Reactions of Silanes and Germanes with Iridium Complexes. Part 2.[1] Adducts of Silyl and Germyl Halides and Related Molecules with *trans*-Carbonylhalogenobis(triethylphosphine)iridium(I)

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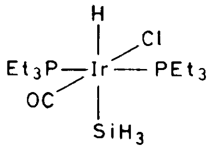
The complex *trans*-$[Ir(CO)X(PEt_3)_2]$ (X = Cl or I) forms equimolar adducts with MH_3Q (M = Si, Q = H, Cl, Br, I, CH_3, or SiH_3; M = Ge, Q = H, Cl, Br, or I). The structures of these adducts have been determined by ^1H and ^{31}P n.m.r. spectroscopy. Addition is always to give *trans*-$[Ir(CO)H(X)(PEt_3)_2(MH_2Q)]$; when M = Si the major (and in most cases the only) product has H *trans* to Si; when M = Ge the major (and in some cases the only) product has H *trans* to X. When X = Cl and Q = Br or I, the silyl adducts contain Cl bound to Si and Br or I bound to Ir; when M = Ge, however, the adduct initially formed contains Cl bound to Ir and Br or I bound to Ge, although the last-named adduct decomposes in solution at room temperature.

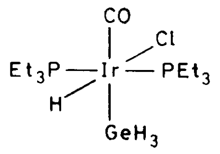
THE formation of equimolar adducts by silanes or germanes with *trans*-carbonylchlorobis(triphenylphosphine)iridium(I), Vaska's compound, has been known for many years,[2,3] but the structures of the adducts have not been easy to determine, for they do not crystallize readily and are only very sparingly soluble in common solvents; much of the evidence on which structures have been assigned comes from i.r. spectroscopy, which is not a reliable technique for this purpose. In a previous study of the reactions between silyl or germyl halides and Vaska's compound[1] we were able to obtain some n.m.r. spectra from the adducts of some germyl compounds because of their transient solubility, and so we were able to base our structural assignments on ^1H n.m.r. spectra. The silyl analogues, however, were so insoluble that we could obtain no useful ^1H n.m.r. spectra at all. Many derivatives of transition-metal complexes of triethylphosphine are much more soluble than their triphenylphosphine analogues.[4] We have therefore investigated the reaction between a range of simple silyl and germyl compounds and *trans*-carbonylchlorobis(triethylphosphine)iridium(I), (1), and *trans*-carbonyliodobis(triethylphosphine)iridium(I), (2), in the hope of obtaining products sufficiently soluble for study by n.m.r. spectroscopy.

RESULTS

Reaction of SiH_4 *with* (1) *and* (2).—The ^{31}P n.m.r. spectrum of the product of the reaction between SiH_4 and (1) appeared as a singlet when proton coupling was eliminated, and as a doublet when only the protons resonating at δ *ca.* 1 were irradiated, showing that in the complex formed the two P nuclei are apparently equivalent under these conditions and therefore mutually *trans*, and that there is one proton bound to iridium. In the ^1H spectrum, the IrH resonance appeared as a triplet of quartets. The triplet splitting was collapsed by irradiating at a frequency corresponding to the chemical shift of the singlet resonance in the ^{31}P spectrum, and so was due to coupling with the two effectively equivalent P nuclei. There was a triplet of doublets in the SiH region; this triplet coupling too was collapsed by irradiation at the same ^{31}P frequency that led to collapse of the triplet coupling in the IrH region, while the magnitude of the doublet splitting was the same as that of the quartet splitting in the IrH resonance. Furthermore, the chemical shift of the IrH resonance was in the region normally associated with H *trans* to a ligand of high *trans* influence, such as CO or Si, but not halogen.[5] If we suppose that the coupling ^3J(HSiIrH) is resolved when H and SiH are mutually *trans* but not when they are mutually *cis* (some evidence to support this assumption is presented in the rest of this paper and elsewhere), we conclude that the complex has structure A below, with mutually *trans* phosphine ligands and with H *trans* to SiH_3. The n.m.r. spectra of the product of the reaction between SiH_4 and (2) are qualitatively very similar, although the ^{31}P chemical shift is substantially different and the IrH resonance moves to low frequency as the halogen bound to iridium is changed from Cl to I; there is no doubt that the two complexes have similar structures. In neither case did we observe any evidence to suggest that a second isomer had been formed. The n.m.r. parameters are set out in the Table. We were able to isolate the product from the reactions with (1) as a solid, whose composition as determined by analysis and whose i.r. spectrum is given in the Experimental section.



