Organometallic Complexes containing Phosphorus(V) bonded to a Transition Metal: Derivatives of Dicarbonyl(η-cyclopentadienyl)ferrate-(1—)

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The complexes $[Fe(\eta-C_5H_5)(CO)_2(PR_2E)]$ [E = S, R = Me (I); E = S, R = OEt (II); E = Se, R = Ph (III)] have been synthesized by the reaction of $Na[Fe(\eta-C_5H_5)(CO)_2]$ with $PBrMe_2S$, $PCl(OEt)_2S$, or PPh_2ClSe. The method seems to be valid for the preparation of a variety of the title complexes and suitable for a wider series of carbonylmetallate anions. On the basis of i.r. and ^1H n.m.r. data, the complexes are believed to contain an Fe–P rather than Fe–E bond. On treating tertiary phosphines, L (PPh_3 or PMe_2Ph), with the complexes (I)—(III), no evidence has been obtained for formation of phosphido-complexes and only substitution products of carbon monoxide have been obtained; using MeI or $[OMe_3][BF_4]$ as reagents, the cations $[Fe(\eta-C_5H_5)(CO)_2\{PR_2(EMe)\}]^+$ are obtained by S- or Se-methylation; EtI and $[OEt_3][BF_4]$ react only with complex (I). The structure of the cationic complexes has been established by i.r. and ^1H n.m.r. spectroscopy.

METAL–CARBONYL complexes containing phosphorus(V) bonded directly to a transition metal are very few in number.[1-3] Complexes of the type $[Fe(\eta-C_5H_5)(CO)_2\{P(CF_3)_2E\}]$ (E = O, S, or Se) have been prepared recently[4] by the action of nitrogen mono-oxide (E = O), sulphur, or selenium on the monomeric phosphido-complex $[Fe(\eta-C_5H_5)(CO)_2\{P(CF_3)_2\}]$; the complex $[Fe(\eta-C_5H_5)(CO)_2\{P(CF_3)_2S\}]$ can be also obtained[4] by treating $P(CF_3)_2(SH)$ with $[Fe(\eta-C_5H_5)(CO)_2Cl]$. Reaction of $S[P(CF_3)_2]_2$ and of $Se[P(CF_3)_2]_2$ with $[\{Fe(\eta-C_5H_5)(CO)_2\}_2]$ gives[5] equimolar amounts of the phosphido-complex $[Fe(\eta-C_5H_5)(CO)_2\{P(CF_3)_2\}]$ and of $[Fe(\eta-C_5H_5)(CO)_2\{P(CF_3)_2S\}]$ or $[Fe(\eta-C_5H_5)(CO)_2\{P(CF_3)_2Se\}]$. In each case, the method of preparation appeared to be specific for the complex containing CF_3 groups bonded to the phosphorus and the authors made no claims as to the generality of the synthetic procedure.

We found that carbonyl complexes containing P^V bonded to a transition metal can be prepared in one step, by treating carbonylmetallate anions with dialkyl- or diaryl-phosphinothioic halogenides, dialkyl- or diaryl-

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phosphinoselenoic halogenides, *OO*-dialkyl or *OO*-diaryl halogenothiophosphates. This method is most suitable for the preparation of a variety of the title complexes. This paper reports the preparation and reactivity of complexes [Fe(η-C_5H_5)$(CO)_2$(PR_2E)] (E = S, R = Me or OEt; E = Se, R = Ph). The synthesis and the reactions of analogous complexes derived from other carbonylmetallate anions will be discussed in forthcoming papers.

RESULTS AND DISCUSSION

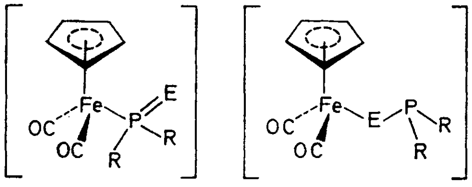
On adding to a tetrahydrofuran (thf) solution of Na[Fe(η-C_5H_5)$(CO)_2$] a slight excess of $PBrMe_2S$, $PCl(OEt)_2S$, or PPh_2ClSe, a reaction occurred, without any evolution of carbon monoxide. After evaporation of the solvent, separation of the reaction products was effected by means of column chromatography, using as eluant methylene dichloride–diethyl ether (3 : 1); the first product eluted from the column was [{Fe(η-C_5H_5)$(CO)_2$}$_2$] followed by a yellow fraction which, as reported in the Experimental section, gave a product formulated as [Fe(η-C_5H_5)$(CO)_2$(PR_2E)] on the basis of the analytical data [E = S, R = Me (I); E = S, R = OEt (II); E = Se, R = Ph (III)]. The complexes are solids, not electrolytes, and are monomers in benzene solution.

