Carbonyl, Hydridocarbonyl, and Hydridoalkoxycarbonyl Complexes of Iridium with Phosphorus–Sulphur Hybrid Ligands, and the Crystal and Molecular Structure of $[IrH(CO_2Me)(Ph_2PCH_2CH_2SEt)_2]BPh_4$†

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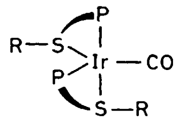
Treatment of *trans*-$[IrCl(CO)(PPh_3)_2]$ with two equivalents of $Ph_2P–CH_2–CH_2–SR$ (R = Me, P–SMe; R = Et, P–SEt) in dichloromethane–methanol affords yellow $[Ir(CO)(P–SR)_2]^+$ complexes, which are isolated as $[BPh_4]^-$ salts. These monocarbonyl complexes react with CO in dichloromethane solution yielding the corresponding dicarbonyl derivatives, identified by i.r. and ^{31}P n.m.r. spectroscopy. Alternatively, treatment of *trans*-$[IrCl(CO)(PPh_3)_2]$with two equivalents of P–SR in dichloromethane–methanol at 70 °C for several hours affords white $[IrH(CO_2Me)(P–SR)_2]^+$ complexes, isolated as $[BPh_4]^-$ salts in good yield. These compounds can also be conveniently obtained by nucleophilic attack of an alcohol molecule on CO of the corresponding dicationic hydrido–carbonyl complexes of Ir^{III}. The $[Ir(CO)(P–SEt)_2]^+$ cation reacts with HY (Y = Cl or BF_4) to afford *cis*- or *trans*-$[IrH(CO)(P–SEt)_2]^{2+}$ derivatives according to the nature of Y; the reactivities and stabilities of these species are discussed. The new compounds have been characterized on the basis of i.r., ^{31}P n.m.r., ^1H n.m.r., and conductivity data. A single-crystal *X*-ray diffractometric study of $[IrH(CO_2Me)(P–SEt)_2]BPh_4$ revealed the octahedral geometry of the complex cation, with *trans*-P atoms and *cis*-S atoms; the bonding of the methoxycarbonyl group is also discussed. Crystal data: orthorhombic system (space group $P2_12_12_1$), a = 12.242(2), b = 16.616(3), c = 26.992(2) Å, Z = 4; the structure was refined to R = 0.0515, R' = 0.0603.

Recently, we have been investigating the reaction chemistry of transition-metal complexes containing unsymmetrical chelating ligands with phosphorus and sulphur donor atoms.[1] The interest in such ligands lies in the facile displacement of the sulphur end of the chelate that such metal complexes often undergo in solution, giving rise to co-ordinatively unsaturated species which could be susceptible to applications in homogeneous catalysis. At the same time, the chelate effect makes these compounds nearly as stable as their diphosphine analogues.

During the course of these studies, we have found that the reactions of ligands of the type $Ph_2P–(CH_2)_2–SR$ (P–SR) with Vaska's compound in alcohol solution can give, beyond the expected $[Ir(CO)(P–SR)_2]^+$ products, also the most unusual hydridoalkoxycarbonyl derivatives, $[IrH(CO_2R')(P–SR)_2]^+$ (R,R' = alkyl). Although nucleophilic attack at the carbon atom of a co-ordinated carbon monoxide molecule by alkoxide ion is frequently observed, the attack of alcohols is less common, and generally a proton acceptor is needed to drive the reaction to completion.[2] Only in a few instances does the reaction with alcohols lead to a final product in which both the RO– and H– groups are present, the former as part of an alkoxycarbonyl ligand, while the latter is bound directly to the metal atom. In the case of carbonyl complexes of iridium, it has been reported that $[Ir(CO)(dmpe)_2]Cl$ [dmpe = 1,2-bis(dimethylphosphino)ethane] readily reacts with ethanol to give a hydridoalkoxycarbonyl derivative according to equation (1).[3]

$$[Ir(CO)(dmpe)_2]Cl + EtOH + NaBPh_4 \longrightarrow trans\text{-}[IrH(CO_2Et)(dmpe)_2]BPh_4 + NaCl \quad (1)$$



R
(**1**) Me
(**2**) Et
(**3**) Ph

Due to the potential interest of alkoxycarbonyl complexes, which are intermediates in a number of synthetically important carbonylation processes,[4] we decided to explore the reactivity of iridium carbonyls with the hybrid ligands P–SR (R = Me, Et, or Ph), and in particular the formation of the hydridoalkoxycarbonyl derivatives. In this paper, we describe some new cationic carbonyl complexes of iridium(I), of the type $[Ir(CO)(P–SR)_2]^+$, as well as the synthesis and characterization of the dicationic iridium(III)–hydridocarbonyl complexes, *cis*- and *trans*-$[IrH(CO)(P–SEt)_2]^{2+}$. Their behaviour in solution is examined by means of ^1H and ^{31}P n.m.r., and the reactivity of these complexes toward alcohols is studied. Moreover, a novel group of hydridoalkoxycarbonyl derivatives of iridium(III), of the type $[IrH(CO_2R')(P–SR)_2]^+$, are described, together with the crystal structure of the complex $[IrH(CO_2Me)(P–SEt)_2]BPh_4$ as determined by single-crystal *X*-ray diffractometry.

