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Reactions of Silanes and Germanes with Iridium Complexes. Part 4.† Reactions with Carbonylhydridotris(triphenylphosphine)iridium(1)

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The title complex, $[IrH(CO)(PPh_3)_3]$ (1), reacts with MH_3O (M = Si or Ge when O = H, F, Cl, Br, or I; M = Si when $O = SiH_3$ or CH₃) to give $[IrH_2(CO)(PPh_3)_2(MH_2O)]$. The products have been characterised by ¹H, ³¹P, and (where appropriate) ¹⁹F n.m.r. spectra. Where M = Ge, the predominant isomer contains mutually *trans* phosphine ligands, whereas when M = Si the predominant (and in some cases the sole) product contains *cis* phosphines. In the isomers with *cis* phosphines, some unusual coupling patterns have been observed in the ¹H n.m.r. spectra. When O = I and M = Si, there is a difference in chemical shift between the two SiH protons of 1.3 p.p.m., and irradiation of one of the peaks at room temperature leads to the disappearance of the other, a phenomenon interpreted as due to saturation transfer; possible mechanisms for the process are discussed.

Some years ago we published a study 1 of the adducts formed by a series of simple silanes and germanes $(MH_3X, where M = Si \text{ or } Ge \text{ and } X = F, Cl, Br, or I)$ trans-carbonylchlorobis(triphenylphosphine)with iridium(I). Our conclusions about the structures of most of these adducts were tentative, because few of the compounds concerned are sufficiently soluble for study by n.m.r. spectroscopy, and adequate crystals for study by X-ray diffraction could not be obtained. Silanes and germanes, however, react with carbonylhydridotris-(triphenylphosphine)iridium(I) (1) to give silvl or germyl derivatives of six-co-ordinated iridium;² these complexes are soluble enough in organic solvents to allow us to obtain their n.m.r. spectra and hence to draw conclusions about the stereochemistry of the products. It has been suggested ²⁻⁴ that triorganosilanes, germanes, and stannanes react with (1) to give products in which the P ligands are mutually *cis* and Si is *trans* to P; our conclusions suggest that the reaction is rather more complicated.

RESULTS

Treatment of solutions of (1) in benzene or toluene with MH_3Q (M = Si; Q = H, F, Cl, Br, I, CH₃, or SiH₃; M = Ge, Q = H, F, Cl, Br, or I) leads to a rapid reaction: the yellow solution turns very pale yellow or colourless, and no gas is evolved. The ³¹P n.m.r. spectrum shows that PPh_a has been evolved; the overall reaction is expressed by the equation. So far we have not succeeded in separating the

$$\begin{array}{r} \mathrm{MH_{3}Q} + [\mathrm{IrH(CO)(PPh_{3})_{3}}] \longrightarrow \\ \mathrm{PPh_{3}} + [\mathrm{IrH_{2}(CO)(PPh_{3})_{2}(MH_{2}Q)}] \end{array}$$

iridium complexes formed from PPh_a , so we have no analytical or crystallographic information. However, the ¹H and ³¹P spectra of the solutions confirm the formulation of the reaction products, and tell us a great deal about their geometries. In most systems more than one isomer is formed, and there are some unexpected features in the ¹H n.m.r. spectrum; the characteristics of the products are presented in an order that has been chosen to allow a simple and logical development of the analysis of the results.

A complex of the molecular formula $[IrH_2(CO)(PPh_3)_2]$

[†] Part 3, E. A. V. Ebsworth, H. M. Ferrier, and T. E. Fraser, J. Chem. Soc., Dalton Trans., 1981, 836.

 (MH_2Q)] can have six different isomeric forms if chirality is ignored (see Figure 1). Two of these, (I) and (II), have equivalent phosphine ligands and so should give singlet ³¹P-{¹H} resonances; similarly, the phosphines in isomer (VI) are equivalent when protons are decoupled. On the



FIGURE 1 Possible isomers of adducts formed by (I) with $MH_a Q$

other hand, ³¹P-{¹H} spectra of (III), (IV), and (V) should give AB patterns. The proton resonance spectra are much more complicated, though they allow more precise distinction between at least some of the isomeric forms. The types of products found are therefore described first in relation to their ³¹P-{¹H} spectra. The details of the ¹H spectra are discussed once the general pattern of products has been established; the spectra are considered in order of increasing complexity.

The ³¹P-{¹H} Spectra.—The product of the reaction

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between (1) and GeH_3I shows a single peak in the ³¹P-{¹H} spectra, besides the resonance due to PPh₃ and some weak and complex multiplets. We therefore suppose that the product of this reaction is essentially a single isomer of type (I), (II), or possibly (VI). In contrast to this, reaction of (1) with SiMeH₃ gives a product where ³¹P-{¹H} spectra

 H_a , happens to be equal to a triplet coupling which is not associated with IrH and which we assign to 3f (HGeIrP). The narrow doublet is due to coupling to the higher-frequency IrH, which we label H_b . Each IrH resonance can be analysed as a set of overlapping triplets [2f (HIrP)] of triplets [3f (HIrGeH)] of doublets [2f (HIrH)]; irradiation



