Complexes with Functional Phosphines. 20.[1] Synthesis of Iron Complexes with Keto Phosphine Ligands and Crystal Structure of the Bis(phosphino enolato) Complex $cis\text{-}\overline{\mathrm{Fe[Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O}}\mathrm{)Ph]_2(CO)_2}$

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Many interesting ruthenium complexes are known with heterodifunctional ligands such as ether, keto, or ester phosphines, where these oxygen–phosphorus ligands (P, O) bind to the metal center more strongly through the phosphorus than the oxygen donor function.[2] This is clearly shown in complexes which are stereochemically nonrigid by virtue of the hemilabile behavior of the P, O ligand: reversible coordination of the oxygen is observed, whereas the metal–phosphorus bond remains intact.[2,3] The lability of the metal–oxygen bond may also be exploited for the reversible binding of small molecules, e.g. carbon monoxide, to the metal center.[3] As part of our ongoing interest for the chemistry of complexes containing P, O ligands or their corresponding enolates, we decided to investigate the iron complexes of such ligands, for which we could find no example in the literature.

Experimental Section

All reactions were performed in Schlenk-type flasks under nitrogen. Solvents were dried and distilled under nitrogen: diethyl ether and tetrahydrofuran from sodium benzophenone ketyl; toluene, pentane, and hexane from sodium; dichloromethane over P_2O_5. Nitrogen (Air liquide R-grade) was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water. Elemental analyses (C, H, and N) were performed by the Service Central de Microanalyses du CNRS. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin-Elmer 398 spectrophotometer or on a Bruker IFS instrument. The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at 200.13 and 81.02 MHz, respectively, on a FT-Bruker WP 200 SY instrument. Chemical shifts, in ppm, are positive downfield relative to external Me_4Si for ^{1}H and to external 85% H_3PO_4 in H_2O for ^{31}P NMR spectra. Absolute ethanol (Carlo Erba) and $Fe(CO)_5$ (BASF) were used as received, and $Ph_2PCH_2C(O)Ph$ (P$\sim$O),[4] $FeBr_2(CO)_4$,[5] $Fe_3(CO)_{12}$,[6] and $[Et_3NH][HFe_3(CO)_{11}]$[7] were prepared according to the literature. Anhydrous $FeBr_2$ was prepared by reaction of Fe metal with Br_2 in refluxing THF.[8]

$Ph_2P(O)CH_2C(O)Ph$. This ligand was prepared by reaction of P$\sim$O with commercial H_2O_2 (30%) in ethanol under reflux (0.5 h). The solvent was evaporated, the oily residue was dissolved in CH_2Cl_2, and the solution was filtered through $MgSO_4$. Evaporation to dryness afforded an oil which was treated with Et_2O, giving a white solid. It was filtered out and dried under vacuum (90% yield). Anal. Calcd for $C_{20}H_{17}O_2P$ (M = 319.89): C, 75.02; H, 5.31. Found: C, 74.56; H, 5.27. ^{1}H NMR ($CDCl_3$): δ 4.14 (d, 2 H, ^2J(P–H) = 15.4 Hz, CH_2), 7.41–8.00 (m, 15 H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 27.2 (s). IR (KBr): ν(C=O) 1681 vs, ν(P=O) 1181 vs cm^{-1}.

$Ph_2P(S)CH_2C(O)Ph$. This ligand was prepared by reaction of P$\sim$O (0.580 g, 1.90 mmol) with elemental S (0.060 g, 1.87 mmol) in toluene (50 mL) at 80 °C for 1 h. The solvent was evaporated, and the residue was extracted in Et_2O (40 mL). Evaporation to dryness afforded a cream solid, which was washed with hexane and dried in vacuo (0.536 g, 84% yield). Anal. Calcd for $C_{20}H_{17}OPS$ (M = 335.9): C, 71.44; H, 5.06. Found: C, 70.83; H, 5.08. ^{1}H NMR ($CDCl_3$): δ 4.32 (d, 2 H, ^2J(P–H) = 14.9 Hz, CH_2), 7.28–8.04 (m, 15 H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 37.5 (s). IR (KBr): ν(C=O) 1679 vs, ν(P=S) 623 s cm^{-1}.

