Reactions of Silanes and Germanes with Iridium Complexes. Part 3.[1] Reactions of some Silyl Derivatives of O, S, Se, N, and P with *trans*-Carbonyliodobis(triethylphosphine)iridium(I)

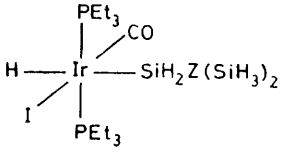
By **E. A. V. Ebsworth,* Hugh M. Ferrier,** and **Thomas E. Fraser,** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The title complex, *trans*-[Ir(CO)I(PEt_3)$_2$], (1), reacts with $Y(SiH_3)_2$ (Y = O, S, or Se) in benzene to give [Ir(CO)HI(PEt_3)$_2$(SiH_2YSiH_3)] or [{Ir(CO)HI(PEt_3)$_2$(SiH_2)}$_2$Y], although when Y = O the formation of the former species is difficult to detect. Reaction between (1) and $P(SiH_3)_3$ leads to the formation of [Ir(CO)HI(PEt_3)$_2$-{$SiH_2P(SiH_3)_2$}], [{Ir(CO)HI(PEt_3)$_2$(SiH_2)}$_2$$PSiH_3$], or [{Ir(CO)HI($PEt_3$)$_2$($SiH_2$)}$_3$P], depending on the proportions of the reactants taken. Reaction between (1) and $N(SiH_3)_3$ gives [Ir(CO)HI(PEt_3)$_2${$SiH_2N(SiH_3)_2$}] and [{Ir(CO)HI(PEt_3)$_2$(SiH_2)}$_2$$NSiH_3$], but no tris(iridiosilylamine) was detected. The compounds have been characterised by ^{1}H and ^{31}P n.m.r. spectroscopy and in some cases by analysis.

Our studies of the reactions between *trans*-[PtHX(PEt_3)$_2$] (X = Cl, Br, or I) and $Y(SiH_3)_2$ (Y = O, S, or Se) or $Z(SiH_3)_3$ (Z = N or P) have led [2] to the identification of derivatives such as [{$PtX(PEt_3)_2(SiH_2)$}$_2$Y] or [{$PtX(PEt_3)_2(SiH_2)$}$_2$$PSiH_3$] when X = I; when X = Cl, exchange processes complicate the reactions. We were not able to detect the formation of a tris(platiniosilyl)-phosphine, even when $P(SiH_3)_3$ was allowed to react with a large excess of the platinum hydride starting material. As part of our study of the oxidative addition of silanes to *trans*-[Ir(CO)X(PEt_3)$_2$] and related compounds, we have investigated the reactions between *trans*-[Ir(CO)I(PEt_3)$_2$], (1), and $O(SiH_3)_2$, $S(SiH_3)_2$, $Se(SiH_3)_2$, $N(SiH_3)_3$, and $P(SiH_3)_3$. The products of the reactions have initially been characterised by n.m.r. spectroscopy.

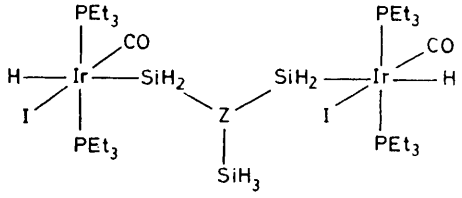
RESULTS

Reactions of trans-[Ir(CO)I(PEt_3)$_2$].—(*a*) *With* $P(SiH_3)_3$. Reaction of (1) with an excess of $P(SiH_3)_3$ in benzene at room temperature was apparently complete within about one minute; we interpret the ^{1}H and ^{31}P n.m.r. spectra as showing that the main product formed under these conditions was complex (2a), below. Our reasons for this conclusion are as follows. The ^{31}P spectrum consists of two resonances, the stronger in the region associated with PEt_3 bound to six-co-ordinated Ir^{III}, and the weaker a very long way to low frequency, in the region associated with P bound to three silicon atoms. With all proton