Spectroscopic data [a]

Complex	$\bar{\nu}$(CO)/cm^{-1}	τ(C_5H_5)	*J*(P–C_5H_5)	τ(P–R)	*J*(P–Me)	τ(E–Me) [b]	*J*(P–EMe) [b]
[Fe(η-C_5H_5)$(CO)_2$(PMe_2S)], (I)	1 978vs, 2 028vs	4.86(d)	*c*	8.10(d)	10.0		
[Fe(η-C_5H_5)$(CO)_2${$P(OEt)_2S$}], (II)	1 996vs, 2 045vs	4.88(d)	1.0	5.83(m) 8.63(t)			
[Fe(η-C_5H_5)$(CO)_2$(PPh_2Se)], (III)	1 985vs, 2 035vs	4.89(d)	1.5				
[Fe(η-C_5H_5)$(CO)_2${PMe_2(SMe)}]I	2 025vs, 2 065vs	4.48(d)	1.5	7.88(d)	10.0	7.57(d)	11.5
[Fe(η-C_5H_5)$(CO)_2${$P(OEt)_2$(SMe)}]I	2 023vs, 2 065vs	4.63(d)	1.0	5.82(m) 8.67(t)		7.63(d)	14.0
[Fe(η-C_5H_5)$(CO)_2${PPh_2(SeMe)}]I	2 018vs, 2 058vs	4.42(d)	1.5			7.9(d)	*ca.* 10
[Fe(η-C_5H_5)$(CO)_2${PMe_2(SEt)}]I	2 015vs, 2 058vs	4.54(d)	1.5	7.87(d)	9.0		
[Fe(η-C_5H_5)(CO)(PPh_3)(PMe_2S)]	1 930vs	*c*		*c*			
[Fe(η-C_5H_5)(CO)(PMe_2Ph)(PMe_2S)]	1 918vs	*c*		*c*			
[Fe(η-C_5H_5)(CO)(PPh_3){$P(OEt)_2S$}]	1 932vs	*c*		*c*			
[Fe(η-C_5H_5)(CO)(PMe_2Ph){$P(OEt)_2S$}]	1 925vs	*c*		*c*			
[Fe(η-C_5H_5)(CO)(PPh_3)(PPh_2Se)]	1 938vs	*c*		*c*			
[Fe(η-C_5H_5)(CO)(PMe_2Ph)(PPh_2Se)]	1 935vs	*c*		*c*			

[a] I.r. spectra in CH_2Cl_2 solution, n.m.r. spectra in [$^2H_6$] acetone; coupling constants, *J*, are in Hz. [b] E=S or Se. [c] See text.

The structure of the products was established from their spectroscopic properties, which are collected in the Table. In the carbonyl-stretching region of the i.r. spectrum two very strong bands were observed, which underwent a slight change on varying the substituents bonded to phosphorus; a band at *ca.* 620 cm^{-1} can be tentatively assigned to the ν(P=S). In the ^{1}H n.m.r. spectrum, in [$^2H_6$]acetone coupling between the hydrogen atoms of the cyclopentadienyl ring and phosphorus was detected [*J*(HP) *ca* 1.2 Hz], giving a sharp doublet at *ca.* τ 4.9 for the cyclopentadienyl resonance. In complex (I), the phosphorus coupling of the C_5H_5 resonance seemed beyond the resolution of the spectrometer but, in the alkylated derivatives of the same product (see below), the doublet was observed. Such coupling is consistent with a structure (A) rather than with (B) where Fe–S–P or Fe–Se–P linkages are present and consequently there is a larger distance between the C_5H_5 ring and the phosphorus atom. Complexes with structure (B) were isolated when R=CF_3 [4] on u.v. irradiation, in non-polar solvents, of the corresponding isomers of structure (A), and their ^{1}H n.m.r. spectrum showed a single sharp peak due to the resonance of the C_5H_5 ring and no coupling to the distant phosphorus atom was detected. Organic substituents bonded to phosphorus should be equivalent as inferred from the ^{1}H n.m.r. spectrum of (I) which shows the methyl resonance as a doublet at τ 8.10 [*J*(P–CH_3) 10.0 Hz].