FIGURE 2 Proton n.m.r. spectra of the GeH (a) and IrH (b) peaks of the adduct of (1) with GeH_aI

consist of an AB quartet; here, too, the product is monoisomeric, but of type (III), (IV), or (V). The product of the reaction of (1) with SiH_3F gives a ³¹P-{¹H} spectrum with the eight lines expected of the AB part of an ABX spectrum, so this product too is mono-isomeric and of type (III), (IV), or (V). All the other products we have studied give ³¹P-{¹H} spectra, showing that isomers with both non-equivalent (AB pattern) and equivalent (singlet) phosphines were present; with all the germyl compounds the predominant of the GeH resonance simplifies each to a triplet of doublets, the doublet couplings being equal. The only question is as to which IrH resonance corresponds to which hydride portion in structure (I). This point will be discussed when the whole series of spectra has been described. The parameters are given in Table 1.

(b) GeH₄. The ³¹P- $\{^{1}H\}$ spectrum of this product showed that a species with a singlet phosphorus resonance had been formed, with a much smaller amount of a second whose

| | | | | | SiH _a - | | | | | |
|--|---------|---------------------|---------------------|--------|--------------------|--------|---------------------------------|---------------------|--------|--------------------|
| | SiH_4 | SiH ₃ Cl | SiH ₃ Br | SiH₃I | (SiH3) b | GeH4 | GeH ₃ F ^e | GeH ₃ Cl | GeH₃Br | GeH ₃ I |
| $\delta H_a/p.p.m.$ | -8.59 | - 8.73 | -8.89 | -8.19 | -8.39 | -9.21 | -9.97 | -9.87 | 10.24 | -10.50 |
| $\delta H_{b}/p.p.m.$ | -10.42 | ca10.21 | 10.15 | -10.06 | -10.19 | -10.37 | -10.25 | -10.33 | -10.26 | - 9.97 |
| δMH/p.p.m. | 2.92 | 5.01 | 4.59 | 3.68 | 2.67 | 2.39 | 6.09 | 5.09 | 4.42 | 3.27 |
| δP/p.p.m. | 12.47 | 12.12 | 11.97 | 11.52 | 12.52 | 12.49 | 11.77 | 11.44 | 11.37 | 11.18 |
| $^{2}/(\mathrm{H_{a}H_{b}})/\mathrm{Hz}$ | 4.2 | 4.2 | 4.0 | 4.0 | 4.3 | 4.1 | 4.0 | 4.0 | n.m. | 3.9 |
| $^{2}/(\mathrm{H_{a}P})/\mathrm{Hz}$ | 17.0 | 17.8 | 17.7 | 17.1 | 16.9 | 15.9 | 15.9 | 15.8 | 16.0 | 15.7 |
| $^{2}J(H_{h}P)/Hz$ | 17.9 | 17.3 | 16 | 17.1 | 17.5 | 18.1 | 17.8 | 17.7 | 17.7 | 17.5 |
| ³ /(HMP)/Hz | 4.7 | 5.5 | 5.5 | 6.1 | n.m. | 4.2 | 2.8 | 5.4 | 5.2 | 5.4 |
| $^{3}/(HMH_{a})/Hz$ | < 0.4 | 2.4 | 2.8 | 3.8 | < 0.4 | 1.5 | 5.3 | 5.6 | 5.5 | 5.9 |
| ³ J(HMH _b)/Hz | 2.0 | 1.8 | 1.8 | 2.1 | 2.2 | 1.8 | 1.6 | 1.5 | 1.5 | 1.5 |

TABLE 1 N.m.r. parameters ^a for products of type (I) from (1) and $MH_{3}Q$

⁶ Measurements in toluene. Chemical shifts given to ± 0.01 p.p.m., and coupling constants to ± 0.2 Hz, unless otherwise stated; n.m. = not measured. ^b $\delta(\text{SiH}_3) = 3.50$ p.p.m.; ³f(HH) = 3.2 Hz. ^c $\delta \text{F} = -224.8$ p.p.m.; ²f(HF) = 41.3, ³ $f(\text{FH}_8) = 9.4$, ³ $f(\text{FH}_9) = 4.0$ Hz.

product had equivalent phosphines, whereas with all the silyl compounds the main product had *cis* phosphines.

The ¹H Spectra.—Product from (a) GeH₃I. The proton resonance spectrum (see Figure 2) shows that this compound is of type (I). There are two IrH resonances of equal intensity in the low-frequency region. The GeH resonance is twice as strong as either, and appears as a 1:3:3:1quartet of narrow doublets. Irradiation at the lower frequency of the two IrH resonances reduces the GeH resonance to a 1:2:1 triplet of narrow doublets, while irradiation at the other IrH resonance collapses the narrow doublet coupling. The quartet pattern is therefore due to a coincidence: coupling to the lower-frequency IrH, which we call ${}^{31}P{-}{^{1}H}$ spectrum was an AB quartet. The ${}^{1}H$ spectra established that the former was an isomer of type (1), and the latter of type (III) or (IV) (see Figure 3).

