PH) 11.8, OMe]	193 [1 P, d, *J*(PP) 46.9, $P(OMe)_3$], 174(1 P, d, μ-P)
4	2056w, 1986vs, 1931m, *1701m*		190 [1 P, d, *J*(PP) 23.8, μ-P], 61.4 (1 P, d, PPh_3)
5a	1998w, 1954s, 1928s, 1891m, *1674m*	1.71 (18 H, m, Me)	184 (1 P, dd, μ-P), 18.4 [1 P, d, *J*(PP) 14.0, PMe_3], 14.4 [1 P, d, *J*(PP) 26.0, PMe_3]
5b *,[f]	2015w, 1945s, 1914vs, 1886(sh), *1656m*	1.70 [9 H, d, *J*(PH) 9.5, Me], 1.57 [9 H, d, *J*(PH) 9.5, Me]	175 (1 P, dd, μ-P), 36.3 [1 P, d, *J*(PP) 14.0, PMe_3], 18.1 [1 P, d, *J*(PP) 68.0, PMe_3]
5c *,[f]			152 (1 P, dd, μ-P), 37.2 [1 P, d, *J*(PP) 52.2, PMe_3], 20.5 [1 P, d, *J*(PP) 20.2, PMe_3]
6b *,[f]	2012w, 1954s, 1898vs, *1655m*	2.12 (12 H, m, CH_2), 1.27 [9 H, d, *J*(PH) 7.5, Me], 1.22 (9 H, d, Me)	181 (1 P, dd, μ-P), 64.4 [1 P, d, *J*(PP) 13.2, PEt_3], 49.0 [1 P, d, *J*(PP) 64.8, PEt_3]
6c [f]		1.90 (br, 12 H, CH_2), 1.06 (br, 18 H, Me)	150 (1 P, dd, μ-P), 69.9 [1 P, d, *J*(PP) 51.6, PEt_3], 59.0 [1 P, d, *J*(PP) 16.8, PEt_3]
7b	2005w, 1953s, 1892m, *1661m*		151 (1 P, dd, μ-P), 77.4 [1 P, d, *J*(PP) 42.4, PPh_3], 63.0 [1 P, d, *J*(PP) 20.0, PPh_3]
8b *	2007w, 1943s, 1887m, *1660m*	3.85 (9 H, s, OMe), 3.76 (9 H, s, OMe)	152 (1 P, dd, μ-P), 77.4 [1 P, d, *J*(PP) 42.0, $P(C_6H_4OMe)_3$], 62.6 [1 P, d, *J*(PP) 20.0, $P(C_6H_4OMe)_3$]
8c			96.3 (1 P, dd, μ-P), 83.9 [1 P, d, *J*(PP) 30.2, $P(C_6H_4OMe)_3$], 77.4 [1 P, d, *J*(PP) 22.0, $P(C_6H_4OMe)_3$]
9a *	2018w, 1967s, 1909m, *1690m*	3.81 [9 H, d, *J*(PH) 9.6, OMe], 3.54 [9 H, d, *J*(PH), 10.9, OMe]	192 [1 P, d, *J*(PP) 67.2, $P(OMe)_3$] 183 [1 P, d, *J*(PP) 16.4, $P(OMe)_3$], 178 (1 P, dd, μ-P)
9b	2022w, 1964s, 1907m, *1681m*	3.47 [9 H, d, *J*(PH) 11.8, OMe], 3.38 [9 H, d, *J*(PH) 12.0, OMe]	194 [1 P, d, *J*(PP) 72.0, $P(OMe)_3$], 179 [1 P, d, *J*(PP) 50.6, $P(OMe)_3$], 163 (1 P, dd, μ-P)
10a	2014w, 1964s, 1907s, *1687m*	4.23, (6 H, m, CH_2), 4.06 (6 H, m, CH_2), 1.35 [9 H, t, *J*(HH) 7.0, Me], 1.23 [9 H, t, *J*(HH) 7.0, Me]	199 [1 P, d, *J*(PP) 67.2, $P(OEt)_3$], 176 [1 P, d, *J*(PP) 14.4, $P(OEt)_3$], 170 (dd, 1 P, μ-P)
10b [f]	1993w, 1929s, 1877m, *1670m*	4.20 (6 H, m, CH_2), 3.92 (6 H, m, CH_2), 1.36 [9 H, t, *J*(HH) 7.0, Me], 1.14 [9 H, t, *J*(HH) 7.0, Me]	191 [1 P, d, *J*(PP) 73.0, $P(OEt)_3$], 175 [1 P, d, *J*(PP) 47.0, $P(OEt)_3$], 166 (1 P, dd, μ-P)
11b [f]	2031m, 1978vs, 1920s, *1679m*		185 [1 P, d, *J*(PP) 63.6, $P(OPh)_3$], 170 (1 P, dd, μ-P), 164 [1 P, d, *J*(PP) 42.0, $P(OPh)_3$]
11d *,[f]			174 [1 P, d, *J*(PP) 25.2, $P(OPh)_3$], 173 (1 P, d, μ-P), 169 [1 P, s, $P(OPh)_3$]
12a	2007m, 1945s, 1899m, *1678m*	4.72 [2 H, pseudo-t, *J*(PH) 10.8, CH_2]	207 [1 P, dd, *J*(PP) 70.0, 26.2, μ-P], 65.7 [1 P, dd, *J*(PP) 85.5, 70.0, PCH_2], 63.4 [1 P, dd, *J*(PP) 85.5, 26.2, PCH_2]
13a	1994w, 1960m, 1923s, *1688m*		176 (1 P, dd, μ-P), 46.2 [1 P, d, *J*(PP) 23.0, PCH_2], 45.3 [1 P, d, *J*(PP) 68.4, PCH_2]
13c	1977w, 1923m, 1892w, *1673m*		177 (1 P, dd, μ-P), 66.8 [1 P, d, *J*(PP) 21.6, PCH_2], 51.4 [1 P, d, *J*(PP) 68.4, PCH_2]
14c *	1980m, 1919s, 1894(sh), *1689m*	4.75–3.90 (8 H, m, C_5H_4)	176 (1 P, dd, μ-P), 66.9 [1 P, d, *J*(PP) 18.0, PPh_2], 45.7 [1 P, d, *J*(PP) 75.6, PPh_2]
15 *	2003w, 1939s, 1887m, *1654m*	3.88 [9 H, d, *J*(PH) 11.0, OMe], 3.54 [9 H, d, *J*(PH) 11.3, OMe], 3.41 [9 H, d, *J*(PH) 12.1, OMe]	197 [1 P, d, *J*(PP) 58.6, $P(OMe)_3$], 180 [1 P, dd, *J*(PP) 57.1, 29.4, $P(OMe)_3$], 175 [1 P, d, *J*(PP) 29.4, $P(OMe)_3$], 159 [1 P, dd, *J*(PP) 58.6, 57.1, μ-P]