Results and Discussion

The room temperature reaction of *trans*-$[IrCl(CO)(PPh_3)_2]$ with two equivalents of the appropriate ligand P–SR (R = Me or Et) in dichloromethane–methanol gives yellow-orange solutions from which the yellow products (**1**) and (**2**) are isolated by addition of sodium tetraphenylborate. With the ligand P–SPh, only impure products are obtained, and

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† Bis[1-(diphenylphosphino)-2-ethylthioethane-*P,S*]hydrido(methoxycarbonyl)iridium(III) tetraphenylborate(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Analytical and physical data

Complex		Colour	M.p. (decomp.)/°C	Yield (%)	Λ_M[a]/S cm^2 mol^{-1}	Analysis[b] (%) C	Analysis[b] (%) H
$[Ir(CO)(P\text{-}SMe)_2]BPh_4$	**(1)**	Yellow	126—128	75	48	62.10 (62.30)	5.05 (5.15)
$[Ir(CO)(P\text{-}SEt)_2]BPh_4$	**(2)**	Yellow	140—142	80	50	62.80 (62.90)	5.40 (5.35)
$[IrH(CO_2Me)(P\text{-}SMe)_2]BPh_4$	**(7)**	White	173—175	55	49	61.65 (61.60)	5.40 (5.35)
$[IrH(CO_2Me)(P\text{-}SEt)_2]BPh_4$	**(8)**	White	182—184	60, 90[c]	50	62.00 (62.20)	5.60 (5.60)
$[IrH(CO_2Et)(P\text{-}SEt)_2]BPh_4$	**(9)**	White	86—88	60, 90[c]	46	62.45 (62.50)	5.70 (5.70)
cis-$[IrH(CO)(P\text{-}SEt)_2][BPh_4]_2$	**(10)**	White	109—111	75	96	68.65 (69.10)	5.85 (5.65)
trans-$[IrH(CO)(P\text{-}SEt)_2][BPh_4]_2$	**(11)**	White	121—123	75	97	68.95 (69.10)	5.60 (5.65)

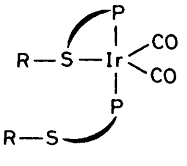
[a] In nitromethane at 22 °C, for 10^{-3} mol dm^{-3} solutions. [b] Required values are given in parentheses. [c] Values refer to method (*a*) and method (*b*), respectively (see text).

Table 2. I.r. and n.m.r. data[a]

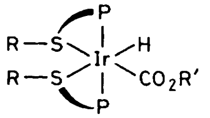
	I.r.[b]/cm^{-1}		N.m.r.							
			$^{31}P\text{-}\{^1H\}$[c]		^1H[d,e]					
Complex	ν(CO)	ν(IrH)	δ/p.p.m.	*J*(P–P')/Hz	$-C_6H_5$	$-OCH_3$	$-CH_2-$	$-CH_3$	Ir–H	*T*[f]/K
(1)	1 930		35.4 (s) 33.8; 37.9	 *g*						308 153
(2)	1 932		35.5 (s) 33.7; 37.0	 *g*						308 153
(3)	1 962[h]		33.7 (s)[i] 31.1; 37.0	 *g*						308 153
(4)	2 000, 1 965[j]		29.2 (d); −4.6 (d)	230						213
(5)	2 005, 1 965[j]		28.7 (d); −5.1 (d)	231						213
(6)	1 998, 1 963[j]		25.9 (d); −6.9 (d)	229						213
(7)[k]	1 642, 1 062[l]	2 155	30.9 (s) 30.4—36.4 (m)[m] (A + B)		6.6—8.2 (m) 6.6—8.2 (m) (A + B)	2.79 (s) 2.97 (s); (A) 2.92 (s) (B)	2.2—3.6 (m) 1.8—3.4 (m) (A + B)	1.57 (s), 1.72 (s) 1.25 (s), 1.39 (s); (A) 1.14 (s), 1.50 (s) (B)	−14.63 (t) [13.2] −13.82 (t) [11.8]; (A) −14.06 (t) [13.2] (B)	353 253
(8)[k]	1 631, 1 073[l]	2 145	30.9 (s) 28.4—33.3 (m)[m] (A + B)		6.6—8.3 (m) 6.6—8.3 (m) (A + B)	2.74 (s) 2.96 (s); (A) 2.88 (s) (B)	1.2—3.7 (m) 1.1—3.4 (m) (A + B)	0.63 (t), 0.91 (t)[n] 0.4—1.1 (m) (A + B)	−14.76 (t) [12.5] −13.79 (t) [10.7]; (A) −14.07 (t) [12.8] (B)	353 253
(9)[k,o]	1 628, 1 047[l]	2 140	32.3—36.5 (m)[m] (A + B)		6.6—8.2 (m) (A + B)		1.4—3.6 (m) (A + B)	0.3—1.4 (m) (A + B)	−13.84 (t) [12.1]; (A) −14.13 (t) [13.2] (B)	253
(10)	2 080	2 135	21.4 (d); 38.0 (d)	253	6.4—8.3 (m)		1.2—3.4 (m)	0.4—1.2 (m)	−11.71 (dd) [7.9, 13.8]	308
(11)	2 055	2 140	24.4 (s)		6.4—8.3 (m)		1.2—3.4 (m)	0.4—1.2 (m)	−13.10 (t) [9.8]	308

[a] Solvents used for ^{31}P n.m.r.: dimethyl sulphoxide (353—308 K), dichloromethane (308—183 K), $CDClF_2$–CD_2Cl_2 (183—153 K); for ^1H n.m.r.: $[^2H_6]$dimethyl sulphoxide (353—308 K), CD_2Cl_2 (308—183 K). [b] In Nujol mull, unless otherwise stated. [c] At 308 K, the spectra of the complexes **(5)**, **(6)**, and **(7)** show two broad signals in the range 27—33 p.p.m. [d] ^1H N.m.r. data are reported only for the hydrido-complexes, since relevant for the discussion. [e] δ values in p.p.m.; *J*(P–H) values in brackets; multiplicity given in parentheses by s = singlet, t = triplet, m = multiplet, dd = doublet of doublets. [f] Temperature refers to both ^{31}P and ^1H n.m.r. spectra. [g] Coupling not resolved. [h] Value from ref. 5. [i] An unreliable value of 17.0 p.p.m. at 223 K is reported in ref. 5. [j] In dichloromethane solution. [k] The n.m.r. spectra of **(7)**, **(8)**, and **(9)** at 253 K indicate the presence of two isomers (A and B) in a molar ratio of *ca.* 1:2, 1:1.5, and 1:2.5, respectively. [l] Stretching frequencies relative to the $-CO_2R$ function. [m] Complex pattern (six main strong lines), possibly arising from the overlapping of two AB spin systems. [n] *J*(H–H') = 7.0 Hz for both triplets. [o] At temperatures higher than 333 K, the complex decomposes giving **(2)**.