The GeH resonance of the major product appeared as a triplet of triplets, but under the highest resolution it became clear that the smaller triplet pattern derived from two nearly equal doublet couplings. Both of these were shown by homonuclear decoupling to be due to ${}^{3}J(\text{HGeIrH})$; the larger triplet coupling is assigned to ${}^{3}J(\text{HGeIrP})$. In the low-frequency region two very similar resonances of equal intensity were observed, each one-third the intensity of the GeH resonance. Their apparently complicated patterns were easily analysed with the help of homonuclear double

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resonance. Each showed the triplet pattern expected from coupling to two equivalent P nuclei; each line of both triplets showed a further doublet splitting, due to ${}^{2}J(HIrH)$, when GeH protons were decoupled, and a quartet splitting [due to ${}^{3}J(HIrGeH)$] when the other IrH resonance was irradiated. Each peak therefore consisted of a pair of overlapping quartets. The overall appearance of the spectrum doublets $[{}^{2}J(H_{c}P_{t})]$ of doublets $[{}^{2}J(H_{c}H_{t})]$; the couplings are easily associated with particular P nuclei by selective irradiation of the H_t peaks. Restoration of coupling to the GeH protons introduces a further quartet splitting on each line that is not very well resolved because of overlap. The GeH resonance appears under even the highest resolution as a triplet of doublets of doublets; each of the doublet



FIGURE 3 Proton n.m.r. spectra of the GeH (a) and IrH (b) peaks of the adduct of (1) with GeH₄. The GeH peaks marked (1) and (III) are due to isomers of types (I) and (III) respectively. The IrH peaks marked a and b are due respectively to H_a and H_b in the isomer of type (I), while those marked c and t are due to H_a and H_t in the isomer of type (II)

was that of two triplets of sextets or septets, since ${}^{2}J(\text{HIrH})$ is between two and three times as large as ${}^{3}J(\text{HGeIrH})$.

The ¹H spectrum of the other isomer is more complicated. We have analysed it as due to an isomer of type (III) or (IV). One of the IrH resonances showed a large coupling (121 Hz) that we assign to ${}^{2}J(H_{t}IrP_{t})$ [for notation see Figure 1 (III)]; there is a smaller doublet coupling that is unaffected by homonuclear double resonance and that we assign to ${}^{2}J(H_{t}IrP_{c})$. Each line appears as a sextet, but decoupling the GeH resonance reduces this to a doublet, which we assign to ${}^{2}J(HIrH)$; in confirmation, the sextets are reduced to narrower quartets by irradiation at H_c. The resonance assigned to H_c is similarly simplified by decoupling the GeH protons to a doublet [${}^{2}J(H_{c}P_{c})$] of couplings can be collapsed by decoupling on one of the IrH protons, but the triplet pattern remains unaffected. We conclude that in this species the two values of ${}^{3}J$ (HGeIrP) happen to be equal. The n.m.r. parameters are collected in Tables 1 and 2, and rough relative abundances of the isomers in Table 3.

(c) SiH_4 . The products of this reaction are similar to those obtained from GeH_4 , except that here ca. 12 times as much of the isomer with cis phosphines was formed as of the other. In addition, a very small amount of a different species containing two P and two H ligands bound to Ir, with one P trans to H, was formed: we could not find any SiH resonance associated with this species.

The resonances due to the main product, of type (III) or

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(IV), were generally similar to those of its germyl analogue. isomer are given in Table 1, and rough relative abundances Here, ${}^{3}J(H_{t}IrSiH)$ is about half ${}^{2}J(H_{c}IrH_{t})$; moreover, the in Table 3.

Here, ${}^{3}J(H_{t}IrSiH)$ is about half ${}^{2}J(H_{c}IrH_{t})$; moreover, the is two values of ${}^{3}J(HSiIrP)$ are substantially different, so that the appearance of the SiH resonance is somewhat different t from that of the GeH resonance in the spectrum of the c germyl complex. The n.m.r. data are collected in Table 2.

(*d*) SiH₃Br. The ³¹P-{¹H} spectrum showed that most of the product was a species with *cis* phosphines. This was confirmed by the ¹H resonance spectrum, which presented some problems of analysis when first recorded. The peaks