(2a) Z = P′
(2b) Z = N

coupling eliminated, the higher-frequency resonance appeared as a doublet and the lower as a triplet, the couplings in the two multiplets being equal: this is consistent with a product in which $P'Si_3$ is linked to an iridium atom to which two mutually *trans* PEt_3 groups are already bound. The ^{1}H n.m.r. spectrum confirms this analysis. The IrH region contains a single multiplet, a triplet of doublets of triplets. The larger triplet coupling is collapsed by irradiating in the ^{31}P region at the frequency of the PEt_3 resonance, while the doublet splitting is collapsed by irradiating at the $P'Si_3$ frequency. Thus the IrH proton is equally coupled to two PEt_3 nuclei (which must therefore both be *cis* to it) and shows resolved coupling both to the $P'Si_3$ phosphorus nucleus and to two other protons. In the SiH region there are two overlapping resonances. One is a simple doublet. The other, the weaker, appears as a doublet of triplets of doublets. The larger doublet splitting is collapsed by irradiating at the frequency of the $P'Si_3$ resonance, which also collapses the coupling in the simple doublet. Thus the two SiH resonances are associated with silicon atoms bound to the same P atom. The triplet splitting in the weaker multiplet is collapsed by irradiating at the PEt_3 frequency, while the splitting of the small



(3a) Z = P′
(3b) Z = N

doublet is of the same magnitude as that of the triplet in the IrH resonance. The chemical shift of the IrH resonance is consistent with H *trans* to Si or CO but not to I; the resolution of ^3J(*H*IrSi*H*) and ^3J(*P*SiIr*H*) is also in keeping with a structure in which H is *trans* to Si.

Reaction of (1) in 2 : 1 molar ratio with $P(SiH_3)_3$ gave a different product. As before, the ^{31}P-{^{1}H} spectrum consisted of two sets of resonances. The peak at the higher frequency, due to the PEt_3 nuclei, was a doublet; that at low frequency, which was much weaker, showed a quintet splitting of the same magnitude as the doublet coupling in the PEt_3 resonance. This implies that the $P'Si_3$ nucleus is equally coupled to four PEt_3 nuclei, and so that oxidative addition from two different SiH_3 groups of a molecule of $P(SiH_3)_3$ has given the product (3a). The H resonances were qualitatively similar to those obtained from the reaction between (1) and an excess of $P(SiH_3)_3$, except that the chemical shifts and coupling constants were somewhat different and the simple doublet was relatively

much less strong. All these observations are consistent with our formulation of the product as the bis(iridiosilyl)-phosphine.

Reaction of a four-fold molar excess of (1) with $P(SiH_3)_3$ was also complete in a few minutes at room temperature. This time the $^{31}P-\{^1H\}$ spectrum was less helpful in characterising the product. By working under conditions of the highest resolution, we were able to resolve the peak due to the PEt_3 groups of the $^{31}P-\{^1H\}$ spectrum as a doublet; the resonance due to the $P'Si_3$ nucleus was clearly a multiplet and could have been a septet, but the envelope was not well enough defined for us to be sure. However, the PEt_3 resonance was a clear doublet when only SiH and and small amounts of both (2a) and (4) were obtained in the reaction between $P(SiH_3)_3$ and (1) in two-fold molar excess; but (4) could be obtained in solution free of (2a) or (3a). We have succeeded in isolating (4) as a white solid, and confirming its constitution by analysis.

(*b*) *With* $N(SiH_3)_3$. Reaction of (1) with an equimolar quantity of $N(SiH_3)_3$ in benzene at room temperature gave a single product whose $^{31}P-\{^1H\}$ n.m.r. spectrum showed a single peak. In the ^1H spectrum there were resonances in the regions associated with SiH, with the protons of co-ordinated PEt_3 groups, and with IrH groups. The IrH resonance appeared as a triplet of triplets: the chemical shift was in the region associated with H *trans* to CO or to Si

TABLE 1

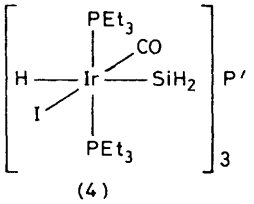
N.m.r. parameters for complexes formed by reaction of (1) with $N(SiH_3)_3$ and $P(SiH_3)_3$ [a]

	Chemical shifts/p.p.m.				
Complex	$\delta(^{15}N/P')$	$\delta(P)$	$\delta(SiH_2)$	$\delta(SiH_3)$	$\delta(IrH)$
(2b)	−6.5	−16.9	4.74	5.33	−9.82
(3b)	−5.2	−16.7	4.85	5.47	−9.75
(2a)	−343.7	−16.9	3.9	4.1	−10.0
(3a)	−299.1	−17.6	4.1	4.2	−9.8
(4) [b]	−259.0	−19.0	4.2		−9.7