$[Ir(CO)(P\text{-}SPh)_2]BPh_4$ **(3)** is most conveniently prepared from $[Ir(P\text{–}SPh)_2]BPh_4$ as reported by Sanger.[5] The new carbonyl compounds **(1)** and **(2)** were characterized by elemental analysis, and found to be 1:1 electrolytes in nitromethane (Table 1). Their i.r. spectra show a strong band at *ca.* 1 930 cm^{-1}, due to the carbonyl absorption (Table 2). The geometry of the cations can be inferred from ^{31}P n.m.r. data. The room temperature $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of **(1)** and **(2)** in



	R
(4)	Me
(5)	Et
(6)	Ph



	R′	R
(7)	Me	Me
(8)	Me	Et
(9)	Et	Et

dichloromethane solution display a single sharp signal. By lowering the temperature, the singlet broadens and then splits into two broad signals (Table 2). Though the limiting low-temperature spectrum is still not reached at 150 K (CD_2Cl_2–$CHClF_2$ solution), the n.m.r. pattern is consistent with a trigonal-bipyramidal structure with an equatorial CO group and the P–SR ligands spanning axial and equatorial positions. The five-co-ordinate cations are stereochemically non-rigid at room temperature on the n.m.r. time-scale but become stereochemically rigid at very low temperature. We observed a similar low temperature (150 K) behaviour for complex (**3**), for which Sanger[5] previously suggested a trigonal-bipyramidal geometry with *trans*-apical P atoms.

When carbon monoxide is bubbled through dichloromethane solutions of the monocarbonyl complexes (**1**)—(**3**), the dicarbonyl derivatives $[Ir(CO)_2(P\text{–}SR)_2]^+$ [R = Me, (**4**); Et, (**5**); or Ph, (**6**)] are immediately formed, as indicated by the i.r. spectra which show two new absorptions in the carbonyl stretching region at about 1 965 and 2 000 cm^{-1} (Table 2). The carbonylation reaction is readily reversible: when argon is bubbled through these solutions, a CO molecule is eliminated from the complexes to reform the starting, monocarbonyl compounds, according to equation (2). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra

$$[Ir(CO)(P\text{–}SR)_2]^+ + CO \rightleftharpoons [Ir(CO)_2(P\text{–}SR)_2]^+ \quad (2)$$

of the solutions containing the dicarbonyl complexes show a single, sharp resonance at room temperature (Table 2). The singlet broadens on lowering the temperature and at −60 °C an AX pattern is observed. The lower field doublet [Δ(co-ord) $\simeq$ 44 p.p.m.] can be assigned to the P atom of a chelate P–SR ligand, while the higher field doublet [Δ(co-ord) $\simeq$ 11 p.p.m.] is attributed to the P atom of a P–SR molecule acting as a monodentate ligand.[6] This shows that the thioether arm of a P–SR chelate has been displaced by CO and that the $[Ir(CO)_2(P\text{–}SR)_2]^+$ cations are five-co-ordinate. The ^2J(P–P′) value of *ca.* 230 Hz suggests a geometry in which the P atoms occupy apical positions. On the basis of spectroscopic data, structures (**4**)—(**6**) are proposed for these complexes. The room temperature ^{31}P n.m.r. behaviour probably arises from a fast (on the n.m.r. time-scale), reversible dissociation of the chelate thioether arm which leads to interchange of the roles of the mono- and bi-dentate P–SR ligands, as already observed for [Ni(NO)(P–SR-*P,S*)(P–SR-*P*)]BPh_4.[7]

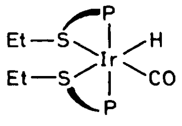
When the reaction between the ligands P–SR (R = Me or Et) and *trans*-$[IrCl(CO)(PPh_3)_2]$ is carried out in boiling methanol–dichloromethane in a ratio of 2:1, the yellow-orange starting solutions turn pale yellow, and white stable crystalline compounds can be isolated by addition of sodium tetraphenylborate. In the case of the ligand P–SPh, only complex (**3**) is recovered from the reaction mixture even after prolonged heating. On the basis of i.r., ^1H and ^{31}P n.m.r. spectra, conductivity, and analytical data, the white products are formulated as $[IrH(CO_2Me)(P\text{–}SR)_2]BPh_4$ [R = Me, (**7**); R = Et, (**8**)]. Along with the ligand and the unco-ordinated anion modes, the i.r. spectra of both compounds exhibit absorptions at 2 145—2 155 cm^{-1}, which can be assigned to a metal–hydride stretching vibration, and at 1 630—1 645 cm^{-1} and 1 060—1 075 cm^{-1}, which we assigned to ν(C=O) and ν(C–O), respectively.[3,8] The room temperature ^1H n.m.r. spectra of (**7**) and (**8**) confirm the presence of the methoxyl and hydride groups: a broad singlet at *ca.* 2.8 p.p.m. is attributed to the methoxyl protons, and a broad signal at *ca.* −14 p.p.m. to the hydride. Moreover, treatment of both compounds with *p*-toluenesulphonic acid in dichloromethane instantly leads to *cis*-$[IrH(CO)(P\text{–}SR)_2]^{2+}$, according to equation (3). The resulting

$$[IrH(CO_2Me)(P\text{–}SR)_2]^+ + H^+ \rightleftharpoons cis\text{-}[IrH(CO)(P\text{–}SR)_2]^{2+} + MeOH \quad (3)$$

hydrido–carbonyl derivatives were identified by ^{31}P n.m.r. and i.r. spectroscopies (see below). Complexes (**7**) and (**8**) do not apparently react with sodium methoxide.