[a] Complexes with asterisks were structurally characterized by single-crystal X-ray diffraction. [b] Measured in CH_2Cl_2 solution; ν(NO) values are italicized. [c] Measured in $(CD_3)_2CO$; s = singlet, d = doublet, t = triplet, m = multiplet. [d] Reported in ppm relative to δ($SiMe_4$) 0. All phenyl protons appear as multiplets at δ 7.90–6.74. [e] Reported in ppm relative to δ(85% H_3PO_4) 0. [f] The NMR spectra were recorded at −60 °C.

Fe–Fe distance [2.812(1) Å] and a larger Fe–P–Fe angle [79.37(5)°] than those in **5b** [2.684(4) Å; 74.2(2)°] and the $\delta_{\mu\text{-P}}$ value of the former (152) appears upfield from that of the latter (175). Two-bond phosphorus–phosphorus coupling constants for the complexes [$(Ph_3P)(OC)_3Fe(\mu\text{-}PPh_2)M(CO)_2(PPh_3)$] (M = Rh or Ir),[16] [$(Ph_3P)(OC)_3Ru(\mu\text{-}PPh_2)Co(CO)_2(PPh_3)$],[17] [$(Me_3P)(OC)_3Fe(\mu\text{-}PBu^t{}_2)Co(CO)_2(PMe_3)$][18] and [$(OC)_3\{(MeO)_3P\}Fe(\mu\text{-}PPh_2)Co(CO)_2\{P(OMe)_3\}$],[3e] which are isoelectronic with [$L(OC)_3Fe(\mu\text{-}PPh_2)Fe(CO)L(NO)$], appear to be dependent on the metals and are perplexing. Nonetheless, structural determinations (see Table 4 for complexes labelled with asterisks) for several complexes in this study greatly facilitate assignments, and some trends could be clarified: (1) the ratio of coupling constant involving μ-P/P$(OR)_3$ *vs.* μ-P/PR_3 is about 1.5–2.5:1, similar to those reported;[3e] (2) in general, the two-bond coupling constant increases as the angle P(1)–Fe–P(2) widens toward 180°, *e.g.* μ-P has larger coupling with the *trans* phosphorus-donor atom on Fe(1); (3) phosphorus atoms on five-co-ordinate iron have larger two-bond phosphorus–phosphorus coupling constants than those on six-co-ordinate iron.