	Coupling constant/Hz						
Complex	$^2J(HP)$	$^2J(H_2Si^{15}N/P')$	$^2J(H_3Si^{15}N/P')$	$^2J(^{15}N/P'P)$	$^3J(HSiIrP)$	$^3J(HH)$	$^3J(HIrSi^{15}N/P')$
(2b)	15.2	4.9	4.3	0.2	6.9	2.3	1.9
(3b)	15.5	4.9	4.1		7.1	2.5	n.r.
(2a)	15.5	*ca.* 10	16.0	0.6	7.0	2.8	7.5
(3a)	15.6	10.4	15.7	1.2	6.3	1.8	7.9
(4) [b]	17.0	12.0		0.7	6.0	1.6	10.0

[a] Measurements in C_6H_6 at room temperature, and considered accurate to ±2 in last figure quoted. All shifts are measured as positive to high frequency of 85% H_3PO_4 (^{31}P), NMe_4^+ (^{15}N), or $SiMe_4$ (^1H); n.r. = not resolved. [b] $^1J(^{29}SiP) = 62.8$ Hz. By homonuclear double resonance, $^2J(HP)$ opposite in sign to $^3J(HSiIrP)$, $^3J(HP')$ opposite in sign to $^2J(H_2SiP')$.

CH protons were decoupled, showing that there was one IrH for each iridium centre, while under the same conditions the $P'Si_3$ resonance was a well defined quartet, showing that there were three IrH groups around the central phosphorus. The IrH resonance appeared as a doublet of triplets, each line of which was broadened but could not be resolved further. The doublet splitting was collapsed by irradiating at the frequency of the $P'Si_3$ resonance, and the triplet coupling by irradiating at the PEt_3 frequency. The SiH resonance appeared as a roughly 1 : 2 : 2 : 2 : 1 quintet; this pattern was shown by heteronuclear double resonance to arise from coupling to the $P'Si_3$ and the PEt_3 phosphorus nuclei, $^2J(HP)$ being roughly twice $^3J(HP)$. Under the highest resolution, a further small doublet splitting could be resolved on each line; we assign this to $^3J(HH)$. The



(4)

most important point, however, is that there was no doublet analogous to the resonances assigned to the SiH_3 groups of (2a) and (3a). We conclude that the product we obtained from this system was the tris(iridiosilyl) complex, (4).

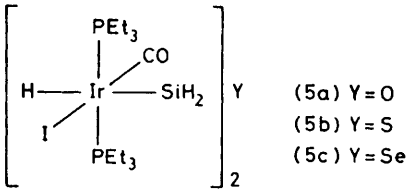
Small amounts of complex (3a) were formed in the reaction between equimolar proportions of (1) and $P(SiH_3)_3$ but not to I; the larger of the triplet couplings could be collapsed by irradiating at the frequency of the PEt_3 resonance. In the SiH region, there were two resonances: the stronger appeared as a singlet, and the weaker as a triplet of narrow doublets, in which the doublet splitting was the same as the smaller triplet splitting in the IrH resonance. The triplet coupling was collapsed by irradiating at the frequency of the P resonance, and the narrow doublet coupling by irradiating at the IrH frequency. We conclude that this product is a species analogous to (2a), with the SiH_2 group *trans* to hydride; the strong singlet in the SiH region is assigned to the unco-ordinated SiH_3 groups. When the experiment was repeated using $^{15}N-(SiH_3)_3$, each line in the SiH and the IrH regions showed an additional small doublet splitting, which was collapsed by irradiating at the same frequency in the ^{15}N region. This shows that the three resonances come from the same molecule. The n.m.r. parameters are given in Table 1. The $^{31}P-\{^1H\}$ resonance of the product obtained for $^{15}N-(SiH_3)_3$ was a narrow doublet. When an excess of (1) was allowed to react with $N(SiH_3)_3$, a similar but different product was obtained. The $^{31}P-\{^1H\}$ resonance was a singlet, as before. The IrH resonance showed a similar pattern, but at a slightly different chemical shift. The two SiH resonances were qualitatively similar, but the singlet due to the free SiH_3 protons was relatively much weaker. The ^{15}N chemical shift was also rather different, and we were unable to resolve $^3J(H^{15}N)$. We conclude that under these conditions the product is a bis(iridiosilyl)amine, (3b), analogous to (3a). Its n.m.r. parameters are set out

in Table 1. We were never able to detect the formation of a tris(iridiosilyl)amine analogous to (4), despite using a variety of reaction conditions. Both of the products [(2b) and (3b)] were isolated as white solids and analysed.