At high temperature (*T* = 80 °C, dimethyl sulphoxide solution), the ^{31}P n.m.r. spectra of both (**7**) and (**8**) consist of a singlet at *ca.* 31 p.p.m. Under the same experimental conditions the ^1H n.m.r. spectrum of (**7**) shows a sharp singlet for the methoxylic protons (2.79 p.p.m.) and a 1:2:1 triplet centred at −14.63 p.p.m. [*J*(P–H) = 13.2 Hz] for the hydride. The methyl protons of the P–SMe ligands appear as two well separated singlets at 1.57 and 1.72 p.p.m. in a 1:1 intensity ratio. The high-field, broader signal can be assigned to the methyl protons of the –SMe group *trans* to the hydride, since selective homodecoupling of the hydride proton results in sharpening of this signal. The ^1H n.m.r. spectrum of (**8**) shows a sharp singlet at 2.74 p.p.m. (methoxyl protons), a 1:2:1 triplet centred at −14.76 p.p.m. [hydride ligand, *J*(P–H) = 12.5 Hz] (Table 2), and two well resolved A_2X_3 systems (ethyl protons of the P–SEt ligands). A selective homodecoupling experiment assigns the 1.92 p.p.m. quartet and the 0.63 p.p.m. triplet to one of the non-equivalent ethyl groups, and the 1.42 p.p.m. quartet and 0.91 p.p.m. triplet to the other one.

Lowering the temperature produces reversible modifications in the n.m.r. spectra of (**7**) and (**8**), which suggest that two isomers [(**A**) and (**B**)] are present in the solutions, in a molar ratio 1:2 and 1:1.5, respectively (Table 2). Integration and homonuclear proton decoupling experiments confirm the assignments. Probably, at high temperature a rapid intramolecular process leads to the observation of averaged spectra, while at low temperature the spectra of the two isomers are distinctly observed. The geometry of these isomers, as well as the nature of the dynamic process actually taking place in solution is so far uncertain. Examples of stereochemical non-rigidity in Ir^{III} complexes of the type $[IrHX(P\text{–}P)_2]^+$ (P–P = diphosphine) have been previously reported and discussed.[9] Among the processes that should be considered, we suggest the possibility of inversion at the co-ordinated sulphur atoms.[10] Since the interpretation of the ^{31}P and ^1H n.m.r. spectra was not conclusive, we undertook a diffractometric analysis of (**8**) in order to ascertain the stereochemistry of these complexes (see below).



(10)

The formation of $[IrH(CO_2R')(P\text{–}SR)_2]^+$ complexes was found to be critically dependent on the nature of the alcohol and of the P–SR ligand. In order to understand the mechanism of this reaction, we have carried out the reaction between Vaska's compound and the P–SR ligands in different alcohols. As found for methanol, the reaction with the ligands P–SMe or P–SEt in boiling ethanol–dichloromethane affords $[IrH(CO_2Et)(P\text{–}SR)_2]^+$ complexes; the P–SEt derivative (**9**) has been isolated and characterized (Table 2). On the contrary, in the presence of 2-propanol or Bu^{t}OH the monocarbonyl derivatives $[Ir(CO)(P\text{–}SR)_2]^+$ are obtained. The latter is the only product formed with P–SPh also, in the presence of methanol or ethanol.

A plausible route to the hydridoalkoxycarbonyl complexes would involve the formation of $[Ir(CO)(P\text{–}SR)_2]^+$ or $[IrH(CO)(P\text{–}SR)_2]^{2+}$ and the subsequent reaction with alcohol or RO^-. To test this hypothesis, we have examined the reactivity of (**2**), and of the corresponding hydridocarbonyl complexes (**10**) and (**11**) with alcohols. The reactions were performed by dissolving complex (**2**) (2×10^{-2} mol dm^{-3}) in dichloromethane containing about 10% of alcohol, and were followed by i.r. spectroscopy. In methanol–dichloromethane solution, at room temperature, complex (**2**) slowly decomposes to afford a mixture of the dicarbonyl derivative (**5**) and possibly $[Ir(P\text{–}SR)_2]^+$. No formation of any detectable amount of (**8**) was observed after 3 d. Under the same experimental conditions, the more acidic trifluoroethanol yields small amounts (*ca.* 10%) of the corresponding hydridoalkoxycarbonyl derivative, as shown by the appearance in the i.r. spectrum of absorptions at 2 135 and 1 643 cm^{-1} [ν(Ir–H) and ν(C=O), respectively]. Unfortunately, the reaction is not clean and also in this case extensive decomposition of (**2**) is observed. No hydridoalkoxycarbonyl complexes are formed with 2-propanol or Bu^{t}OH. It should be noted that if complex (**2**) in methanol–dichloromethane is briefly heated to 50 °C, the formation of (**8**) immediately occurs. In all these cases, the solution i.r. studies do not reveal the presence of detectable amounts of hydrido intermediates. However, the hydrido complexes $[IrH(CO)(P\text{–}SR)_2]^{2+}$ can be easily obtained by direct protonation of complex (**2**) with strong acids.