Preparation of $Fe_3(CO)_{11}(P\sim O)$ (1). Solid P$\sim$O (0.300 g, 0.99 mmol) was added to a THF solution (100 mL) of $Fe_3(CO)_{12}$ (0.510 g, 1.00 mmol) at −78 °C. Under constant stirring, Me_3NO (0.074 g, 0.99 mmol) in THF (100 mL) was added over a period of 15 min. The reaction mixture was then slowly brought to room temperature (2 h). The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel. Elution with toluene/pentane (1:1) afforded *cis*-$\overline{\mathrm{Fe(CO)_2[Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O}}\mathrm{)Ph]_2}$ (**5**) (0.017 g) (see below). Elution with toluene/pentane (3:1) gave green **1**, which was recrystallized from pentane (0.523 g, 67% yield). This complex should be stored below −15 °C. Anal. Calcd for $C_{31}H_{17}Fe_3O_{12}P$ (**1**) (M = 779.24): C, 47.73; H, 2.18. Found: C, 47.99; H, 2.45. ^{1}H NMR ($CDCl_3$): δ 4.32 (d, 2 H, ^2J(P–H) = 7.83 Hz, CH_2), 7.10–7.90 (m, 15 H, Ph). ^{31}P{^{1}H} NMR (THF/C_6D_6): δ 40.6 (s). IR (THF): ν(C≡O) 2083 m, 2030 s, 2008 vs cm^{-1}. IR (KBr): ν(CO) 2085 m, 2003 vs br, 1785 m, ν(C=O) 1676 mw cm^{-1}.

Pyrolysis of 1. A solution of **1** (0.039 g, 0.05 mmol) in toluene (10 mL) was heated at 60 °C for 45 min. The color changed from green to red. The solution was filtered through a Celite-padded filter funnel and concentrated. Addition of pentane afforded a yellowish powder of $Fe(CO)_4(P\sim O)$ (**2**) (0.023 g, 97% molar yield), which was identified by comparison with an authentic sample prepared as described below.

Preparation of $Fe(CO)_4(P\sim O)$ (2). Solid P$\sim$O (2.31 g, 7.60 mmol) was added to a THF solution (50 mL) of $Fe(CO)_5$ (1 mL, 7.61 mmol) at −78 °C. Under constant stirring, Me_3NO (0.570 g, 7.60 mmol) in THF (50 mL) was added over a period of 15 min. The reaction mixture was then slowly brought to room temperature (2 h). The solvent was evaporated under reduced pressure, and the residue was chromatographed on alumina (it decomposes on silica gel). Elution with CH_2Cl_2/pentane (1:3) afforded an orange-red solution of the product. Recrystallization from CH_2Cl_2/hexane afforded yellowish, air-stable microcrystals (1.89 g, 53% yield). Anal. Calcd for $C_{24}H_{17}FeO_5P$ (**2**) (M = 471.7): C, 61.05; H, 3.60. Found: C, 61.24; H, 3.69. ^{1}H NMR ($CDCl_3$): δ 4.22 (d, 2 H, ^2J(P–H) = 9.2 Hz, CH_2), 7.35–7.78 (m, 15 H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 66.5 (s). IR (CH_2Cl_2): ν(C≡O) 2051 s, 1977 m, 1945 s, 1931 s, ν(C=O) 1675 mw cm^{-1}. IR (KBr): ν(C≡O) 2050 s, 1983 m, 1946 s, 1930 s, ν(C=O) 1673 ms cm^{-1}.

Preparation of $Fe(CO)_3(P\sim O)_2$ (3). Solid P$\sim$O (2.60 g, 8.55 mmol) was added to a n-BuOH solution (80 mL) of $[Et_3NH][HFe_3(CO)_{11}]$ (2.50, 4.32 mmol). After 2 h of reflux, the mixture was cooled to room temperature, and a yellow solid precipitated from the dark solution. It was filtered off, washed with pentane (3 × 15 mL), and extracted with CH_2Cl_2. This solution was concentrated, and addition of methanol afforded the yellow, air-stable microcrystalline product (1.47 g, 46% molar yield). Anal. Calcd for $C_{43}H_{34}FeO_5P_2$ (**3**) (M = 747.55): C, 69.02; H, 4.54. Found: C, 68.81; H, 4.58. ^{1}H NMR ($CDCl_3$): δ 4.25 (d, 2 H, ^2J(P–H) = 7.9 Hz, CH_2), 7.28–7.79 (m, 15 H, Ph). ^{31}P{^{1}H} NMR (THF/C_6D_6): δ 78.3 (s). IR ($CHCl_3$): ν(C≡O) 1890 s, 1870 s cm^{-1}. IR (KBr): ν(C≡O) 1871 vs br, ν(C=O) 1666 ms cm^{-1}.