TABLE 2 N.m.r. parameters ^a for products of type (III) from (1) and MH_3Q

| | | | | | | | SiH | | | | |
|---|--------------|---------------------------------|---------------------|---------------------|--------------------|---|-------------|---------|---------------------------------|---------------------|--------|
| | SiH4 | SiH _a F ^b | SiH ₃ Cl | SiH ₃ Br | SiH ₃ I | SiH ₃ CH ₃ ^c | $(SiH_3)^d$ | GeH_4 | GeH ₃ F ^e | GeH ₃ Cl | GeH₃Br |
| δH•/p.p.m. | -10.42 | -10.22 | -10.02 | -10.03 | -10.07 | -10.32 | -10.53 | -10.81 | -10.61 | -10.31 | -10.48 |
| $\delta H_{o}/p.p.m.$ | 9.67 | -9.35 | -9.52 | -9.54 | -9.40 | -9.43 | -9.46 | -9.82 | 9.65 | -9.79 | 9.71 |
| $\delta H_1/p.p.m.$ |] 0.70 | 6.64 | 6.15 | 5.68 | 5.14 | 4.42 | 3.47 | 1915 | 1669 | 6.14 | 5.60 |
| $\delta H_{a}/p.p.m.$ | 3.76 | $(\delta < 0.1)$ | 5.47 | 4.89 | 4.08 | 4.29 | 3.20 | 5 9.19 | 0.08 ع | 5.33 | 4.57 |
| $\delta P_t/p.p.m.$ | 5.68(4 | l) 6.73 | 5.82(4) | 5.79(4 | 6.51(4) | 7.07 | 5.44 | 4.47 | 4.05 | 4.03 | 4.48 |
| δP _c /p.p.m. | 3.52(4 | ý 1.74 | 2.77(4) | 2.77 (4 | 1) 1.12(4) | 3.04 | 3.49 | 5.91 | 5.29 | 5.82 | 5.15 |
| ² /(H ₁ H ₂)/Hz | 4.0 | 4.4 | 4.2 | 4.0 | 4.1 | 3.7 | 4.0 | 3.8 | 3.8 | 3.9 | 4.0 |
| ² I(H,P,)/Hz | 115.7 | 109.9 | 112.4 | 112.6 | 113.1 | 114.8 | 115.4 | 121.0 | 115.0 | 117.5 | 118.3 |
| $^{2}I(H_{c}P_{t})/Hz$ | 15.0 | 14.8 | 14.7 | 14.5 | 14.5 | 15.3 | 14.9 | 15.2 | 14.6 | 14.9 | 15.1 |
| ² /(H _t P _c)/Hz | 18.7 | 19.3 | 19.5 | 19.4 | 19.6 | 19.1 | 19.3 | 18.3 | 17.7 | 18.8 | 17.6 |
| $^{2}I(H_{c}P_{c})/Hz$ | 20.8 | 20.9 | 20.3 | 20.2 | 19.7 | 21.7 | 20.9 | 20.4 | 19.6 | 19.3 | 19.3 |
| $^{2}/(H_{0}H_{1})/Hz$ | n.o. | 15.3 | 12.6 | 12.4 | 12.7 | 7.8 | n.m. | n.o. | 24.5(5) | 18.9 | 22.0 |
| ² J(P _t P _c)/Hz | 15.9 | 18.0 | 17.4 | 17.4 | 16.7 | 16.3 | 15.4 | 13.7 | 14.7 | 14.8 | 1.7 |
| $^{3}/(H_{1}P_{c})/Hz$ | 100 | (10) | 12.9 | 11.2 | 14.0 | n.m. | n.m. | أمه | n.m. | 23.6 | 21.6 |
| $^{8}/(H_{q}P_{c})/Hz$ | 9.0 ر | (11) | 13.7 | 14.0 | ca. 12 | 7.8 | n.m. | 5 5.2 | n.m. | 24.2 | 22.0 |
| $^{3}/(H_{l}P_{t})/Hz$ | l = 7 | (10) | 8.5 | 8.6 | 8.0 | n.m. | n.m. | 309 | n.m. | 7.3 | 6.8 |
| $^{3}J(\mathrm{H}_{q}\mathrm{P}_{t})/\mathrm{H}z$ | f 0.1 | (11) | 9.8 | 10.6 | ca. 12 | 5.3 | n.m. | 5 0.2 | n.m. | 8.8 | 9.7 |
| $^{3}J(H_{l}H_{c})/Hz$ | <u>]</u> 9 1 | 4.2 | 5.8 | 5.0 | 7.6 | 4.2 | 4.4 | 329 | 5.1 | 6.1 | 5.9 |
| $J(H_qH_c)/Hz$ | 5.1 | 1.0 | 1.3 | 1.3 | < 0.4 | < 0.4 | < 0.4 | 1 2.0 | < 0.4 | < 0.4 | < 0.4 |
| $J(H_lH_t)/Hz$ | 118 | 320 | 4.4 | 6.1 | 4.1 | < 0.4 | < 0.4 | }18 | < 4.0 | 4.3 | 4.2 |
| $J(H_qH_t)/Hz$ | 1.0 | J 2.0 | 0.4 | 0.6 | < 0.4 | < 0.4 | < 0.4 | J 1.0 | 1.3 | < 0.4 | < 0.4 |
| | | | | | | | | | | | |

^a Measurements from solutions in toluene. Chemical shifts are to ± 0.01 p.p.m. and coupling constants to ± 0.2 Hz unless otherwise indicated. Values in parentheses were obtained from simulations of spectra; n.m. = not measured, n.o. = not observed.