As found for the analogous complex $[Ir(CO)(dppe)_2]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane], the oxidation of (**2**) with HBF_4 in dichloromethane–2-propanol affords *cis*-$[IrH(CO)(P\text{–}SEt)_2]^{2+}$ (**10**), while HCl gives the *trans* isomer (**11**), which is thermodynamically the more stable.[11] These geometries are assigned on the basis of the spectroscopic data. The i.r. spectrum of (**10**) shows Ir–H and C≡O bands at 2 135 and 2 080 cm^{-1}, respectively; the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of this compound appears as an AB pattern [*J*(P–P) = 253 Hz], indicating the presence of inequivalent *trans*-P atoms, while the hydride signal in the ^1H n.m.r. spectrum is a doublet of doublets (X part of an ABX system). Complex (**11**) exhibits Ir–H and C≡O stretching frequencies at 2 140 and 2 055 cm^{-1}, respectively; its $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows a sharp singlet, while the hydride resonance in the ^1H n.m.r. spectrum is a triplet. These data are consistent with a *trans* arrangement for the hydrido and carbonyl ligands, but do not allow us to distinguish between the two structures in which the P atoms of the P–SEt ligands occupy either *cis* or *trans* positions. On standing in dichloromethane solution, the *cis* isomer, (**10**), slowly yields the *trans* isomer, (**11**); this reaction is strongly accelerated when chloride ions are added to the solution. Therefore, it is likely that (**11**) is obtained in the HCl oxidation reaction by means of chloride-induced isomerization of the kinetically formed *cis* complex, (**10**). These results are similar to those reported for *cis*- and *trans*-$[IrH(CO)(dppe)_2]^{2+}$.[11]

Table 3. Selected bond distances (Å) and angles (°), with estimated standard deviations in parentheses, for complex (**8**)

Ir–S(1)	2.421(6)	Ir–C(1)	2.01(2)
Ir–S(2)	2.447(5)	C(1)–O(1)	1.19(2)
Ir–P(1)	2.312(6)	C(1)–O(2)	1.38(3)
Ir–P(2)	2.316(6)	O(2)–C(58)	1.46(4)
S(1)–Ir–S(2)	85.8(2)	P(1)–Ir–P(2)	177.0(2)
S(1)–Ir–P(1)	85.9(2)	P(1)–Ir–C(1)	93.4(6)
S(1)–Ir–P(2)	93.2(2)	P(2)–Ir–C(1)	87.7(6)
S(1)–Ir–C(1)	178.3(6)	Ir–C(1)–O(1)	129(2)
S(2)–Ir–P(1)	96.0(2)	Ir–C(1)–O(2)	113(1)
S(2)–Ir–P(2)	86.8(2)	O(1)–C(1)–O(2)	117(2)
S(2)–Ir–C(1)	92.8(6)	C(1)–O(2)–C(58)	116(2)

Both isomers, (**10**) and (**11**), are readily deprotonated by bases such as hydroxide and alkoxide ions, or triethylamine, and no reaction is observed between the *trans* isomer, (**11**), and weak nucleophiles such as methanol and ethanol. By contrast, the *cis* isomer, (**10**), readily undergoes nucleophilic attack by methanol and ethanol at the carbon atom of the carbonyl ligand, with the formation of the corresponding hydridoalkoxycarbonyl derivatives (**8**) and (**9**), respectively. Since a larger steric crowding is present in the complex having *cis* geometry, the reason for the higher reactivity of (**10**) is probably of electronic nature. It seems plausible that the electronic density at the carbonyl is greater when the position *trans* to CO is occupied by the hydride rather than the thioether; this is also suggested by the CO stretching frequencies of the two complexes [ν(CO) = 2 080 and 2 055 cm^{-1} for (**10**) and (**11**), respectively]. Hence, the carbon atom of the carbonyl ligand is more electron-rich in the case of the *trans* isomer, (**11**), and nucleophilic attack is less likely.

The reaction of (**10**) with alcohol was monitored by i.r. spectroscopy; mixing (**10**) with a slight excess of methanol or ethanol in dichloromethane leads to quantitative formation of the hydridoalkoxycarbonyl derivatives (**8**) or (**9**), as shown by the appearance of absorptions at *ca.* 2 140 and *ca.* 1 630 cm^{-1} [ν(Ir–H) and ν(C=O), respectively]. No reaction was observed with either the more basic and sterically demanding alcohols such as 2-propanol and Bu^{t}OH, or with the more acidic trifluoroethanol. Also, with water, nucleophilic attack at co-ordinated CO does not occur, but rather isomerization of (**10**) to (**11**) is observed.

In conclusion, it seems likely that the reaction of the P–SR ligands with Vaska's compound involves the initial formation of $[Ir(CO)(P\text{–}SR)_2]^+$; this first step can be eventually followed by the reaction with alcohol. The instability of the carbonyl complexes in dichloromethane–alcohol solutions prevents kinetic studies, and therefore the mechanism of formation of the hydridoalkoxycarbonyl complexes remains uncertain.

Perhaps the more interesting feature of the formation of complexes (**8**) and (**9**) is that the carbonyl complex (**2**) reacts with methanol and ethanol only at high temperature. A tentative interpretation of this fact is that the dissociation of a thioether arm occurs in these conditions, affording a co-ordinatively unsaturated species which then undergoes O–H oxidative addition of an alcohol molecule. In the resulting hydridoalkoxo derivative of Ir^{III}, the reco-ordination of the thioether arm could