Preparation of $FeBr_2(CO)_2(P\sim O)_2$ (4). Solid P$\sim$O (1.38 g, 4.54 mmol) was added to a CH_2Cl_2 solution (100 mL) of $FeBr_2(CO)_4$ (0.740 g, 2.25 mmol) at room temperature. After stirring was maintained for 2 h, the solution was filtered through a Celite-padded filter funnel and concentrated. Addition of ethanol induced precipitation of a yellow microcrystalline product (1.72 g, 86% yield). Anal. Calcd for $C_{42}H_{34}Br_2FeO_4P_2$ (**4**) (M = 879.4): C, 57.31; H, 3.86. Found: C, 57.47; H, 4.05. ^{1}H NMR (CD_2Cl_2): δ 5.02 (virtual t, 2 H, ^{2+4}J(P–H) = 9.58 Hz, CH_2), 7.19–7.96 (m, 15 H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 35.9 (s). IR (CH_2Cl_2): ν(C≡O) 2042 s, 1992 s, 1984 sh cm^{-1}. IR (KBr): ν(C≡O) 2041 s, 1999 s, ν(C=O) 1675 m, 1671 m cm^{-1}.

Preparation of $cis\text{-}\overline{\mathrm{Fe[Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O}}\mathrm{)Ph]_2(CO)_2}$ (5). A solution of

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Table I. Crystallographic Data for *cis*-$Fe[Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph]_2(CO)_2$ (**5**·$THF\cdot{}^1/_2C_6H_6$)

formula	$C_{49}H_{43}O_5P_2Fe$	V, Å^3	2048.5
fw	829.7	Z	2
cryst system	triclinic	ρ(calcd), g cm^{-3}	1.345
space group	$P\bar{1}$	T, °C	–100
a, Å	13.090 (4)	F(000)	866
b, Å	16.482 (5)	λ(Cu Kα), Å	1.5418
c, Å	10.274 (3)	μ, cm^{-1}	40.807
α, deg	92.98 (2)	R^a	0.039
β, deg	108.87 (2)	$R_w{}^b$	0.060
γ, deg	100.40 (2)		

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$.

NaOH (0.21 g, 5.25 mmol) in EtOH (15 mL) was added to a solution of **4** (1.00 g, 1.13 mmol) in THF (100 mL). Progressive precipitation of NaBr occurred, and after stirring for 1 h, the solvent was removed under reduced pressure. The solid was extracted with CH_2Cl_2; this solution was filtered through a Celite-padded filter funnel and concentrated. Addition of hexane produced a yellow precipitate of the air-stable product (0.70 g, 86% yield). Anal. Calcd for $C_{42}H_{32}FeO_4P_2$ (**5**) (M = 717.6): C, 70.23; H, 4.45. Found: C, 70.77; H, 4.50. ^1H NMR ($CDCl_3$): δ 5.29 (s, 1 H, CH), 7.10–7.92 (m, 15 H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 63.5 (s). IR (THF): $\nu(C{\equiv}O)$ 2024 s, 1970 vs, [$\nu(C\overset{\cdots}{-}O) + \nu(C\overset{\cdots}{-}C)$] 1514 m cm^{-1}. IR (KBr): $\nu(C{\equiv}O)$ 2029 s, 1971 s, [$\nu(C\overset{\cdots}{-}O) + \nu(C\overset{\cdots}{-}C)$] 1510 s cm^{-1}.

Preparation of $Fe[(O)PPh_2CH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph]_2$ (6). Solid $Ph_2P(O)CH_2C(O)Ph$ (0.59 g, 1.84 mmol) was added to a solution of $FeBr_2$ (0.20 g, 0.93 mmol) in toluene (40 mL). The brown-red suspension was refluxed for 3 h under constant agitation. The solvent was removed under reduced pressure, and the residue was dissolved in THF (40 mL). Solid KH was added in excess to the reaction mixture, and stirring was maintained overnight. The resulting red solution was filtered through a Celite-padded filter funnel, and the solvent was removed under reduced pressure, affording the red, air-stable microcrystalline product (0.49 g, 77% yield). Anal. Calcd for $C_{40}H_{32}FeO_4P_2$ (**6**) (M = 693.6): C, 69.20; H, 4.61. Found: C, 69.99; H, 4.88. Mass spectrum (FAB$^+$): m/z = 694 (34%, M$^+$), 321 (100%, $Ph_2P(O)CH_2C(O)$ Ph + H$^+$). IR (KBr): [$\nu(C\overset{\cdots}{-}O) + \nu(C\overset{\cdots}{-}C)$] 1514 s; 1484 s, 1437 s, 1374 s br, $\nu(P{=}O)$ 1125 s cm^{-1}.