A



B

Reactions of GeH_4 *with* (1) *and* (2).—The ^{31}P n.m.r. spectrum of the product of the reaction between (1) and GeH_4 when proton coupling was eliminated showed two singlets of apparent relative intensity *ca.* 2 : 1, implying that two different isomers were present. Besides the complex peaks due to protons bound to co-ordinated PEt_3 groups, the ^1H n.m.r. spectrum showed two sets of IrH and two sets of GeH resonances. The higher-frequency IrH resonance and the lower-frequency GeH resonance were the weaker; they showed patterns (triplet of quartets for IrH, triplet of doublets for GeH) that were the same as those obtained from the products of the reactions of SiH_4 with (1) or (2). In these multiplets the triplet splittings were both collapsed by irradiating in the ^{31}P region with a frequency that corresponds to the chemical shift of the weaker of the two P resonances, and it therefore appears that the less abundant of the two isomers was of type A.

The other resonances in both IrH and GeH regions appeared under normal conditions as simple triplets; both multiplets were collapsed by irradiating at a frequency corresponding to the stronger of the two lines in the ^{31}P spectrum. If, as suggested above, we assume that ^3J(HGe-IrH) is substantially larger when H and GeH_3 are mutually *trans* than when they are *cis*, it follows that this isomer must have either CO or Cl *trans* to H. The chemical shift of the IrH resonance was in the region associated with H *trans* to halogen [5] but not with H *trans* to a ligand of high *trans* influence, such as CO; we therefore conclude that the more abundant isomer has GeH_3 *trans* to CO and H *trans* to Cl, as in structure B. The spectra of the product of the reaction between (2) and GeH_4 are very similar; the less abundant isomer gave IrH and GeH resonances whose patterns confirm that this compound was of type A. The patterns due to the more abundant isomer were the same as those obtained from (1) and GeH_4, except that in an expansion of the GeH resonances it proved possible to resolve a small additional doublet splitting that we could not detect in the spectra of the products of reaction with (1). We were not able to expand the IrH resonances to establish the equivalent quartet coupling, but we assume that the doublet splitting is derived from ^3J(HGeIrH).

The IrH chemical shifts confirmed that in these isomers H was *trans* to halogen. In isomers of type A, as the halogen bound to iridium is changed from Cl to I the IrH resonance moves by *ca.* 2 p.p.m. to low frequency. In the more abundant isomer, the IrH resonance moves to high frequency as the halogen bound to iridium is changed from Cl to I, a change in the same direction as had been observed in other complexes of iridium in which H is *trans* to halogen.[6] The chemical shifts and coupling constants are given in the Table.

Other Reactions of (2).—(*a*) *With* SiH_3I. The ^{31}P spectrum with protons decoupled showed a sharp single peak, indicating that only one isomer had been formed. The presence of a proton resonance in the region associated with metal hydrides shows that SiH_3I was added as $ISiH_2$ and H rather than as SiH_3 and I. The IrH resonance appeared as a triplet of triplets: the larger triplet coupling was collapsed by irradiation at a frequency corresponding to the chemical shift of the peak in the ^{31}P spectrum. At low temperatures the SiH resonance appeared as a triplet of doublets: the triplet splitting was collapsed by irradiation at the same ^{31}P frequency, and the magnitude of the doublet splitting was the same as that of the smaller of the triplet splittings in the IrH resonance. We conclude that the only isomer formed was of type A. There was, however, an unexpected change in the appearance of the SiH resonance with temperature. At temperatures below −30 °C the pattern of a triplet of doublets was clear and well defined. As the solution was allowed to warm towards room temperature, the individual peaks broadened, and at +30 °C the separate components could no longer be distinguished, although a symmetrical triplet pattern could still be made out; irradiation at the frequency of the ^{31}P resonance collapsed this triplet form into a broad symmetrical single line. As the temperature was further increased, the original pattern of a triplet of doublets re-emerged as the component lines became sharper, and at 80 °C they were sharp and fully resolved. This behaviour was reversible; the chemical shift and the two coupling constants were much the same at +80 and −30 °C. The ^{31}P and the IrH resonances changed little over the same temperature range, and showed no signs of broadening; the broadening cannot therefore be associated with exchange. Since it was observed only in the spectrum of the product of the reaction of (2) with SiH_3I, we are forced to conclude that it is associated with the presence of I bound to Si, and may therefore reflect restricted rotation that is slow at the low temperature and fast at 80 °C on the n.m.r. time scale; it is of course