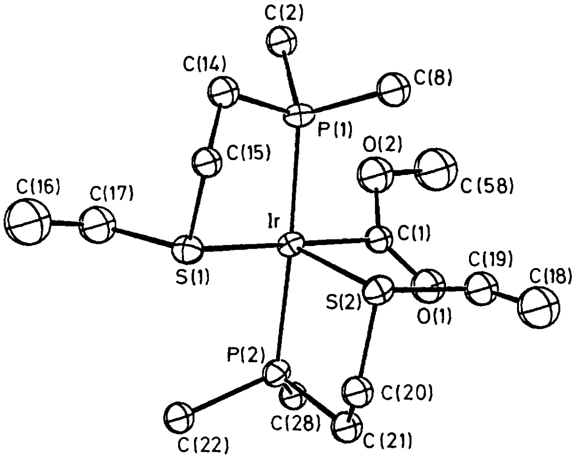


Figure. The molecular structure of $[IrH(CO_2Me)(P\text{-}SEt)_2]^+$, (**8**), with the atom numbering scheme. Phenyl rings have been omitted for clarity

induce an intramolecular MeO^- migration, yielding the methoxycarbonyl group. In agreement with this hypothesis, complex (**3**), in which the ligand P–SPh induces a lower basicity at the iridium atom, does not form any hydridoalkoxycarbonyl derivatives. Since RO^- readily deprotonates complex (**10**), the methoxide migration route appears to be more likely than a displacement–nucleophilic attack mechanism. It should be noted, however, that with the corresponding complexes $[Ir(CO)(P\text{-}P)_2]^+$ the reaction with alcohol to give hydridoalkoxycarbonyl derivatives occurs when the ligand is dmpe, but not when the diphosphine is dppe.[3] In this case, a dissociative pathway involving the diphosphine arms is unlikely, since the $-PMe_2$ groups are tightly bound to the iridium. Alternative routes which involve carbon monoxide dissociation, or the protonation by alcohol of the five-co-ordinate complex (**2**), should also be considered.

Description of the Crystal Structure of (**8**).—The results of the *X*-ray diffraction study on (**8**) are summarized in Table 3, and the co-ordination around the iridium atom is shown in the Figure, together with the atomic numbering scheme. The crystal is built up of discrete $[IrH(CO_2Me)(P\text{-}SEt)_2]^+$ cations and $[BPh_4]^-$ anions, held together by electrostatic and van der Waals interactions. The BC_4 core of the anion has an approximate tetrahedral geometry with a mean B–C distance of 1.63 ± 0.03 Å, and C–B–C angles in the range 107—114°. The co-ordination around the iridium atom can be described in terms of a slightly distorted square-based pyramid, five co-ordination positions being occupied by the chelating P–SEt ligands and by the methoxycarbonyl group. The phosphorus atoms occupy *trans* positions; the S(1) atom is *cis* to S(2) and *trans* to the methoxycarbonyl group. Though the hydride hydrogen atom is not located, the overall geometry of the complex supports spectroscopic evidence for an Ir–H species, and suggests that the hydride ligand occupies the co-ordination position *trans* to S(2), completing the octahedral co-ordination of the iridium atom.

The methoxycarbonyl group is planar, within experimental error, and the C(1)–O(1)–O(2) plane nearly bisects the Ir–S(2)–C(20)–C(21)–P(2) ring, making a dihedral angle of 44(1)° with the plane passing through Ir, S(1), and S(2). The Ir–C(1) bond length of 2.01(2) Å can be compared with those found for other methoxycarbonyl complexes of Ir^{III}, such as $[IrCl(CO_2Me)(Me_2PCH_2CH_2PMe_2)]FSO_3$[8] [2.073(8) Å] and $[Ir(I)_2(CO_2Me)(CO)(phen)]$[12] (phen = 1,10-phenanthroline) [2.05(2) Å]. The other interatomic distances in the ester group are normal. The significant distortions observed in the C(1) sp^2 geometry [Ir–C(1)–O(1) = 129(2), Ir–C(1)–O(2) = 113(1)°] are not unusual. In fact, the *X*-ray structures of several methoxycarbonyl derivatives of different metals show similar angular patterns.[2b,c,8,12,13]

The Ir–P and Ir–S distances are close to those observed in analogous compounds containing mixed-donor phosphorus–sulphur ligands.[14] The difference between the Ir–S distances suggests a stronger *trans* influence of the hydride as compared to the methoxycarbonyl ligand. The co-ordination angles around the Ir atom show minor distortions from the ideal octahedral geometry (Table 3). The chelate bite angles are typical of five-membered rings,[14] the average value being 86.3°. The Ir–P(1)–C(14)–C(15)–S(1) ring can be described in terms of an envelope conformation: Ir, S(1), P(1), and C(14) are nearly coplanar (±0.02 Å), while C(15) is displaced by 0.62(2) Å from their mean plane. The conformation of the Ir–S(2)–C(20)–C(21)–P(2) ring is near to the ideal half-chair: C(20) and C(21) are displaced from the Ir–S(2)–P(2) plane by 0.41(2) and −0.26(2) Å, respectively. All distances and angles within the P–SEt ligands are unexceptional. The geometry of both sulphur atoms is pyramidal, with the ethyl groups nearly lying in the S(1)–Ir–S(2) plane (±0.40 Å), and oriented away from each other (Figure). On the basis of steric considerations, the configuration observed at S(1) and S(2) should be the most favoured also in solution. However, we cannot rule out the possibility that other diastereoisomers are actually present in the solutions of (**7**) and (**8**), and that a fast interconversion process is operative at high temperature, as suggested above.

Experimental

All reactions were carried out under argon. Solvents were purified by standard methods. All chemicals used were of reagent grade or comparable purity. The phosphorus–sulphur hybrid ligands were synthesized and purified as previously described.[15] The complexes $[Ir(CO)(P\text{-}SPh)_2]BPh_4$[5] and *trans*-$[IrCl(CO)(PPh_3)_2]$[16] were prepared by published procedures. Infrared spectra were obtained on a Jasco DS 702 G spectrophotometer calibrated with the 1 601.4 cm^{-1} band of polystyrene film; samples were prepared as Nujol mulls or dichloromethane solutions. Proton and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were collected on a Bruker WP 80 SY Fourier transform spectrometer equipped with a variable temperature unit. Spectra at temperatures lower than −80 °C were run in CD_2Cl_2–$CHClF_2$ solutions. Positive ^{31}P chemical shifts are downfield of 85% H_3PO_4, external standard; ^1H chemical shifts are referenced to $SiMe_4$. Conductance data were obtained on a Metrohm E 518 conductivity bridge. Melting points were determined on analytically pure samples on a Büchi 512 capillary melting point apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Laboratory, Istituto di Chimica, Udine, Italy. Analytical and physical data for the complexes are collected in Table 1, while selected spectroscopic data for the complexes are given in Table 2.