Preparation of $Fe[Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph]_2$ (7). A solution of $FeBr_2$ (0.50 g, 2.30 mmol) in THF was added to a THF solution of Li [$Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph$] (5.10 mmol) at – 78 °C. The solution turned instantaneously from red to green and stirring at room temperature was maintained for 2 h. The solvent was removed under reduced pressure, and the green solid was recrystallized from Et_2O at –15 °C (1.40 g, 92% yield). Anal. Calcd for $C_{40}H_{32}FeO_2P_2$ (**7**) (M = 662.1): C, 72.49; H, 4.83. Found: C, 71.27; H, 5.35. Mass spectrum (FAB$^+$): m/z = 663.1 (MH$^+$). IR (KBr): 1659 m ($\nu(C{=}O)$ of free P~O), [$\nu(C\overset{\cdots}{-}O) + \nu(C\overset{\cdots}{-}C)$] 1534 s cm^{-1}. ^1H NMR ($CDCl_3$, 298 K): δ 3.74 br, PCH_2 of free P~O), 5.44 (s br, 1 H, PCH), 6.7–7.9 (m, 15 H, Ph). $^{31}P\{^1H\}$ NMR (THF/C_6D_6, 296 K): δ –18.6 (free P~O), 30.4 (s).

X-ray Data Collection, Structure Solution, and Refinement. Single crystals of **5**·$THF\cdot{}^1/_2C_6H_6$ suitable for X-ray diffraction were obtained by slow diffusion of pentane into a THF/benzene solution. A yellow crystal of dimensions 0.22 × 0.28 × 0.33 mm was mounted on a Philips PW1100/16 diffractometer, equipped with a local-built low-temperature device. A total of 3029 reflections ($3 < 2\theta < 44°$) were collected, of which 2404 were observed [$I > 3\sigma(I)$]. Empirical absorption corrections and Lorentz and polarization corrections were applied to the data. All non-hydrogen atoms were located by the heavy-atom method (Patterson and Fourier synthesis), and they were refined anisotropically. The benzene molecule lies on a crystallographic inversion center. The hydrogen atoms, except those of C_6H_6, were included as idealized contributions (C–H = 0.95 Å, B(H) = $1.3B_{\text{equiv}}$(C)). All computations used MOLEN on a VAX computer.[9] GOF = 1.39, and final residual density = 0.28 e Å^{-3}. The pertinent data are summarized in Table I, and the final positional parameters are given in Table II. Tables of bond distances and angles and anisotropic thermal parameters are available (see paragraph at the end of paper regarding supplementary material).