(A) (B)

The extent of the Fe ⟶ P π bonding in phosphine-oxide, phosphine-sulphide, and phosphine-selenide complexes having structure (A) has been discussed on the basis of spectroscopic data and, as far as phosphine-oxide complexes are concerned, on the basis of the bond distances as determined by *X*-ray crystallography.[6,7] We observe that the ν(CO) values in our complexes are lower than those previously reported [4] for the analogous complexes [Fe(η-C_5H_5)$(CO)_2${$P(CF_3)_2E$}] and are comparable to those reported for the phosphido-complex [Fe(η-C_5H_5)$(CO)_2${$P(CF_3)_2$}]. Furthermore, the ν(CO) stretching frequencies increase with the electron-withdrawing power of the organic substituents bonded to phosphorus; thus, the highest values were observed for complexes where R = CF_3, whereas the complex containing Me groups showed the lowest ν(CO) values suggesting a higher electron-density donation $d_\pi \longrightarrow p_\pi^*$ from the metal to carbon monoxide in the methyl derivative than in the CF_3-containing complex. According to i.r. data, the highest η-C_5H_5 resonance in the ^{1}H n.m.r. spectrum was observed when R = Me (τ 4.95, compared with the value of τ 4.36 observed for the CF_3 derivative [4]). A similar spectroscopic trend was also observed in the phosphine-selenide complexes.

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Tervalent phosphorus has a high affinity for free and bonded sulphur, which has led to many useful synthetic reactions.[8] Accordingly we tried to prepare new phosphido-complexes [Fe(η-C_5H_5)(CO)$_2$(PR_2)] by treating (I) and (II) with PPh_3 or PMe_2Ph; at room temperature, in ligroin (80—120 °C) solution, no reaction was observed, whereas on heating the reaction mixture under reflux the complexes [Fe(η-C_5H_5)(CO)L(PR_2S)] (L=PPh_3 or PMe_2Ph) were obtained. Complex (III) reacted with ligands L giving [Fe(η-C_5H_5)(CO)L(PPh_2Se)]. Qualitatively, we observe that the better σ donor PMe_2Ph reacts more rapidly than PPh_3 and that the phosphine-selenide complex reacts easier than phosphine-sulphide complexes. Satisfactory ^1H n.m.r. spectra for complexes containing tertiary phosphines could not be obtained because of their low solubility; the i.r. spectra of these complexes showed, in the ν(CO) stretching region, only one band at lower wavenumbers than their precursors, indicating the better σ-donor ability of the tertiary phosphines compared with CO.

Complexes (I)—(III), at room temperature and in CH_2Cl_2 solution, reacted with [OMe_3][BF_4] or MeI by S- or Se-methylation to give the ionic complexes [Fe(η-C_5H_5)(CO)$_2${PR_2(EMe)}]$^+$ which were also isolated as tetraphenylborate salts. The assumption that the methylation occurs at the sulphur or selenium atom is based on spectroscopic data and on some examples reported in the literature.[9] Methylation at the carbon atom of the co-ordinated carbon monoxide would seem to be ruled out by the i.r. spectrum, which showed, for all the cationic complexes, two very strong ν(CO) bands shifted to higher frequency compared to the precursor, as expected from the overall charge of the complex, and no band attributable to ν(CO) of an acetyl group. Hydrogen-1 n.m.r. spectra of methylation products showed a new methyl resonance, as a doublet; some other slight differences from the spectra of the precursors were observed, mainly a shift towards low field of the C_5H_5 resonance and of organic groups bonded to phosphorus, in accordance with the higher formal charge on the phosphorus atom. Alkylation at the sulphur or selenium atom would not be expected to substantially influence either the geometry or the electronic structure of the complex. The only apparent alternative to methylation at sulphur or selenium would be methylation at phosphorus; this would yield a metal complex of the ligand $PMeR_2E$ (R = Me or OEt, E = S; R = Ph, E = Se), which can form stable complexes having the chalcogen as donor atom.[10] In this case, however, an isomerization process, leading to an Fe–E–P bond, is to be expected and in the ^1H n.m.r. spectrum the C_5H_5 resonance would be a single sharp peak, and not a doublet as observed. In the absence of any kinetic data, we observe that methylation is easier for complex (I) than (II).

Ethyl iodide or [OEt_3][BF_4] reacted only with (I) to give an S-alkylated cationic complex; in this case the reaction is slower than with MeI or [OMe_3][BF_4], and the reaction product shows spectral characteristics very similar to those of the methylated complexes.