N.m.r. parameters for the adducts of *trans*-$[Ir(CO)X(PEt_3)_2]$ with MH_3Q

				δ(MH)	δ(IrH)	δ(P)	^2J(PIrH)	^3J(PIrMH)	^3J(HIrMH)
X	M	Q	Solvent		p.p.m.			Hz	
I	Si	H	bz	3.2 (t/d)	−10.1 (t/q)	−15.7	15.0	5.6	3.0
I	Si	Cl	tl	5.0 (t/d)	−10.4 (t/t)	−15.5	15.0	8.0	4 0
I	Si	Br	tl [a]	4.7 (t/d)	−10.4 (t/t)	−17.3	15.0	8.3	3.2
I	Si	I	tl	4.0 (t/d)	−10.2 (t/t)	−18.5	15.0	8.0	4.0
I	Ge	H	bz [b]	3.4 (t/d)	−16.3 (t/q)	−23.1	12.0	6.2	0.5
			[c]	2.7 (t/d)	−10.5 (t/q)	−17.5	16.0	4.4	2.6
I	Ge	Cl	tl	5.4 (t/d)	−15.8 (t/t)	−23.3	12.0	8.0	0.8
I	Ge	Br	tl	4.8 (t/d)	−15.6 (t/t)	−24.1	13.0	8.0	0.9
I	Ge	I	tl	3.7 (t/d)	−15.4 (t/t)	−25.0	13.0	8.1	0.9
Cl	Si	H	tl	2.9 (t/d)	−8.1 (t/q)	−4.6	16.0	5.2	3.0
Cl	Si	Cl	tl [b]	4.8 (t/d)	−8.6 (t/t)	−5.3	16.0	7.0	3.0
			[d]	n.o.	−16.0 (t)	−3.2	12.0	n.o.	n.o.
Cl	Si	Br	tl [b]	4.9 (t/d)	−9.2 (t/t)	−9.2	16.0	7.0	3.5
			[d]	n.o.	−15.1 (t)	n.a.	12.0	n.o.	n.o.
Cl	Si	I	tl [b]	5.1 (t.d)	−10.5 (t/t)	16.5	16.0	7.8	4.0
			[d]	n.o.	−14.2 (t)	n.a.	11.0	n.o.	n.o.
Cl	Si	CH_3	bz [e]	3.6 (q/t/d)	−7.7 (t/t)	−4.4	16.0	4.0	2.2
Cl	Si	SiH_3	bz [f]	2.7 (q/t/d)	−8.0 (t/t)	−5.9	16.0	5.0	2.3
Cl	Ge	H	bz [b]	3.0 (t)	−18.8 (t)	−13.6	10.0	6.0	n.o.
			[c]	2.4 (t/d)	−8.5 (t/q)	−6.9	16.0	5.0	3.0
Cl	Ge	Cl	tl [b]	5.1 (t)	−18.3 (t)	−14.4	13.0	7.5	n.o.
			[d]	n.o.	−9.2 (t/t)	−13.0	18.0	n.o.	n.o.
Cl	Ge	Br	tl [b]	4.9 (t)	−18.6 (t)	−14.9	12.0	8.0	n.o.
			[d]	n.o.	−9.5 (t/t)	n.a.	16.0	n.o.	n.o.
Cl	Ge	I	tl [g]	3.4 (t)	−18.0 (t)	−13.3	12.0	8.6	n.o.

All chemical shifts measured as positive to high frequency of $SiMe_4$ for ^1H or 85% H_3PO_4 for ^{31}P; bz = benzene, tl = toluene. [a] Shown by homonuclear tickling that signs of *J*(PIrH) and *J*(PIrSiH) are opposite. [b] Major product. [c] Minor product. [d] Very minor product. [e] δ(CH) = 0.6 p.p.m., ^3J(HCSiH) = 4.0 Hz. [f] δ(SiH_3) = 3.6 p.p.m., ^3J(HSiSiH) = 5.0 Hz. [g] At −20 °C. n.o. = Not observed; n.a. = not assigned.

possible that the quadrupole moment of the iodine nucleus is involved. The n.m.r. data are given in the Table.