It is worth noting that the bis(iridiosilyl)amine is an initial product of the reaction between (1) and $N(SiH_3)_3$, even when an initial excess of the latter is taken; over a period of hours the bis product reverts to the mono-species.

(*c*) *With* $O(SiH_3)_2$. Reaction between $O(SiH_3)_2$ and (1) in 1 : 2 mol ratio gave a product whose ^{31}P-{^1H} spectrum consisted of a single line. We believe this to have been the complex (5a).

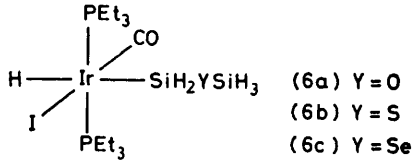
The proton resonance spectrum contained peaks due to IrH, to PEt_3, and to SiH protons. The IrH resonance appeared as a triplet of triplets; the SiH resonance as a triplet of doublets. The larger triplet coupling in each case was shown by heteronuclear double resonance to derive



(5a) Y = O
(5b) Y = S
(5c) Y = Se

from coupling to phosphorus nuclei; the smaller triplet coupling in the IrH resonance was of the same magnitude as the doublet splitting in the SiH resonance. The absence of any resonance that could be assigned to protons of a free SiH_3 group is significant. The complex was isolated as a white air-stable solid and characterised by analysis and by determining its molecular weight in solution. The n.m.r. parameters are given in Table 2. Reaction between (1) and an excess of $O(SiH_3)_2$ in benzene gave a solution with the same ^{31}P-{^1H} spectrum; the ^1H spectrum was also the same except for a sharp singlet at a chemical shift corresponding to the resonance of free $O(SiH_3)_2$. This peak had ^{29}Si satellites, and ^1J(SiH) was the same as in $O(SiH_3)_2$. On removing all volatile materials, a white solid residue remained which gave the same analytical results and the same molecular weight as did the product from the equimolar reaction described above. We conclude that under these conditions we have again obtained complex (5a), leaving an excess of $O(SiH_3)_2$. When the reaction was allowed to occur in light petroleum, an immediate precipitate was formed; this was soluble in benzene, and the proton resonance spectrum contained peaks due to (5a) and additional resonances that we assign to the complex (6a). The n.m.r. parameters are included in Table 2.

Weak peaks corresponding to those of complex (6a) were observed in addition to those due to (5a) in a solution in benzene containing (1) and a large molar excess of $O(SiH_3)_2$. In this solution the resonance due to excess of $O(SiH_3)_2$ degraded over a period of hours, and a peak due to SiH_4 became progressively stronger, together with a number of weak peaks in the region normally associated with Si*H*O species.



(6a) Y = O
(6b) Y = S
(6c) Y = Se

(*d*) *With* $S(SiH_3)_2$. The reaction of (1) with $S(SiH_3)_2$ followed a slightly different course. With the reactants in a 2 : 1 mol ratio, two singlets of roughly equal intensity were observed in the ^{31}P-{^1H} n.m.r. spectrum. When only protons resonating at about δ = 0—5 p.p.m. were irradiated, each ^{31}P line split into a doublet, showing that each species was a monohydride complex; when only PEt_3 protons were decoupled, each ^{31}P line appeared as a doublet of triplets, showing that in each complex there were two equivalent protons coupling to P and with chemical shifts around δ = 4—6 p.p.m. The ^{31}P chemical shifts were in the region associated with PEt_3 bound to Ir^{III}. All these observations are consistent with the formation of complexes (5b) and (6b), analogous to (5a) and (6a) above, and this interpretation is confirmed by the ^1H spectrum. In this, two IrH resonances were observed, each appearing as a triplet of triplets, with the larger triplet coupling associated with coupling to P. In the SiH region we observed a sharp singlet and two triplets of doublets, with each of the triplet couplings associated with phosphorus. The triplet splittings in the higher frequency of the IrH and the higher frequency of the SiH multiplets were both collapsed by irradiating at the same frequency, which corresponded to the lower frequency of the two ^{31}P resonances. These three resonances are therefore due to the same molecular species. Reaction with the reagents in 1 : 1 mol ratio gave spectra with the same resonances, but in which the singlet in the SiH region and the lower frequency SiH and IrH multiplets were relatively stronger. We conclude that these peaks and the higher frequency of the two ^{31}P resonances are due to the complex of type (6b). We were unable to obtain samples of either species uncontaminated by the other. The n.m.r. parameters are given in Table 2.