The sulphur or selenium atom in complexes (I)—(III) has a lone pair which may be available for σ-bond formation with a metal; because of this, such complexes could be used as ligands. We are now investigating this possibility and the results will be discussed in a forthcoming paper.

EXPERIMENTAL

The starting materials Na[Fe(η-C_5H_5)(CO)$_2$],[11] $PCl(OEt)_2S$,[12] and PPh_2ClSe [13] were prepared by literature methods; $PBrMe_2S$ was a Strem product. Alkyl iodides were purified before use by distillation from sodium thiosulphate. Other reagents were used as obtained from commercial sources. The chromatographic separations were effected on an alumina column. Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer using a polystyrene film for calibration. A Varian A60 MHz spectrometer was used to obtain ^1H n.m.r. spectra. Molecular weights were determined with a Knauer vapour-pressure osmometer. A conductivity meter WTW LBR was used for conductivity measurements. Elemental analyses were by Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany. All reactions were carried out under an atmosphere of oxygen-free nitrogen.

Preparation of Dicarbonyl(η-cyclopentadienyl)(dimethylphosphinothioato)iron, (I). To a solution of Na[Fe(η-C_5H_5)(CO)$_2$], obtained from [{Fe(η-C_5H_5)(CO)$_2$}$_2$] (0.50 g, 1.4 mmol) in freshly distilled tetrahydrofuran solution, $PBrMe_2S$ (0.50 g, 3.0 mmol) was added and the mixture was left at room temperature for *ca.* 4 h. After filtration, the resulting red solution was evaporated to dryness and the crude product chromatographed on an alumina column, eluting with methylene dichloride–diethyl ether (3 : 1). The first product eluted from the column was [{Fe(η-C_5H_5)(CO)$_2$}$_2$] followed by a yellow fraction which, after evaporation of the solvent at reduced pressure and crystallization from methylene dichloride–hexane, gave the product as bright yellow *crystals* (yield 32%) (Found: C, 40.5; H, 4.15; S, 11.85. $C_9H_{11}FeO_2PS$ requires C, 40.2; H, 4.10; S, 11.95%). *Dicarbonyl(η-cyclopentadienyl)(*OO*-diethyl thiophosphato)iron*, (II), was prepared in the same way from Na[Fe(η-C_5H_5)(CO)$_2$] and $PCl(OEt)_2S$ and was isolated as a yellow-brown *powder* (yield 57%) (Found: C, 40.1; H, 4.60; S, 9.65. $C_{11}H_{15}FeO_4PS$ requires C, 40.0; H, 4.60; S, 9.70%).

Preparation of Dicarbonyl(η-cyclopentadienyl)(diphenylphosphinoselenoato)iron, (III). A thf solution (*ca.* 100 cm^3) of Na[Fe(η-C_5H_5)(CO)$_2$], obtained from [{Fe(η-C_5H_5)(CO)$_2$}$_2$] (1 g), was added to a filtered benzene solution of PPh_2ClSe, freshly prepared from PPh_2Cl (1.5 g, 6.8 mmol) and selenium red powder. The resulting solution was stirred for *ca.* 4 h and filtered. On evaporation of the solvent to dryness, a red solid was obtained. This was chromato-

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graphed on an alumina column, eluting with methylene chloride–diethyl ether (3 : 1). The pure product was obtained from the yellow-orange fraction, by partial evaporation of the solvent and adding hexane (yield 53%) (Found: C, 51.9; H, 3.55; Se, 17.3. $C_{19}H_{15}FeO_2PSe$ requires C, 51.75; H, 3.40; Se, 17.2%).