(*b*) *With* SiH_3Br *and with* SiH_3Cl. The ^{31}P and ^1H n.m.r. spectra of the products of these reactions were qualitatively very much like those of the product of the reaction with SiH_3I, except that the SiH resonances were sharp at all temperatures studied. The ^{31}P and IrH chemical shifts were all similar, whereas the SiH chemical shifts varied by *ca.* 1 p.p.m., a change of the same order as the change in chemical shift from SiH_3I to SiH_3Cl. All these observations imply that there has been no halogen exchange. This was as expected, since in each of these systems any exchange equilibrium would be expected to leave iodine bound to Ir and the lighter halogen bound to silicon. It should be noticed that no other isomer was detected in any of these systems. The n.m.r. parameters are set out in the Table.

(*c*) *With* GeH_3I, GeH_3Br *or* GeH_3Cl. The n.m.r. spectra of the products of each of these reactions were all qualitatively identical. The ^{31}P spectra with proton coupling eliminated were all singlets, showing that in each case only one isomer had been formed; the ^{31}P chemical shifts were all similar, implying that in each species iodine remained bound to iridium. The IrH and the GeH resonances each appeared as triplets, whose splittings were collapsed by irradiation at the frequency of the appropriate ^{31}P resonance; small doublet splittings could be resolved in the GeH resonance on expansion. The IrH chemical shift was almost identical in the three species, whereas the GeH chemical shift moved to high frequency in the series I, Br, Cl; this is also consistent with structures in which the halogen bound to germanium was the same in the product as in the starting material. Since we did not resolve coupling to the IrH protons we cannot prove directly that the complexes contained GeH_2 groups, but off-resonance decoupling leaves the ^{31}P spectra as doublets, showing that in each product there is one hydride bound to Ir. These compounds are therefore of type B, formed by addition of GeH_2X and H to Ir.

Other reactions of (1).—(*a*) *With* SiH_3Cl. Here there is no possibility of the formation of different isomers as a consequence of halogen exchange. The main product was a complex of type A: this was established by the observation of a singlet in the ^{31}P spectrum when proton coupling was eliminated, which appeared as a doublet of triplets when only the protons of the PEt_3 groups were decoupled. The IrH and the SiH resonances both showed the expected patterns (IrH, triplet of triplets; SiH, triplet of doublets), and the couplings to phosphorus were identified by heteronuclear double resonance.

A second and much weaker peak was observed in the ^{31}P spectrum; this was shown by off-resonance decoupling to be associated with a molecule containing a single hydride bound to Ir. A weak peak was also observed in the ^1H spectrum in the region associated with H bound to iridium and *trans* to chloride. This peak was too weak to allow the determination of the associated ^{31}P chemical shift by heteronuclear double resonance, nor could we detect any corresponding SiH resonance, perhaps because of overlap with peaks due to the predominant isomer. Our suggestion that the weak peaks in both ^{31}P and ^1H spectra were due to the presence of a very small amount of an isomer of type B is therefore put forward very tentatively.

(*b*) *With* SiH_3Br *and with* SiH_3I. In these systems, halogen exchange, which would lead to the formation of SiCl and IrBr or IrI bonds, is likely to be favoured thermodynamically. Such exchange is normally faster [6] in compounds of four-co-ordinated Ir^I than in derivatives of six-co-ordinated Ir^{III}, so it is reasonable to suppose that any exchange is more likely to occur before rather than after addition.