(*e*) *With* $Se(SiH_3)_2$. The products of the reactions

TABLE 2

N.m.r. parameters for complexes formed by reaction of (1) with $Y(SiH_3)_2$ (Y = O, S, and Se) [a]

	Chemical shift/p.p.m.				Coupling constants/Hz		
Complex	δ(P)	δ(Si*H*$_2$)	δ(Si*H*$_3$)	δ(Ir*H*)	^2J(HP)	^3J(HP)	^3J(HH)
(6a)	−13.8	5.71	4.89	−9.83	15.9	6.7	3.01
(6b)	−16.6	4.4	4.5	−10.2	15.7	8.0	3.2
(6c)	−17.1	4.3	4.6	−10.1	16.0	8.0	3.2
(5a) [b]	−13.8	5.78		−9.80	15.9	7.1	3.0
(5b)	−17.2	5.3		−9.95	15.5	8.0	2.3
(5c)	−17.3	5.2		−9.95	16.2	7.2	2.5

[a] Measurements in C_6H_6 at room temperature; considered inaccurate to ±2 in last figure quoted. All shifts taken as positive to high frequency of 85% H_3PO_4 (^{31}P) or $SiMe_4$ (^1H, ^{29}Si). [b] $\delta(^{29}Si)$ = −30.1 p.p.m.; ^2J(SiP) = 10.7; ^1J(SiH) = 196.0; ^2J(SiH) = 10.4 Hz. By homonuclear double resonance, ^2J(PH) opposite sign to ^3J(PIrSi*H*).

between (1) and $Se(SiH_3)_2$ in both 1 : 1 and 2 : 1 molar ratio gave ^{31}P and ^1H n.m.r. spectra that were qualitatively the same as those described above. We conclude that similar products of types (5c) and (6c) have been formed, and the n.m.r. parameters are included in Table 2.

DISCUSSION

The process of oxidative addition by which these species are formed is essentially the same as that invoked to explain the reactions between (1) and silyl halides;[1] the ^1H n.m.r. parameters suggest that the stereochemical arrangement of ligands round iridium is the same. The relatively easy formation of the tris(iridiosilyl)phosphine is surprising, because the molecule must be stereochemically crowded; we hoped to determine the crystal structure, but have been unable to grow crystals. It should be noted that reaction between $[PtHI(PEt_3)_2]$ and $P(SiH_3)_3$ gave $[\{PtI(PEt_3)_2(SiH_2)\}_2PSiH_3]$ as the most substituted product formed, even though Pt^{II} is presumably less stereochemically demanding than is six-co-ordinated iridium(III). A similar change in degree of substitution is found with $N(SiH_3)_3$; here we were able to identify mono- and bis-(iridiosilyl)-amines but no tris species, whereas with $[PtHI(PEt_3)_2]$ we were only able to identify a mono-platiniosilyl species. Reaction between (1) and $S(SiH_3)_2$ or $Se(SiH_3)_2$ gave both mono- and bis-(iridiosilyl) complexes, but the reaction between (1) and $O(SiH_3)_2$ was somewhat different. Even with an excess of $O(SiH_3)_2$ the only product we could detect in benzene was the bis species (6a), save in the presence of a large excess of $O(SiH_3)_2$, and we were only able to determine the n.m.r. parameters of (6a) by allowing the reaction between (1) and $O(SiH_3)_2$ to occur in a solution from which the products were precipitated as soon as they were formed. This implies that the free SiH_3 group of (6a) reacts with (1) significantly faster than does $O(SiH_3)_2$. The alternative explanation that exchange of Si led to the formation of (5a) and $O(SiH_3)_2$ is shown to be wrong by our observing peaks due to (5a) and (6a) together from the product of reaction in light petroleum after redissolving it in benzene. The decomposition of excess of disiloxane in the presence of (5a) recalls the catalytic effect of $[Ir(CO)H(PPh_3)_2(Si_2Me_4O)]$ on the redistribution of Si–O and Si–H bonds in organosiloxanes.[3]