Reactions with Tertiary Phosphines.—Complex (I) (0.50 g, 1.85 mmol) in ligroin (b.p. 80—120 °C) was treated with excess of PPh_3 and the reaction mixture was heated under reflux. The progress of the reaction was followed by i.r. spectroscopy. After *ca.* 40 h, the red-brown precipitate which formed $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(PMe_2S)]$, was separated by filtration, washed several times with diethyl ether, and dried (Found: C, 61.75; H, 5.20; S, 6.30. $C_{26}H_{26}FeOP_2S$ requires C, 61.9; H, 5.20; S, 6.35%). The following complexes were prepared and isolated similarly: $[Fe(\eta\text{-}C_5H_5)(CO)(PMe_2Ph)(PMe_2S)]$, red solid, reaction time *ca.* 15 h (Found: C, 50.6; H, 5.95; S, 8.45. $C_{16}H_{22}FeOP_2S$ requires C, 50.55; H, 5.85; S, 8.45); $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)\{P(OEt)_2S\}]$, red-brown solid, reaction time *ca.* 30 h (Found: C, 59.6; H, 5.40; S, 5.60. $C_{28}H_{30}FeO_3P_2S$ requires C, 59.6; H, 5.35; S, 5.70); $[Fe(\eta\text{-}C_5H_5)(CO)(PMe_2Ph)\{P(OEt)_2S\}]$, brown solid, reaction time *ca.* 10 h (Found: C, 49.15; H, 6.00; S, 7.30. $C_{18}H_{26}FeO_3P_2S$ requires C, 49.1; H, 5.95; S, 7.30%); $[Fe(\eta\text{-}C_5H_5)(CO)(PPh_3)(PPh_2Se)]$, yellow solid, reaction time *ca.* 8 h (Found: C, 64.2; H, 4.50; Se, 11.5. $C_{36}H_{30}FeOP_2Se$ requires C, 64.0; H, 4.45; Se, 11.7%); and $[Fe(\eta\text{-}C_5H_5)(CO)(PMe_2Ph)(PPh_2Se)]$, yellow solid, reaction time *ca.* 2 h (Found: C, 56.45; H, 5.05; Se, 14.3. $C_{26}H_{26}FeOP_2Se$ requires C, 56.55; H, 4.90; Se, 14.3%).

Alkylation Reactions.—*Method* (*a*). A solution of complex (I) (0.52 g, 1.85 mmol) in MeI (4 cm^3) was left, with vigorous stirring, for *ca.* 1 h. A pale yellow solid was obtained, $[Fe(\eta\text{-}C_5H_5)(CO)_2\{PMe_2(SMe)\}]I$, which was separated by filtration, washed several times with pentane, and dried (Found: C, 28.95; H, 3.50; S, 7.90. $C_{10}H_{14}FeIO_2PS$ requires C, 29.15; H, 3.40; S, 7.80%). The following complexes were prepared and isolated similarly, using the appropriate alkylating agent: $[Fe(\eta\text{-}C_5H_5)(CO)_2\{P(OEt)_2(SMe)\}]I$, yellow solid (Found: C, 30.7; H, 3.90; S, 6.80. $C_{12}H_{18}FeIO_4PS$ requires C, 30.55; H, 3.85; S, 6.80%); $[Fe(\eta\text{-}C_5H_5)(CO)_2\{PPh_2(SeMe)\}]I$, yellow-brown solid (Found: C, 41.3; H, 3.15; Se, 13.6. $C_{20}H_{18}FeIO_2PSe$ requires C, 41.2; H, 3.10; Se, 13.55%); and $[Fe(\eta\text{-}C_5H_5)(CO)_2\{PMe_2(SEt)\}]I$, brown (Found: C, 31.2; H, 3.7; S, 7.70. $C_{11}H_{16}FeIO_2PS$ requires C, 31.0; H, 3.80; S, 7.50%).

Method (*b*). To a solution of complex (I) in dichloromethane, a slight excess of $[OMe_3][BF_4]$ was added and the mixture was left with vigorous stirring. The progress of the reaction was followed by i.r. spectroscopy. The brown solution was evaporated to dryness; extraction with methanol gave, after partial evaporation of the solvent, the product $[Fe(\eta\text{-}C_5H_5)(CO)_2\{PMe_2(SMe)\}][BF_4]$ (Found: C, 32.45; H, 3.85; S, 8.75. $C_{10}H_{14}BF_4FeO_2PS$ requires C, 32.3; H, 3.80; S, 8.60%). Working-up as above and using the appropriate alkylating agent, the complexes $[Fe(\eta\text{-}C_5H_5)(CO)_2\{P(OEt)_2(SMe)\}][BF_4]$, $[Fe(\eta\text{-}C_5H_5)(CO)_2\{PPh_2(SeMe)\}][BF_4]$, and $[Fe(\eta\text{-}C_5H_5)(CO)_2\{PMe_2(SEt)\}][BF_4]$ were obtained.

Tetraphenylborate Salts. The complexes $[Fe(\eta\text{-}C_5H_5)(CO)_2\{PR_2(ER)\}][BPh_4]$ were prepared by adding $Na[BPh_4]$, dissolved in methanol, to a solution of $[Fe(\eta\text{-}C_5H_5)(CO)_2\{PR_2(ER)\}]Y$ ($Y = I$ or BF_4) in the same solvent. They closely resemble the corresponding iodide or tetrafluoroborate salts except for a lower solubility in organic solvents.

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