Exchange in Disubstituted Complexes.—A very interesting feature in this study is the fluxional behaviour of several isomeric pairs of complexes even at low temperature. Although the ^{31}P NMR signals of the two phosphorus-donor ligands in complexes of type **a** remain sharp at temperatures up to 45 °C, interconversion of isomers **b** and **c** for [$Fe_2(CO)_4(PR_3)_2(NO)(\mu\text{-}PPh_2)$] (R = Me **5**, Et **6** or Bu^n **16**) is very facile in the solution, and the separation of one from the other is difficult. The three isomeric pairs have very similar variable-temperature spectra and should follow very similar exchange processes. We were able to grow single crystals of **5c** and **5b** in pure form from thf–hexane and from CH_2Cl_2–

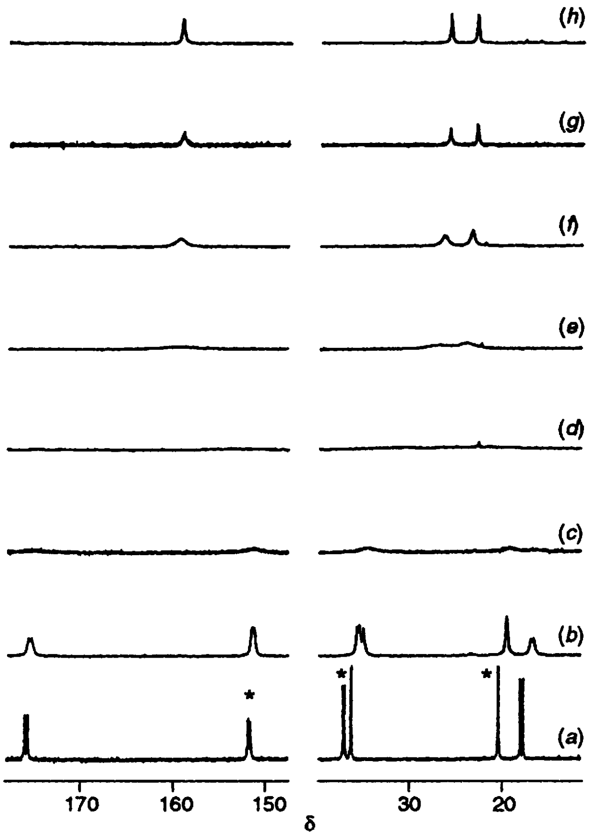


Fig. 4 Variable-temperature $^{31}P-\{H\}$ NMR spectrum of complexes **5b**, **5c** in [$^2H_8$]toluene at (*a*) 213, (*b*) 253, (*c*) 273, (*d*) 293, (*e*) 313, (*f*) 333, (*g*) 353 and (*h*) 373 K. Peaks marked with an asterisk are from **5c**

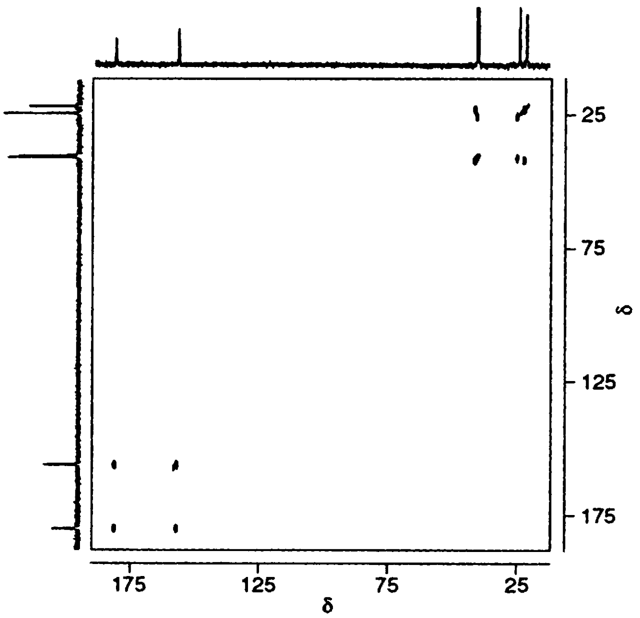


Fig. 5 The EXSY $^{31}P-\{H\}$ two-dimensional homonuclear correlation *via* dipolar coupling for complexes **5b**, **5c** in [$^2H_8$]toluene at 243 K