Table II. Positional Parameters and B Values and Their Esd's

atom	x	y	z	B,^{a} Å^2
Fe	0.30829 (6)	0.20474 (5)	0.98789 (7)	2.52 (2)
P1	0.4471 (1)	0.25533 (8)	0.9119 (1)	2.51 (3)
C1	0.3758 (4)	0.3083 (3)	0.7797 (5)	2.6 (1)
C2	0.2658 (4)	0.2953 (3)	0.7559 (5)	2.4 (1)
O1	0.2157 (3)	0.2503 (2)	0.8275 (3)	2.81 (9)
C3	0.1911 (4)	0.3353 (3)	0.6456 (5)	2.5 (1)
C4	0.2218 (4)	0.3659 (3)	0.5381 (5)	3.5 (1)
C5	0.1499 (5)	0.4016 (3)	0.4356 (5)	4.2 (2)
C6	0.0491 (5)	0.4076 (3)	0.4462 (6)	4.1 (2)
C7	0.0188 (4)	0.3787 (3)	0.5522 (5)	3.6 (1)
C8	0.0893 (4)	0.3423 (3)	0.6510 (5)	2.9 (1)
C9	0.5040 (4)	0.1780 (3)	0.8414 (5)	2.5 (1)
C10	0.5043 (4)	0.1766 (3)	0.7067 (6)	3.7 (1)
C11	0.5434 (5)	0.1164 (4)	0.6512 (5)	4.3 (2)
C12	0.5838 (4)	0.0573 (4)	0.7285 (6)	4.3 (2)
C13	0.5858 (5)	0.0588 (3)	0.8626 (6)	4.2 (2)
C14	0.5453 (4)	0.1182 (3)	0.9180 (5)	3.1 (1)
C15	0.5662 (4)	0.3277 (3)	1.0291 (5)	2.6 (1)
C16	0.6554 (5)	0.3024 (3)	1.1185 (6)	4.0 (2)
C17	0.7422 (5)	0.3578 (3)	1.2134 (6)	4.4 (2)
C18	0.7435 (5)	0.4398 (4)	1.2212 (6)	5.0 (2)
C19	0.6576 (6)	0.4669 (4)	1.1337 (9)	8.5 (2)
C20	0.5697 (6)	0.4110 (4)	1.0397 (8)	7.2 (2)
C21	0.3186 (4)	0.2993 (3)	1.0824 (5)	3.1 (1)
O2	0.3219 (3)	0.3616 (2)	1.1422 (4)	5.2 (1)
P2	0.1559 (1)	0.13804 (8)	1.0271 (1)	2.62 (3)
C101	0.1275 (4)	0.0451 (3)	0.9182 (5)	2.9 (1)
C102	0.1990 (4)	0.0446 (3)	0.8447 (5)	3.3 (1)
O101	0.2866 (3)	0.1027 (2)	0.8656 (3)	2.61 (8)
C103	0.1886 (4)	–0.0309 (3)	0.7510 (5)	2.7 (1)
C104	0.2801 (4)	–0.0559 (3)	0.7407 (5)	3.0 (1)
C105	0.2706 (4)	–0.1272 (3)	0.6572 (5)	3.5 (1)
C106	0.1703 (5)	–0.1742 (3)	0.5837 (5)	3.7 (2)
C107	0.0765 (5)	–0.1493 (4)	0.5888 (6)	4.2 (2)
C108	0.0853 (4)	–0.0780 (3)	0.6725 (5)	3.8 (1)
C109	0.0292 (4)	0.1777 (3)	0.9834 (5)	2.8 (1)
C110	–0.0266 (4)	0.1838 (3)	0.8470 (5)	3.5 (1)
C111	–0.1268 (4)	0.2080 (3)	0.8075 (5)	3.8 (2)
C112	–0.1710 (5)	0.2257 (4)	0.9043 (6)	4.6 (2)
C113	–0.1179 (5)	0.2188 (4)	1.0402 (6)	5.7 (2)
C114	–0.0186 (5)	0.1954 (4)	1.0797 (5)	4.3 (2)
C115	0.1821 (4)	0.1151 (3)	1.2038 (5)	2.6 (1)
C116	0.1728 (4)	0.0343 (3)	1.2371 (5)	3.2 (1)
C117	0.1980 (5)	0.0183 (3)	1.3735 (6)	4.2 (2)
C118	0.2326 (5)	0.0830 (4)	1.4780 (5)	4.2 (2)
C119	0.2423 (5)	0.1623 (3)	1.4479 (5)	3.8 (2)
C120	0.2177 (4)	0.1787 (3)	1.3127 (5)	3.5 (1)
C121	0.3956 (4)	0.1692 (3)	1.1317 (5)	2.8 (1)
O102	0.4539 (3)	0.1486 (2)	1.2283 (4)	4.1 (1)
O200	0.4943 (4)	0.6129 (3)	0.4473 (6)	9.3 (2)
C201	0.4595 (8)	0.6556 (7)	0.5471 (8)	10.9 (3)
C202	0.3370 (8)	0.6540 (8)	0.457 (1)	17.0 (4)
C203	0.325 (1)	0.6102 (7)	0.340 (2)	19.6 (5)
C204	0.401 (1)	0.5620 (7)	0.354 (1)	14.1 (4)
C205	0.041 (1)	0.4686 (7)	0.106 (1)	19.1 (5)
C206	0.013 (1)	0.5408 (8)	0.099 (1)	16.5 (5)
C207	–0.068 (2)	0.553 (1)	–0.009 (2)	11.5 (6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Results and Discussion