$$\begin{split} ^{b} \delta F &= -173.5 \ \text{p.p.m.;} \ ^{2} J(\text{HF}) = 49.9, \ ^{3} J(\text{FP}_{t}) = 13.6, \ ^{3} J(\text{FP}_{c}) = 24.3, \ ^{3} J(\text{FH}_{c}) = 12.2, \ ^{3} J(\text{FH}_{t}) = 16.4 \ \text{Hz.} \ ^{c} \delta(\text{CH}_{3}) = 0.7 \ \text{p.p.m.;} \ ^{3} J(\text{HH}) = 4.2, \ ^{4} J(\text{HP}_{t}) = 4.2 \ \text{Hz.} \ ^{\delta} \delta(\text{Si}) = 62.5 \ \text{p.p.m. relative to SiMe}_{1}; \ ^{2} J(\text{SiP}_{t}) = 99 \ \text{Hz.} \ ^{\delta} \delta(\text{CH}_{3}) = 1.3, \ ^{\delta} \delta(\text{CH}_{3}) = 1.3, \ ^{\delta} \delta(\text{Si}) = 62.5 \ \text{p.p.m. relative to SiMe}_{1}; \ ^{2} J(\text{SiP}_{t}) = 99 \ \text{Hz.} \ ^{\delta} \delta(\text{CH}_{3}) = 1.3, \ ^{\delta} \delta(\text{CH}_{3}) = 1.3, \ ^{\delta} \delta(\text{CH}_{3}) = 1.3, \ ^{\delta} \delta(\text{Si}) = 12.2, \ ^{3} J(\text{FP}_{t}) = 12.5, \ ^{3} J(\text{FP}_{c}) = 22.5, \ ^{3} J(\text{FH}_{t}) = 12.3, \ ^{3} J(\text{FH}_{c}) = 9.0 \ \text{Hz.} \end{split}$$

The ¹H spectrum of the isomer of type (I) is less easy to characterise, for the peak due to the lower-frequency hydride ligand is partly overlapped by that due to the unidentified product mentioned above. Moreover, coupling

TABLE 3

Rough percentages a of isomers of type (I) and type (III) formed by reaction between (1) and MH₃Q at room temperature

| • | | |
|---------------------------------|---------------|-----------------|
| МН ₃ Q | % of type (1) | % of type (III) |
| SiH₄ | 8 | 92 |
| $SiH_{3}(CH_{3})$ | 0 | 100 |
| SiH ₃ F | 0 | 100 |
| SiH ₃ Cl | 10 | 90 |
| SiH ₃ Br | 12 | 88 |
| SiHaI | 25 | 75 |
| $SiH_{3}(SiH_{3})$ | 10 | 90 |
| GeH ₄ | 65 | 35 |
| GeH ₃ F [•] | major | minor |
| | (ca. 80%) | (ca. 20%) |
| GeH ₃ Cl | 85 | 15 |
| GeH_3Br | 90 | 10 |
| GeH_I | 100 | 0 |

^a The smaller values in each case are probably accurate to at least ± 2 . ^b For GeH₃F, the resonances overlapped so much that satisfactory integration was not possible.

between the SiH protons and the other IrH proton is not resolved. However, the relationships between the peaks were easily established by irradiating across the lowerfrequency hydride resonance. The parameters for this due to a small amount of the isomer of type (I) were easily recognised. Part of the resonance due to H_b is overlapped by peaks from the more abundant isomer, but most of the parameters were easily measured and are given in Table 1. Once these peaks had been accounted for, there remained two SiH and two IrH resonances of equal intensity: in order of decreasing frequency, these are labelled L, Q, C, and T (see Figure 4). Peaks L and Q were in the SiH, and C and T in the IrH regions of the spectra. Peaks L and C under low resolution appeared as complex multiplets, Q as a broad quartet, and T as a wide doublet (J ca. 100 Hz) of doublets of triplets. These observations could be understood with the help of homonuclear double resonance. Irradiation at C or T affects both L and Q; it follows that L, Q, C, and T come from the same species, of type (III) or (IV). The Ir atom in such a species is a chiral centre: we must conclude that resonances L and Q are due to the two non-equivalent protons of the SiH₂ group. When L was decoupled, T simplified to a doublet of doublets of doublets; under the very highest resolution, it became clear that each line showed a further very small doublet coupling that was removed by decoupling Q. We conclude that T is due to H_t in a species of type (III) or (IV): the largest coupling is due to P_t , the next to P_c ; couplings to H_c and to one of the SiH protons (H_l) are nearly equal, while coupling to the other SiH proton (H_a) is smaller and can only just be detected. Under very high resolution, C shows a pattern that can easily be analysed as due to coupling to two different P nuclei





FIGURE 4 Proton resonance spectra of the isomer of type (III) formed by (1) and SiH₃Br. (a) Peaks L, Q, C, and T. The weak multiplet at the low frequency end of the diagram is due to H_b in the isomer of type (I); (b) Q under higher resolution showing (second spectrum) the effects of line narrowing; couplings are assigned as indicated; (c) L under higher resolution, the second drawing showing the effects of line narrowing; couplings are assigned as indicated

(20.2 and 14.5 Hz), one IrH proton (4.0 Hz), and two different SiH protons (5.0 and 6.1 Hz). These conclusions were confirmed by homo- and hetero-nuclear double resonance. Of the two SiH resonances, H_1 could be resolved into a set of 32 overlapping lines [see Figure 4(c)]; the apparent quartet Q could similarly be interpreted [see Figure 4(b)]

(a)

easily be assigned to a complex of type (III) or (IV) with SiHCl₂ as ligand. However, ³¹P-{¹H} and ¹H resonances due to isomers of type (I) (minor product) and type (III) or (IV) (main product) could easily be identified, and in general they were very like the analogous peaks in the spectrum of the adduct of SiH₃Br. Some of the details were different:



-20 Hz

FIGURE 5 IrH resonances of the adduct of (1) with SiH_3F . (a) Resonances due to H_c and H_t ; (b) half of one of the multiplets due to H_t , with line narrowing; couplings are assigned as indicated

and all the couplings could be related by double resonance. The parameters are collected in Table 2, relative abundances of the isomers in Table 3, and some relative signs of coupling constants in Table 4.