At −80 °C the n.m.r. spectra of a solution of SiH_3Br and (1) in toluene were unchanged. At −50 °C the only iridium(I) species which remained was a small amount of *trans*-$[IrBr(CO)(PEt_3)_2]$, and at room temperature this had completely disappeared; there were peaks in the ^{31}P spectrum due to one major and four minor iridium(III) products. The main product could be identified from the patterns of its IrH and SiH resonances as an isomer of type A; peaks due to a small amount of $[IrCl(CO)H(PEt_3)_2(SiH_2Cl)]$ (3) were also identified. There was also a weak Ir*H* resonance whose chemical shift is consistent with a structure of type B; a weak peak in the ^{31}P spectra may also be associated with this isomer. The reaction between SiH_3I and (1) gave similar results, except that the minor products were present in relatively greater amounts. The main product was an isomer of type A; the only minor product to be identified with certainty was $[Ir(CO)H(I)(PEt_3)_2(SiH_2I)]$ (4), although an Ir*H* resonance that could be assigned to an isomer of type B was also observed. There remains the question of the halogen distribution in the two major products: are they bromo- or iodo-silyl derivatives containing chloride bound to iridium, or has halogen exchange led to the formation of two chlorosilyl complexes in which the heavier halogens are bound to iridium? We cannot be certain, but we believe that halogen exchange has occurred. The SiH chemical shifts are very similar in these two compounds and in (3). This would be expected if all three were chlorosilyl compounds, but would be surprising if the three compounds each contained a different halogen bound to silicon. Moreover, the Ir*H* and ^{31}P chemical shifts in the three compounds are significantly different. Such a pattern would be expected if each contained a different halogen bound to iridium, but would be surprising if each contained chlorine bound to iridium. If we are right, and exchange has occurred, the product of the reaction between SiH_3I and (1) should be the same as that obtained from SiH_3Cl and (2). The proton chemical shifts and the coupling constants are indeed very similar. There is a difference in the ^{31}P chemical shifts of 1 p.p.m.; although such a difference should be outside error, it is small, and we put it down to minor variations in conditions such as temperatures or concentrations.

(*c*) *With* GeH_3Cl. The main product was an isomer of type B. This was established by the ^{31}P spectrum, a singlet when all protons were decoupled and a doublet under off-resonance decoupling, and by the triplet patterns of IrH and GeH resonances; both the splittings were collapsed by ^{31}P decoupling. Furthermore, the IrH chemical shift was in the region associated with Cl as the *trans* ligand. The proton spectrum also contained a weak triplet of triplets in the region associated with H bound to iridium and *trans* to a ligand of high *trans* influence. The resonance was too weak to allow heteronuclear double resonance, and so we cannot positively associate a phosphorus frequency with this peak, but a weak singlet under proton-noise decoupling in the phosphorus spectrum that becomes a doublet under off-resonance decoupling may be due to the same species. It seems likely that the compound is an isomer of type A, the GeH resonance being obscured by the GeH resonance of the more abundant isomer.

(*d*) *With* GeH_3Br *and* GeH_3I. The reaction between (1) and GeH_3Br at low temperature gave rise to a single predominant product and five or six minor products. The peaks in both ^1H and ^{31}P n.m.r. spectra due to the minor products were too weak to allow us to make positive identification of any of the species concerned. The predominant species gave the singlet in the ^{31}P spectrum (when proton coupling is eliminated), together with the triplet patterns for both IrH and GeH resonances, that characterizes an isomer of type B. The ^{31}P chemical shift was much the same as in $[IrCl(CO)H(GeH_2Cl)(PEt_3)_2]$ (5), where we know that Cl is bound to Ir, whereas the GeH chemical shift was slightly different; the data would be consistent with either form, but seem to us to be more in keeping with that in which no halogen exchange has occurred (Br is still bound to Ge, and Cl to Ir). The reaction between (1) and GeH_3I at low temperature gives a small amount of a compound identified from its n.m.r. parameters as *trans*-$[Ir(CO)(GeH_2Cl)H(I)(PEt_3)_2]$ (6), but the main product is a different species whose ^{31}P and ^1H n.m.r. spectra show it to be a compound of type B. Here too the ^{31}P chemical shift is close to that found for (5), and some 10 p.p.m. to high frequency of the shifts in compounds of this type that are known to contain I bound to Ir, such as $[Ir(CO)(GeH_2I)H(I)(PEt_3)_2]$ (7). The GeH chemical shift is close to that for (7), and is some 1.5 p.p.m. to low frequency of the GeH chemical shift in (5). Here too we conclude that no exchange has occurred at low temperatures, and that the product contains I bound to Ge and Cl bound to Ir. Since separate resonances are observed for the different products, and since the spectra we have obtained from the products of the reaction between GeH_3I and (1) are quite different from those we have obtained from the products of the reaction between GeH_3Cl and (2), there can be no halogen exchange in the main products of the reactions. It follows that with GeH_3X the addition of GeH to iridium is faster than exchange, in marked contrast to the behaviour of silyl halides with the same iridium starting material.