TABLE 3

Analytical, molecular weight, and i.r. spectral data

Complex	Analysis (%) [a] C	H	N	Infrared data [b] $\tilde{\nu}$(IrH)/cm^{-1} (w)	$\tilde{\nu}$(CO)/cm^{-1} (s)	M [a]
(5a)	25.1 (25.3)	5.3 (5.3)		2 090	1 940	1 323 (1 242)
(2b)	22.7 (22.6)	5.4 (5.4)	2.3 (2.0)	2 090	1 980	
(3b)	24.3 (24.5)	5.6 (5.4)	0.9 (1.1)	2 090	1 960	
(4)	24.9 (24.9)	5.2 (5.3)		2 025	1 968	

[a] Found (calc.). [b] w = Weak, s = strong.

EXPERIMENTAL

Volatile materials were manipulated using a standard vacuum system fitted with greased or with Sovirel Teflon taps; involatile materials that were sensitive to air were handled in a V.A.C. model HE-493 glove-box fitted with a model HE-493 Dri-Train under dried nitrogen gas. Infrared spectra were obtained of gases or of solids dispersed in Nujol by means of Perkin-Elmer 457 (250—4 000 cm^{-1}) or 577 (200—4 000 cm^{-1}) instruments. N.m.r. spectra were recorded by means of the following spectrometers: FX90Q (^{31}P), XL100 (^{31}P), WH 360 (^1H, ^{29}Si), and HA100 CW, whose probe had been double-tuned [4] to accept an additional radiofrequency for ^1H-{^{31}P} or ^1H-{^{15}N} experiments. Compounds were dissolved in C_6H_6 or C_6D_6, and where necessary $SiMe_4$ was added as a proton lock.

Silyl starting materials were prepared by established methods; *trans*-$[Ir(CO)I(PEt_3)_2]$, (1), was made from the corresponding chloride [5] and NaI.

Most of the reactions between (1) and silyl compounds were carried out in the following manner. Compound (1) (0.2 mmol) was weighed into an ampoule fitted with a Teflon tap and to whose side an n.m.r. tube was attached. Benzene was then distilled into the ampoule and (1) was allowed to dissolve; the appropriate silyl compound was then distilled into the solution and reaction allowed to occur for a few minutes. Volatile material was distilled away and fresh benzene distilled into the ampoule to dissolve the residual gum, and this process was repeated. Finally, the reaction products were washed into the n.m.r. tube using C_6H_6 or C_6D_6, any locking material added, and the tube sealed. In some cases reactions were allowed to occur in n.m.r. tubes without removing any volatile material. The isolation of solid products was achieved using Schlenk equipment in conjunction with the glove-box. Products were analysed by microanalysis, and solution molecular weights determined osmometrically using Perkin-Elmer model 115 molecular weight apparatus. Analytical and i.r. data for the compounds that were isolated are summarised in Table 3.

We are grateful to Johnson Matthey Ltd. for the loan of chemicals, and to the S.R.C. for maintenance grants (to H. M. F. and T. E. F.).

[0/1321 *Received*, 22nd *August*, 1980]

REFERENCES

[1] Part 2, E. A. V. Ebsworth and T. E. Fraser, *J. Chem. Soc., Dalton Trans.*, 1979, 1960.
[2] E. A. V. Ebsworth, J. M. Edward, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1976, 1673.
[3] M. D. Curtis and J. Greene, *J. Am. Chem. Soc.*, 1978, **100**, 6362.
[4] A. Charles and W. McFarlane, *Mol. Phys.*, 1968, **14**, 299.
[5] K. Banfield, *Inorg. Synth.*, 1974, **15**, 18; T. E. Fraser, Ph.D. Thesis, University of Edinburgh, 1978.