(e) SiH₃Cl. The reaction between (1) and SiH₃Cl is not clean, even in toluene at -30 °C: the products include the adduct of SiH₄ and the ¹H spectrum shows peaks that can

for example, ${}^{2}J(H_{c}IrH_{t})$ could not be distinguished from ${}^{3}J(H_{1}SIIrH_{t})$, and ${}^{3}J(H_{q}SIIrH_{t})$ was not resolved, while the differences in the couplings to H_{1} made the appearance of H_{1} rather different. The n.m.r. parameters are given in Tables 1 and 2, rough values for the relative abundances of the isomers in Table 3, and relative signs of some of the coupling constants for the isomer of type (III) or (IV) in Table 4.

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(f) $\operatorname{SiH}_3(\operatorname{CH}_3)$. The product of this reaction was monoisomeric; the ³¹P-{¹H} spectrum gave an AB pattern. At 100 MHz the SiH_2 resonance was an unresolved 'hedgehog'; the CH_3 resonance was a quartet which became a triplet under ³¹P decoupling. This suggests that Si is *trans* to P, and so that the product is of type (III). In keeping with this, the ²⁹Si-{¹H} spectrum showed a single large (100 Hz) doublet coupling, which we assign to ²J(SiP_t); in the ¹³C resonance due to CO there was no coupling larger than 2—3 Hz. In the IrH region of the ¹H spectrum, H_t was found to couple only to the P nuclei and to H_c, but H_c showed

resonances of the type associated with an isomer of type (I), and in addition peaks in the IrH and SiH regions that were qualitatively very like those given by the product obtained from (1) and SiH₃(CH₃). The main difference was that the SiH₃ resonances were to high frequency of the SiH₂ peaks, so that the SiH₃ peak from the product of type (I) overlapped one of the SiH₂ peaks from the product of type (III). The product of type (III) was the more abundant; n.m.r. parameters for both are given in Tables 1 and 2.

(*h*) GeH₃Cl. The main product is of type (I). A small proportion of an isomer with cis phosphines is also formed:



FIGURE 6 Saturation transfer in the SiH resonances of the isomer of type (111) formed by (1) with SiH₃I. (a) Peaks due to L and Q at 298 K with no double irradiation; (b) effect on Q of irradiation at L at room temperature with ca. 0.05 W power. The multiplet at the low-frequency end of the drawing is due to the SiH resonance of the isomer of type (I)

roughly equal couplings to H_t and to one of the SiH protons. At 360 MHz the SiH peaks were clearly resolved into two. The one at the higher frequency was a poorly resolved and complex multiplet; the other was an overlapping triplet of doublets of quartets. The quartet splitting was shown by double resonance to be due to ${}^{3}J(\text{HCSiH})$; the other

TABLE 4

| Relative | signs * | of | coupling | constants | in |
|----------|---------------------|-----|-------------------------------------|-----------|----|
| [] | rH ₂ (CO |)(F | Ph ₃) ₂ (SiF | $I_2Br)]$ | |

| $^{2}J(\mathrm{H_{l}H_{q}})$ | | $^{3}J(\mathrm{H_{q}H_{t}})$ | |
|---------------------------------------|-----------|--|---|
| | (assumed) | | |
| $^{2}/(H_{t}H_{c})$ | + | $^{3}/(H_{g}H_{c})$ | - |
| $^{2}J(\mathrm{H_{t}P_{t}})$ | _ | $^{3}/(H_{1}H_{t})$ | |
| $^{2}/(\mathrm{H_{t}P_{c}})$ | + | ${}^{3}/({\rm H_{1}H_{c}})$ | |
| $^{2}/(\mathrm{H_{c}P_{c}})$ | t- | $^{3}/(\mathrm{H_{q}P_{t}})$ | _ |
| $^{2}/(\mathrm{H_{c}P_{t}})$ | + | $^{3}/(H_{a}P_{c})$ | _ |
| $^{2}I(\mathbf{P}_{c}\mathbf{P}_{t})$ | + | ${}^{3}I(\mathbf{H_{i}P_{t}})$ | |
| 0 (- V) | | ³ /(H ₁ P _c) | _ |

* These were determined by homo- and hetero-nuclear double resonance, irradiating peaks due to H_1 , H_q , H_c , H_t , P_t , and P_c at low power. ${}^2J(H_1H_q)$ is assumed to be negative, as in other molecules where ${}^2J(HSiH)$ has been determined.

couplings were with the two P and the other SiH nuclei. By analogy we suppose that ${}^{2}J(HH)$ is roughly equal to ${}^{3}J(HP_{c})$.