The product of the reaction between (1) and GeH_3I was thermally unstable: when the n.m.r. tube was warmed to room temperature, the peaks due to the major product disappeared. At least 17 lines could be distinguished in the ^{31}P spectrum; all were shown by off-resonance decoupling to be due to species containing one hydride bound to Ir, but the only species we could identify from the ^{31}P and ^1H spectra were (6) and (7), both formed in substantial amounts.

(*e*) *With* $SiH_3(CH_3)$. The product of this reaction gave ^{31}P and IrH spectra expected for an adduct of type A, with H *trans* to CH_3SiH_2; the SiH resonance was complicated by coupling to P, to IrH, and to CH_3, but the resonance could be simplified into a quartet [due to ^3J(HCSiH)] of doublets [due to ^3J(HSiIrH)] by decoupling ^{31}P. The CH proton resonance appeared to low frequency of the SiH resonance as a simple triplet.

(*f*) *With* Si_2H_6. The n.m.r. spectra of the product of this reaction were very much the same as those obtained from the reaction between (1) and $SiH_3(CH_3)$ and described above in (*e*). There were two SiH resonances. The one at higher frequency, which appeared as a simple triplet, was assigned to the SiH_3 resonance of Si_2H_5 bound to iridium; as with the CH_3 resonance in the spectrum of the CH_3SiH_2 derivative, the only coupling observed was to the SiH_2 protons. The other SiH resonance appeared as a complex multiplet, but under ^{31}P decoupling it simplified to a quartet of doublets, the quartet splitting arising from coupling to the SiH_3 protons and the doublet splitting from coupling to the *trans*-hydride ligand bound to iridium. It is clear that Si_2H_6 has added as Si_2H_5 and H, rather than as two SiH_3 groups, to give an isomer of type A.

DISCUSSION

The structures of the compounds described here can be assigned with confidence on the basis of the n.m.r. spectra. Indeed, the principle set out at the beginning of this paper from which the details of the structures of the adducts have been deduced become more firmly based in the light of the spectra of the complete series of compounds. It is in those isomers of the germyl derivatives in which the chemical shift of the hydride ligand implies a *trans*-halogen ligand that ^3J(HIrGeH) is so small as to be barely resolved or not resolved at all; it is in those silyl isomers where ^3J(HIrSiH) is between five and ten times larger that the hydride chemical shift is consistent with a structure in which H is *trans* to Si. On this basis, almost every adduct of a silyl compound that we have studied here is of type A, with the silyl and the hydride ligands mutually *trans*; in contrast, most of the germyl adducts are of type B, and where a germyl isomer of type A is formed it is in no case the most abundant product. We cannot account for this difference in behaviour. It is unlikely to be due to steric factors, for germyl and silyl groups are not very different in size; moreover, all silyl compounds we have studied give the same type of product, irrespective of the size of any substituent bound to silicon. We have no evidence at all as to the mechanism of addition; ionic mechanisms are perhaps unlikely to be important with such hydrides in non-polar solvents, nor do radical mechanisms seem very probable under such very mild conditions, but neither can be excluded. It is unsafe to base conclusions about the stereochemistry of the initial attack upon the stereochemistry of the ultimate products, but the simplest explanation of our results is that SiH adds to this iridium complex in the *trans* mode, whereas GeH can add either *trans* or *cis*. We have no evidence at all to suggest that either type of isomer tends to rearrange.

These structural conclusions should be compared with those we drew from our earlier study of the adducts of silyl and germyl halides and related compounds with Vaska's compound. The earlier study was hampered by the insolubility of many of the products. The adducts of the germyl halides remained in solution for a short time, and we were able to use ^1H n.m.r. spectra to determine their geometries; the structures we assigned were of type B, with germyl chloride giving a type A isomer as well. While there is no reason why Vaska's compound and its triethylphosphine analogue should give adducts of the same structure, it is both reasonable and satisfying to find that the conclusions about the two sets of germyl compounds are similar. We were not able to obtain any n.m.r. spectra from the adducts of Vaska's compound with silyl halides, and so our earlier conclusions about the structures of these derivatives were based entirely on the i.r. spectra of the solids. On the basis of the IrH and IrCl stretching frequencies we suggested that these adducts too were of type B, with hydride *trans* to halogen and CO *trans* to Si. This type of evidence, however, is far from decisive; the n.m.r. spectra we have obtained here show that Si is *trans* to H in the adducts of the triethylphosphine analogue of Vaska's compound, and it is at least possible that the adducts of Vaska's compound itself have this structure too. In the two silyl adducts of the triethylphosphine analogue of Vaska's compound that we have isolated, the ν(CO) stretching frequencies are very similar to their values in the analogous adduct of Vaska's compound. Unless these adducts have isomerized on crystallization, they certainly contain CO *trans* to halogen.