Reactions involving the P~O ligand are summarized in Scheme I. Treatment of $Fe_3(CO)_{12}$ with 1 equiv of P~O in the presence of Me_3NO in THF led to the monosubstituted derivative $Fe_3(CO)_{11}$(P~O) (**1**), whose IR data are typical of $Fe_3(CO)_{11}L$ clusters,[10] and a small quantity of the mononuclear, bis(phosphino enolate) complex *cis*-$Fe[Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph]_2(CO)_2$ (**5**) (see below). Thermal treatment of this cluster led to fragmentation

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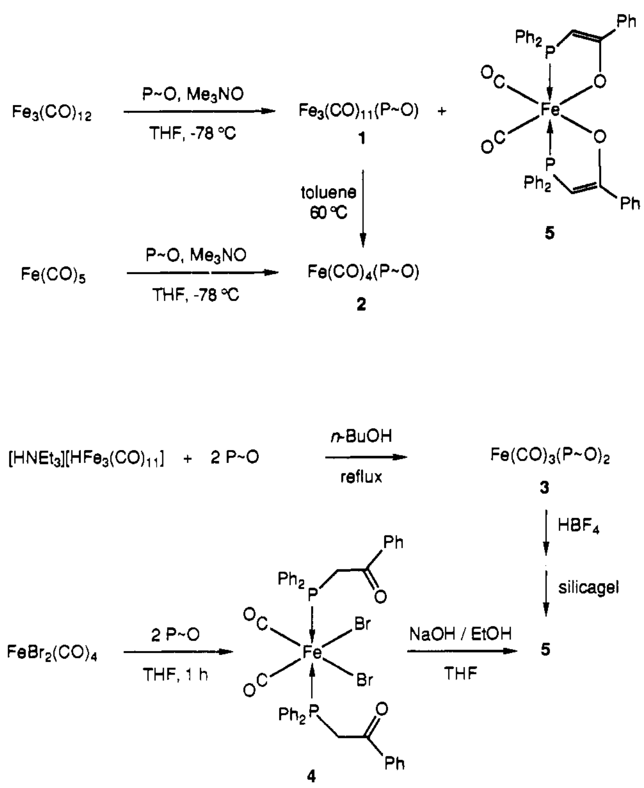
Scheme I



to Fe(CO)$_4$(P$\sim$O) (**2**), which is also conveniently obtained from Fe(CO)$_5$. Reaction of the anion [HFe$_3$(CO)$_{11}$]$^-$ with P$\sim$O occurred with cluster fragmentation and yielded the disubstituted mononuclear derivative Fe(CO)$_3$(P$\sim$O)$_2$ (**3**), which was also obtained in the direct reaction of Fe(CO)$_5$ with Na(BH$_4$) and 2 equiv of P$\sim$O in refluxing 1-butanol. The spectroscopic properties and structures of **1**–**3** are similar to those of their PPh$_3$ analogues.

Whereas **3** was unreactive toward NaOH, it reacted with excess HBF$_4$ in THF at room temperature to give a yellow, cationic complex [ν(BF$_4$) (Nujol) 1078 cm^{-1}; ν(CO) (Nujol) 2046 s, 1999 s cm^{-1}; δ(PCH_2) 4.70 (d, 2 H, ^2J(PH) = 17 Hz)], which, after chromatography through a silica gel column, yielded the Fe(II) complex **5**. In order to prepare **5** in a more rational way and in better yields, we first prepared FeBr$_2$(CO)$_2$(P$\sim$O)$_2$ (**4**), in a manner similar to that for FeBr$_2$(CO)$_2$(PPh$_3$)$_2$[5b] from FeBr$_2$(CO)$_4$ and 2 equiv of P$\sim$O, and reacted it with NaOH in THF. Deprotonation of the PCH$_2$ groups occurred, yielding the desired complex with the chelating phosphino enolate ligands. Complex **5** appears to be the first of its type in iron chemistry. Its IR spectrum contains two strong ν(CO) absorptions, of similar intensities, at 2023 and 1969 cm^{-1}, consistent with a cis arrangement of these ligands. These absorptions are very similar to those observed in the octahedral complexes of the type FeX$_2$(CO)$_2$(PR$_3$)$_2$, where the carbonyls occupy a position trans to the halide X,[5b,11] or in an iron(II) phosphino thioenolato carbonyl complex.[12] The band at 1510 cm^{-1} is typical for a ν(C$\overset{\cdots}{-}$O) + ν(C$\overset{\cdots}{-}$C) vibration of the enolate moiety.[4] The ^{1}H NMR spectrum of the PCH protons consists of a singlet at 5.29 ppm, owing to a very small (or zero) ^2J(PH) coupling, as already encountered in related complexes.[13] The molecular structure of **5** has been determined by X-ray diffraction (see below).