Synthesis of the Complexes.—$[Ir(CO)(P\text{-}SMe)_2]BPh_4$, (**1**). The complex *trans*-$[IrCl(CO)(PPh_3)_2]$ (0.390 g, 0.5 mmol) and the ligand P–SMe (0.260 g, 1.0 mmol) were dissolved in dichloromethane–methanol (1:1 ratio, 40 cm^3); a methanol solution (20 cm^3) of $NaBPh_4$ (0.342 g, 1.0 mmol) was added. The dichloromethane was removed under vacuum and a yellow product was obtained. Recrystallization from dichloromethane–ethanol gave the desired compound.

$[Ir(CO)(P\text{-}SEt)_2]BPh_4$, (**2**). This complex was prepared from *trans*-$[IrCl(CO)(PPh_3)_2]$ (0.390 g, 0.5 mmol) and P–SEt (0.274 g, 1.0 mmol) in a similar manner as that described for (**1**) above.

[IrH(CO$_2$Me)(P–SMe)$_2$]BPh$_4$, (**7**). The complex *trans*-[IrCl(CO)(PPh$_3$)$_2$] (0.390 g, 0.5 mmol) and the ligand P–SMe (0.260 g, 1.0 mmol) were dissolved in dichloromethane (20 cm^3). Methanol (20 cm^3) was added and the solution refluxed, under vigorous stirring, for 6 h; the solution was then allowed to cool to room temperature. After addition of a methanol solution of NaBPh$_4$ (0.342 g, 1.0 mmol), the dichloromethane was pumped off and an off-white powder precipitated. The crude product was recrystallized twice from dichloromethane–methanol to give a white product.

[IrH(CO$_2$Me)(P–SEt)$_2$]BPh$_4$, (**8**). (*a*) The complex was obtained from *trans*-[IrCl(CO)(PPh$_3$)$_2$] (0.390 g, 0.5 mmol) and P–SEt (0.274, 1.0 mmol) as described above for the analogue (**7**).

(*b*) Complex (**10**) (0.423 g, 0.3 mmol) was stirred for 10 min in a dichloromethane–methanol (30–10 cm^3) mixture. Evaporation of the dichloromethane *in vacuo* yielded the desired product.

[IrH(CO$_2$Et)(P–SEt)$_2$]BPh$_4$, (**9**). This complex was obtained following both methods (*a*) and (*b*) as described for (**8**), using ethanol instead of methanol.

cis-[IrH(CO)(P–SEt)$_2$][BPh$_4$]$_2$, (**10**). Complex (**2**) (0.544 g, 0.5 mmol) was dissolved in dichloromethane (20 cm^3), and a 2-propanol solution of HBF$_4$ (0.5 cm^3, 1.2 mol dm^{-3}) slowly added. After addition of a 2-propanol solution of NaBPh$_4$ (0.342 g, 1.0 mmol), the dichloromethane was pumped off affording a white-cream solid, which was recrystallized from dichloromethane–2-propanol.

trans-[IrH(CO)(P–SEt)$_2$][BPh$_4$]$_2$, (**11**). Complex (**2**) (0.5 g, 0.5 mmol) was dissolved in dichloromethane (20 cm^3), and a 0.5 cm^3 sample of 1.1 mol dm^{-3} HCl (2-propanol solution) slowly added. A 2-propanol solution of NaBPh$_4$ (0.342 g, 1.0 mmol) was then added, and the dichloromethane removed under reduced pressure affording a white-cream product, which was recrystallized from dichloromethane–2-propanol.

Crystal Structure Determination of Compound (**8**).—Large crystals of (**8**) were grown by slow diffusion of methanol into a dichloromethane solution of the complex.

Crystal data. C$_{58}$H$_{62}$BIrO$_2$P$_2$S$_2$, M = 1 120.2, orthorhombic, space group $P2_12_12_1$ (determined from preliminary Weissenberg and precession photographs), a = 12.242(2), b = 16.616(3), c = 26.992(2) Å, U = 5 491(1) Å^3 (by least-squares refinement on setting angles of 24 randomly selected reflections with $24 < 2\theta < 34°$, λ = 0.710 69 Å), Z = 4, D_c = 1.36, D_m = 1.35 g cm^{-3}, $F(000)$ = 2 280, μ(Mo-K_α) = 25.9 cm^{-1}. White, platelet-shaped crystal (approximate dimensions 0.2 × 0.6 × 0.8 mm) cut from a polycrystalline mass.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, continuous ω/θ scans with ω-scan width = $(1.5 + 0.35 \tan\theta)°$, ω-scan speed = 0.6—6.7° min^{-1}, graphite-monochromated Mo-K_α radiation; no statistical variation over the course of data collection for four standard reflections monitored every 4 000 s of exposure time; 5 367 reflections measured ($3 < \theta < 25°$, hkl); absorption correction by the empirical ψ-scan method (transmission factors, min., max.: 0.7169, 0.9993, average value 0.9283);[17] 2 655 unique data with $I > 3\sigma(I)$.