The n.m.r. parameters of all the adducts make up a self-consistent set. As has already been discussed, the ^{31}P chemical shifts appear to be characteristic of the halogen bound to iridium, and the IrH chemical shifts to some extent characteristic of the ligand *trans* to hydride. The nature of the *cis* ligands, too, particularly if these are halides, has a substantial effect on the hydride chemical shift. Apart from the general assumption that couplings between protons and other protons or phosphorus nuclei are larger when the nuclei involved are mutually *trans* than when they are *cis*, there is little on which to remark in the coupling constants we have determined.

EXPERIMENTAL

Volatile compounds were manipulated in conventional vacuum apparatus fitted with greased glass or with greaseless polytetrafluoroethylene (Sovirel) taps. Involatile solids were handled under dry nitrogen in a glove-box made by Vacuum Atmospheres on a conventional N_2 line. Infrared spectra were recorded by means of a Perkin-Elmer 457 double-beam spectrometer (250—4 000 cm^{-1}). Continuous-wave ^1H n.m.r. spectra were recorded using a Varian Associates HA100 spectrometer whose probe had been double-tuned for heteronuclear double resonance; ^1H and ^{31}P Fourier-transform spectra were obtained with a Varian Associates XL100 spectrometer.

Solvents were obtained commercially and purified by standard methods; silyl and germyl starting materials were prepared as described elsewhere.[7] The iridium complexes (1) and (2) were prepared from $[Ir_2Cl_2(\text{cyclo-octene})_4]$ [for (1)] and by treating (1) with NaI [for (2)].

Reactions of (1).—In a typical experiment, (1) (0.2 mmol) was weighed into an n.m.r. tube and evacuated; solvent and a small amount of $SiMe_4$ were distilled into the tube, followed by MH_3Q (0.2 mmol). The tube was then sealed. For Q = H, CH_3, or SiH_3 the n.m.r. spectra were then recorded at room temperature. For Q = halogen the tube was not allowed to warm above −80 °C and the first spectra were obtained at that temperature; the system was then slowly allowed to warm in steps of *ca.* 10°, and spectra were recorded until reaction was complete. The only product that proved unstable when allowed to warm to room temperature was that formed with GeH_3I. After reaction was complete, attempts were made to isolate the products; the n.m.r. tubes were opened and the solvent was pumped off. A gum remained; addition and removal of cyclohexane left a solid only in the case of the adduct of SiH_4, although the other adducts could be redissolved by adding fresh solvent. The adduct of (1) with SiH_4 was characterized by analysis and its i.r. spectrum and melting point were measured (Found; C, 27.5; H, 6.1. $C_{13}H_{34}ClIrOP_2Si$ requires C, 29.8, H, 6.5%), ν(SiH) at 2 095, ν(CO) at 1 975 cm^{-1}, ν(IrH) presumably under ν(SiH); m.p. 77—78 °C. The compound appeared to melt without decomposition.

Reaction of (2).—Despite every care, almost all the samples of (2) we prepared contained small amounts of the adduct of (2) with O_2. The ^{31}P peak due to this compound remained unchanged throughout the reactions studied, so we conclude that it did not interfere with the reactions themselves, but this made it very difficult for us to isolate pure samples of any of the silyl or germyl adducts of (2). We succeeded in obtaining a solid sample of the adduct with SiH_3Br, and characterized this by analysis, by its i.r. spectrum, and by its melting point (Found: C, 22.6; H, 4.7. $C_{13}H_{34}IIrOP_2Si$ requires C, 22.4; H, 4.5%), ν(SiH) at 2 066, ν(CO) at 1 977 cm^{-1}, ν(IrH) presumably under ν(SiH); m.p. 87—88 °C.

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