(g) SiH_3SiH_3 . The ³¹P-{¹H} spectrum of the products of this reaction showed peaks due to isomers with both *cis* and *trans* phosphines. In the ¹H spectrum there were

as with its silvl analogues, there is a large internal chemical shift between the two GeH protons. Here the coupling between one of the GeH protons, H_q , and the two IrH protons was not observed. The main parameters are given in Tables 1 and 2.

(i) GeH_3Br . Here too the main product is of type (I). The ¹H spectrum in the hydride region is complicated because the two IrH resonances almost coincide, giving an ABM₂X₂ pattern. We have resolved this by studying the product obtained from GeD_3Br and (1). In such a reaction, the product will contain one IrH and one IrD group in each molecule unless intermolecular H-D exchange occurs. The main IrH resonance due to an isomer of type (I) consists of two broadened triplets of equal intensity, showing that H is randomly distributed between the two possible sites. No sign of the multiplets due to molecules containing two H's was detected, so significant intermolecular H scrambling did not occur in the system. Peaks due to both hydrides in the isomer with *cis* phosphines were also present. We were not able to identify the peaks due to the GeH resonances of the isomer of type (III) or (IV) with certainty, but resonances were observed that we assign tentatively to these groups, and their parameters are given in Table 2.

(j) GeH₃F. The main product here contains mutually *trans* phosphines. The ¹H and ³¹P spectra are complicated by coupling to fluorine; ³J(HIrGeF) is small. One of the IrH resonances appears somewhat unsymmetrical, because of overlap with one of the IrH resonances from the species

with cis phosphines. The ¹H resonances of the latter were not fully resolved. We were able to identify about threequarters of the complex overlapping multiplets due to H_c and H_t, and so could establish values for the couplings that are consistent with the observed patterns. Couplings involving H_t are well determined, because one of the two multiplets was separate from other peaks; some couplings involving H_e are not so well determined, and these values are included in brackets in Table 2. The GeH resonance was on the edge of the very strong peaks due to the phenyl protons, and so we cannot analyse it. The value given for the chemical shift is the position of the strongest line. We have assigned ${}^{2}J(\text{HGeH})$ as the separation between the weak, narrow doublet to lowest frequency and the next narrow doublet in the multiplet pattern. The n.m.r. parameters are collected in Tables 1 and 2.

(k) SiH_3F . This product contains mutually cis phosphines. Both values of ${}^{3}J(FSiIrP)$ are much bigger than for the germyl adduct, but the one to Pe is roughly double that to P_t , so we suggest that Si is *trans* to P_c , and that the product is of type (III). Here too the ¹H spectrum shows some unexpected features. The resonance due to H_t appears as a wide doublet of triplets of quartets: this unexpected pattern arises because ${}^{2}J(H_{t}IrP_{c})$ happens to be numerically about equal to ${}^{3}J(H_{t}IrSiF)$, giving a near triplet, and because ${}^{3}I(HIrSiH)$ is half ${}^{2}I(HIrH)$, giving a near quintet (see Figure 5). It should be noted that here the two SiH protons couple equally to H_t . The resonance due to H_c is complicated but the pattern obtained at 360 MHz can be analysed very simply as a first-order system. The SiH resonance is much more complicated. Values of $^{3}I(H_{e}IrSiH)$ and $^{3}I(H_{t}IrSiH)$ are obtained from the IrH peaks, and of ² J(HSiF) from the ¹⁹F spectrum; patterns obtained under phosphorus decoupling, however, consist of two fairly narrow multiplets separated by ${}^{2}J(HSiF)$, so the internal chemical shift must be small. Weak outer lines in the SiH-{IrH} spectrum give values of ${}^{2}J$ (HSiH), and the proton spectra can then be simulated, leading to the values for the coupling constants given in Table 2.

(*l*) SiH₃I. Two isomers are formed, the minor of type (I), with *trans* phosphines, and the major of type (III) or (IV). The ¹H n.m.r. spectra are like those of the adducts of SiH₃Br or SiH₃Cl: the IrH resonances are extremely similar to the analogous resonances in the adducts of chloride or bromide, and the two SiH resonances are separated by over 1 p.p.m. Here, though, while one appears as a quartet the lines are broad. The other peak is a featureless lump, though sharp components are resolved if one or other of the IrH resonances is irradiated.

The most dramatic observation in recording this spectrum was made when we attempted to decouple one SiH from the other: on irradiating L, Q disappeared (see Figure 6). This is a spectacular case of saturation transfer, which will be discussed further below. Reducing the power of irradiation at room temperature showed that saturation transfer is much more efficient than decoupling: no observable resonance appears at Q without a quartet structure. However, at -40 °C the efficiency of saturation transfer is reduced enough to allow us to turn Q into a broadened triplet by irradiation at L. Careful experiments, using peaks due to the trans isomer as standards, show that irradiation at Q or L does not lead to any transfer of saturation to the IrH resonances. Analogous experiments show that with irradiation at L with about 0.05 W power, the transfer of saturation leads to loss of ca. 60% of the intensity of Q in the spectrum of the adduct of SiH_3Br and 40% for the adduct of the chloride at 298 K. In each of these two spectra Q could be reduced to a near triplet by irradiation at L