hexane, respectively, and clarify the ^{31}P NMR spectra for both at low temperature. There is dramatic change in the relative quantities of **b** to **c** in solvents of different polarities. The ratio [**b**]:[**c**] for [$Fe_2(CO)_4(PR_3)_2(NO)(\mu-PPh_2)$] in acetone at −10 °C decreases as R increases in size (2.5:1 for R = Me, 1:2 for Et, 1:6 for Bu^n). The energy differences between **c** and **b** were calculated to be 0.46, −0.24 and −0.9 kcal mol^{-1} for R = Me, Et and Bu^n, respectively. On the contrary, in toluene a complex of type **b** is found only for **5** (L = PMe_3). The ratio of [**5b**]:[**5c**] is 1:1.4 at −20 °C and the energy difference between the two is −0.17 kcal mol^{-1}. Another interesting feature of the $^{31}P-\{H\}$ NMR spectra is the inversion of the order of $\delta(PR_3)$ as one goes from **c** to **b**. Fig. 4 shows the variable-temperature $^{31}P-\{H\}$ NMR spectra for **5b**, **5c** in [$^2H_8$]toluene. There is considerable line broadening at −20 °C. The peaks of **5b** and **5c** collapse into the baseline at 0 °C and coalesce at 40 °C. The fast-exchange limit could not be reached even at 150 °C [in $(CD_3)_2SO$] when **5b**, **5c** decomposed completely. Recently Pregosin[19] and Müller[20] and co-workers demonstrated that two-dimensional exchange spectroscopy (EXSY) could be used to study the chemical exchange behaviour of organometallic complexes. We were able to confirm the mutual exchange for **5b**, **5c** (Fig. 5) as well as for **6b**, **6c** and **16b**, **16c** (SUP 57083) *via* such experiments.[21] The exchange processes cease at −50, −30 and −20 °C, for **5b**, **5c**, **6b**, **6c** and **16b**, **16c**, respectively.

It is not possible for the exchange process to involve the dissociation of PR_3 since we did not observe any disubstituted derivatives with mixed phosphorus ligands when a different phosphine was added to the mixture of **5b** and **5c**. Breakage of the Fe–(μ-P) is disfavoured in view of the stability of similar phosphide-bridged diiron complexes. Interconversion of **5b** and **5c** is likely *via* the following sequence: (1) breakage of the Fe–Fe bond; (2) rotation of $Fe(CO)(PMe_3)(NO)$ around the Fe–(μ-P) bond; (3) reformation of the Fe–Fe bond. An alternative exchange mechanism for **5b** and **5c** does not involve any bond breakage and is similar to Berry's pseudo-rotation at a trigonal-bipyramidal iron centre. Both mechanisms are consistent with the following observations: (*a*) the $^{31}P-\{H\}$ NMR spectra of diphosphine-bridged **14c** and **13c** remain static and show no line broadening over the temperature range of 25–100 °C; (*b*) **8b** and **8c** could not be converted into each other at temperatures below their decomposition. The much more restricted motion in these complexes would greatly raise the activation energy for both mechanisms.

The $^{31}P-\{H\}$ NMR spectrum of [$Fe_2(CO)_4\{P(OMe)_3\}_2(NO)(\mu-PPh_2)$] **9b** at −40 °C is consistent with its solid-state structure. Complexes **9b** and [$Fe_2(CO)_4\{P(OEt)_3\}_2(NO)(\mu-PPh_2)$] **10b** should have similar structures because of the similarity of their spectra. Complexes **9b** and **10b** behave similarly in solution and the $^{31}P-\{H\}$ NMR signals of the two $P(OR)_3$ and μ-P show significant broadening from room temperature to 90 °C. The nature of this fluxional process has not yet been elucidated. It is somewhat surprising that a new structural type, **d**, is found in addition to **b** in the complex [$Fe_2(CO)_4\{P(OPh)_3\}_2(NO)(\mu-PPh_2)$] **11**. Furthermore, a two-dimensional EXSY experiment (SUP 54083) confirmed that **11b** and **11d** are converted into each other readily even at −30 °C.

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