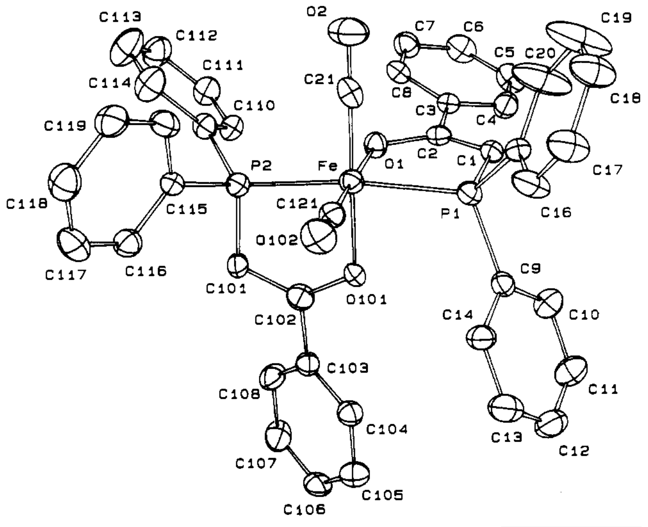


Figure 1. View of the molecular structure of cis-$\overline{\text{Fe[Ph}_2\text{PCH}\overset{\cdots}{-}\text{C}(\overset{\cdots}{-}\text{O}}$)Ph]$_2(CO)_2$ (**5**). Thermal envelopes of 20% are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. Selected bond lengths (Å) and angles (deg) are as follows: Fe–C21 = 1.753 (8), C21–O2 = 1.156 (7), Fe–C121 = 1.752 (7), C121–O102 = 1.150 (6), Fe–O1 = 1.978 (4), Fe–O101 = 1.966 (4), Fe–P1 = 2.246 (2), Fe–P2 = 2.263 (2), P1–C1 = 1.753 (6), P2–C101 = 1.756 (6), C1–C2 = 1.354 (8), C101–C102 = 1.380 (8), C2–C3 = 1.505 (8), C102–C103 = 1.491 (8), C2–O1 = 1.309 (7), C102–O101 = 1.304 (7); P1–Fe–P2 = 169.38 (6), O1–Fe–C121 = 177.0 (2), C21–Fe–O101 = 174.2 (2), P1–Fe–O1 = 84.7 (1), P1–Fe–O101 = 86.0 (1), P1–Fe–C121 = 93.1 (2), O1–Fe–C21 = 85.4 (2), O1–Fe–P2 = 90.7 (1), O1–Fe–O101 = 88.8 (1), C21–Fe–P2 = 95.4 (2), C21–Fe–C121 = 92.7 (3), Fe–C21–O2 = 177.8 (6), Fe–C121–O102 = 177.7 (5), O101–Fe–C121 = 93.1 (2), O1–C2–C1 = 124.1 (5), P2–Fe–O101 = 84.4 (1), O101–C102–C101 = 123.5 (5), P1–Fe–C21 = 93.8 (2), P2–Fe–C121 = 91.8 (2), P1–C1–C2 = 114.1 (5).

Following our observations that a metal template effect may lead to highly selective coupling reactions between the coordinated phosphino enolate moiety and PPhCl$_2$,[14] complex **5** was treated with PPhCl$_2$ in THF. The reaction was monitored by ^{31}P{^{1}H} spectroscopy (THF/C$_6$D$_6$). After 24 h in refluxing THF, the signals due to free P$\sim$O (−18.7), **5** (63.85), and PPhCl$_2$ (163.6) were observed, in addition to a dd pattern at δ 135.8 and 6.8 (J(PP) = 235 Hz) which could be indicative of a P–O coupling product. Unfortunately, the latter disappeared with time (48 h reflux) and was not further characterized.