Structure analysis and refinement. Conventional Patterson and Fourier methods. Full-matrix least-squares refinement, with anisotropic thermal parameters for the Ir, S, and P atoms. Hydride ligand not detected on the difference Fourier maps. The contribution of the remaining hydrogen atoms (located at

Table 4. Atomic positional parameters (fractional co-ordinates), with estimated standard deviations in parentheses, for complex (**8**)

Atom	x	y	z
Ir	0.844 82(7)	0.937 66(5)	0.865 57(3)
S(1)	0.813 5(5)	0.969 4(3)	0.779 2(2)
S(2)	0.666 2(4)	0.871 8(3)	0.862 8(2)
P(1)	0.778 8(5)	1.065 3(4)	0.881 9(2)
P(2)	0.919 2(5)	0.812 9(4)	0.847 6(2)
O(1)	0.854(1)	0.849 3(9)	0.958 5(6)
O(2)	0.911(1)	0.974(1)	0.964 2(7)
C(1)	0.866(2)	0.912(1)	0.937 5(7)
C(2)	0.863(2)	1.139(1)	0.912 7(8)
C(3)	0.815(3)	1.207(2)	0.932(1)
C(4)	0.890(3)	1.267(2)	0.957(1)
C(5)	0.993(3)	1.247(2)	0.956(1)
C(6)	1.044(2)	1.186(2)	0.936(1)
C(7)	0.975(2)	1.130(2)	0.913(1)
C(8)	0.653(2)	1.064(2)	0.917 8(8)
C(9)	0.654(2)	1.057(2)	0.967 7(8)
C(10)	0.553(2)	1.047(2)	0.994(1)
C(11)	0.463(2)	1.056(2)	0.969(1)
C(12)	0.449(2)	1.071(2)	0.921(1)
C(13)	0.553(2)	1.072(2)	0.894 8(9)
C(14)	0.746(2)	1.116(1)	0.822 3(9)
C(15)	0.717(2)	1.053(1)	0.784 4(8)
C(16)	0.928(3)	1.046(2)	0.705(1)
C(17)	0.935(2)	1.019(2)	0.757(1)
C(18)	0.505(3)	0.808(2)	0.925(1)
C(19)	0.617(2)	0.840(2)	0.922 8(9)
C(20)	0.701(2)	0.777(1)	0.834 4(8)
C(21)	0.809(2)	0.742(1)	0.852 0(8)
C(22)	0.981(2)	0.799(1)	0.785 0(8)
C(23)	1.082(2)	0.830(1)	0.776 3(9)
C(24)	1.122(2)	0.822(2)	0.728(1)
C(25)	1.062(2)	0.795(2)	0.692 1(9)
C(26)	0.960(2)	0.767(2)	0.699(1)
C(27)	0.915(2)	0.769(2)	1.749(1)
C(28)	1.027(2)	0.799(1)	0.887 9(7)
C(29)	1.036(2)	0.697(2)	0.901(1)
C(30)	1.119(2)	0.678(2)	0.933(1)
C(31)	1.195(2)	0.727(2)	0.950 2(9)
C(32)	1.189(2)	0.804(1)	0.935 3(9)
C(33)	1.104(2)	0.834(1)	0.905 8(9)
C(34)	0.466(2)	0.929(1)	0.673 7(8)
C(35)	0.430(2)	0.872(2)	0.640(1)
C(36)	0.483(2)	0.799(2)	0.626(1)
C(37)	0.578(3)	0.785(2)	0.649(1)
C(38)	0.625(2)	0.834(2)	0.680(1)
C(39)	0.572(2)	0.906(2)	0.694(1)
C(40)	0.339(2)	1.004(1)	0.741 1(8)
C(41)	0.370(2)	0.949(1)	0.778 8(8)
C(42)	0.317(2)	0.952(2)	0.825 1(9)
C(43)	0.238(2)	1.007(2)	0.837(1)
C(44)	0.209(2)	1.056(2)	0.799 6(9)
C(45)	0.260(2)	1.056(2)	0.755 4(9)
C(46)	0.495(2)	1.087(1)	0.694 9(9)
C(47)	0.488(2)	1.150(2)	0.729 3(9)
C(48)	0.565(2)	1.213(2)	0.731(1)
C(49)	0.645(2)	1.212(1)	0.695 9(9)
C(50)	0.663(3)	1.156(2)	0.662(1)
C(51)	0.588(2)	1.090(1)	0.660 5(9)
C(52)	0.324(2)	1.035(1)	0.643 5(8)
C(53)	0.356(2)	1.080(1)	0.603 4(8)
C(54)	0.282(2)	1.097(2)	0.562(1)
C(55)	0.181(2)	1.062(2)	0.563 2(9)
C(56)	0.147(2)	1.018(1)	0.601 7(9)
C(57)	0.217(2)	1.003(2)	0.640(1)
C(58)	0.933(3)	0.958(2)	1.016(1)
B	0.409(2)	1.012(2)	0.688 3(9)

calculated positions, with C–H = 1.0 Å, $U = 5.0$ Å^2), held constant, was included in the final cycles. The function minimized was $w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma(F_o) + (0.02F_o)^2 + 1.0]$; 2 655 unique reflections having $I > 3\sigma(I)$ were used in the calculations; anomalous scattering terms were included. The structure was refined to $R = 0.0515$ ($R' = 0.0603$). The goodness of fit was 1.10, and the maximum shift/e.s.d. in the final cycle was 0.15. No peaks of chemical significance in the final difference Fourier calculation [highest peak (1.0 e Å^{-3}) located at *ca.* 1.0 Å from the Ir atom]. Least-squares refinement using the enantiomeric structure generated from final co-ordinates gave $R = 0.0653$ ($R' = 0.0770$), supporting the absolute configuration assigned to the cation. Neutral-atom scattering factors were taken from the literature.[18] All data processing performed on a PDP11/44 computer, using the Enraf-Nonius SDP program library.[17] The final fractional atomic co-ordinates of the non-hydrogen atoms are given in Table 4.

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

Acknowledgements

Support of this work by the Italian C.N.R., Rome, is gratefully acknowledged. We wish to thank Professor L. Randaccio (Dipartimento di Scienze Chimiche, Università di Trieste) for data collection and computing facilities, and Mr. F. Tubaro and Mr. P. Polese for technical assistance.

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Received 9th *February* 1988; *Paper* 8/00515J