Attempts to form a complex of the type FeBr$_2$(P$\sim$O)$_2$ from FeBr$_2$ and P$\sim$O in refluxing toluene for 3 h under N$_2$ only led to a poor yield of a complex formulated as $\overline{\text{Fe[(O)PPh}_2\text{CH}\overset{\cdots}{-}\text{C}(\overset{\cdots}{-}\text{O}}$)Ph]$_2$ (**6**) on the basis of its elemental analysis and infrared and mass spectra. However, its ^{1}H NMR spectrum only contained broad resonances, indicating a paramagnetic Fe(II) complex. The formation of this phosphine oxide complex must have resulted from the presence of adventitious air and indicates the low tendency to form FeBr$_2$(P$\sim$O)$_2$ and/or the lability of such complexes. The latter view is supported by the instability often encountered for complexes of the type FeX$_2$(PR$_3$)$_2$.[15] We then decided to prepare **6** by the reaction of the phosphine oxide ligand with FeBr$_2$ followed by deprotonation in situ (eq 1). This reaction afforded red **6** in almost quantitative yield. In order to evaluate the nucleophilicity of the enolate oxygen atom and with the intention to form O–P coupling product(s),[13] we reacted **6** with PPh$_2$Cl or PPhCl$_2$ in THF. In the former case, an almost insoluble yellow product formed, with IR absorptions at 1675 m, 1592 m, 1485 m, and 1437 s cm^{-1}, which has not yet been fully identified. In the latter case, the red solution turned yellow, but no product

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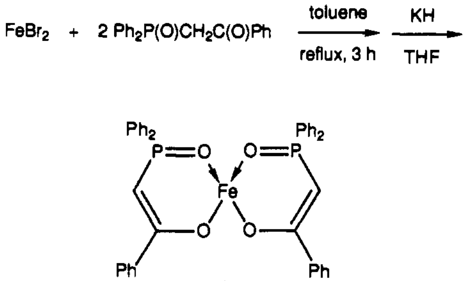

6

(1)

could be characterized. Attempts to isolate a complex related to **6** from $Ph_2P(S)CH_2C(O)Ph$ were also unsuccessful.

Finally, reaction of the lithium phosphino enolate $Li[Ph_2PCH{\cdots}C({\cdots}O)Ph]$ with $FeBr_2$ in THF yielded a green microcrystalline compound **7**, which was recrystallized from Et_2O at −15 °C. Despite several attempts, it proved impossible to obtain this complex completely free of the P∼O ligand, as indicated in the IR spectrum and by the PCH_2 resonance at 3.74 ppm in the ^1H NMR spectrum, which also contained the expected resonance for the PCH enolate proton at δ 5.44. Bubbling CO at room temperature through a toluene solution of **7** afforded small yields of **5** and other, yet unidentified, compounds.

Molecular Structure of *cis*-$\overline{Fe[Ph_2PCH{\cdots}C({\cdots}O}Ph]_2(CO)_2$ (5). The coordination about the Fe(II) center is octahedral (Figure 1), with the carbonyl ligands in the cis position and the phosphorus donor atoms trans to one another. There is no symmetry element for the molecule, and the two enantiomers are present in the unit cell. The atoms in the orthogonal five-membered ring chelates are almost coplanar (maximum deviations from the least-squares planes: P(1) [0.055 (1) Å] and Fe [−0.050 (1) Å], and C(102) [0.043 (5) Å] and O(101) [−0.019 (5) Å], respectively). These planes from a dihedral angle of 16.4 (3) and 34.3 (2)° with the phenyl rings attached to C(2) and C(102), respectively. The Fe–P distances compare with those in a $PMePh_2$ complex (2.260 (2) and 2.276 (2) Å)[16] and with the average value of 2.237 Å in PPh_3 complexes of iron.[17] The Fe–O distances are longer than those found for the terminal alkoxy groups in $LiFe(OCHBu^t{}_2)_4{\cdot}Bu^t{}_2CHOH$ (1.806 (2) and 1.829 (2) Å)[18] and for the Fe–OMe distance in a porphyrin complex of Fe(III) (1.8155 (15) Å), in agreement with the presence of an Fe(II) center in **5**.[19] These distances are however slightly shorter than the average Fe–O distance in carboxylato complexes (2.033 Å).[17] The dimensions within the enolato moiety are comparable to those in e.g. related bis(phosphino enolato) complexes of Ni(II)[20] (to the best of our knowledge, there are no iron complexes available for comparison).

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Supplementary Material Available: Tables of crystallographic and collection data (Table S-I), hydrogen atomic coordinates (Table SII), anisotropic thermal parameters (Table S-III), and bond distances and angles (Table S-IV) (10 pages). Ordering information is given on any current masthead page.

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