DISCUSSION

(a) Assignment.—The one remaining question of assignment in these spectra concerns the two IrHresonances in the isomers of type (I). While in the spectra of the species containing MH₃ the two resonances look very similar, in all the others the IrH resonance labelled H_a shows much larger coupling to MH than does the other. We believe that this proton is *trans* to M. In all the isomers of the species we have studied, Ht must be *cis* to M, and [if we are right to assign structure (III) to all the isomers with cis phosphines] so must H_c . The resonances due to both H_t and H_e move more or less to higher frequency for a given M as Q changes from H through F, Cl, and Br to I. One of the IrH resonances in the series of isomers of type (I) shifts in the same sense; the other shifts in the *opposite* sense. We assign the former to H cis to M, and the latter to H trans to M. This assignment coincides with the one based on the magnitude of ${}^{3}/(HMIrH)$. Patterns of change with changing M and Q in the chemical shifts of the other hydrides support this analysis.

(b) The Relative Abundance of the Isomers.—The proportions of each type of isomer found at room temperature are given in Table 3. These proportions do not seem to change with time. We have assumed that all isomers with *cis* phosphines are of the same type. There seems to be a very rough correlation between the size of M or its attached groups and the type of isomer formed: the smaller the attached group, the smaller the proportion of the isomer with type (I). Since the difference in size between Ge and Si is very small, the considerable difference in isomer distribution between silvl and germyl products is a little surprising. Furthermore, CH_3 presents a minor discrepancy in this analysis.

(c) The N.M.R. Parameters.--There is nothing remarkable about the ³¹P chemical shifts: the peak due to the isomer with trans phosphines in a given system is always to higher frequency of the other resonances. The changes in IrH chemical shift with M and with substituent at M follow regular trends if our structural assignments are correct. The most striking observation in relation to chemical shifts is the internal shift between H_1 and H_{α} in isomers of type (III). The magnitude of this shift depends dramatically on the nature of the substituent at M: it is very small when the substituent is F, CH_3 , or SiH₃ but large when the substituent is Cl, Br, or I, and increases in that order. It seems likely that the shift is derived from conformational effects. It enables us to record some values of ${}^{2}J(\text{HMH})$ in these molecules. The most unexpected feature of the many coupling constants recorded is the very wide range of values of ${}^{3}J(\text{HIrMH})$ in isomers of type (III). When the substituent at Si is F, ${}^{3}/(H_{t}IrSiH_{a})$ and ${}^{3}/(H_{t}IrSiH_{l})$ are effectively equal, whereas ${}^{3}J(H_{c}IrSiH_{q})$ and ${}^{3}J(H_{c}IrSiH_{l})$ are 1.7 and 4.4 Hz respectively; in the complex containing SiH₃,

 ${}^{3}J(H_{t}IrSiH)$ is not detected, while of the two possible values of ${}^{3}J(H_{c}IrSiH)$, one is 4.3 Hz and the other too small to be detected. When the substituent at Si is Cl or Br, the couplings from H_{1} and H_{q} to both H_{c} and H_{t} are substantially different. Here too the differences are likely to be related to conformational effects: they lead to resonances whose appearances are in some cases both simple and misleading.

We have also determined the relative signs of a number of the coupling constants in the spectrum of the adduct between (1) and SiH₃Br, using low-power homoand hetero-nuclear double resonance. The signs, given in Table 4, are all related to the sign of ${}^{2}J(\text{HSiH})$, which we have assumed to be negative. All three-bond couplings are negative, and all but two of the two-bond couplings are positive; apart from ${}^{2}J(\text{HSiH})$, the other negative two-bond coupling involves mutually *trans* H and P.

(d) The Saturation Transfer.—The mechanism by which saturation of H_1 is transferred to H_q is by no means clear. Since there is no transfer of saturation to either of the IrH resonances, the process responsible cannot involve reductive elimination of SiH₃I; it must simply interchange H_{α} and H_{i} . This could be achieved by inversion at Ir, but we have no evidence to indicate that this process takes place. In view of the dependence of saturation transfer upon the nature of the other group bound to silicon, the most logical explanation would involve ionisation of the halogen, perhaps under the influence of the excess of PPh₃ that is present in solution. If the co-ordination round the silicon atom were to become planar, interchange of H_1 and H_q would become possible. Alternatively, co-ordination of PPh₃ to silicon might lead to a similar result by pseudo-rotation in a species containing five-co-ordinated silicon. Further experiments are in hand to explore this unexpected phenomenon.

(e) Stereospecificity of the Addition.—Fawcett and Harrod⁴ have suggested that the initial reaction between (1) and MR_3H is stereospecific, H_t being derived from the silane; they then proposed that a further interchange process involving free MH leads to equili-

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bration between H_t and H_c . In our system we believe that the processes are more complicated than suggested by this simple analysis; preliminary results, for example, suggest that while reactions between (1) and Si(CH₃)D₃ initially lead to a product in which D is *trans* to P, randomisation of H and D between positions *cis* and *trans* to P_t takes place without formation of SiH. Randomisation begins in less than 5 min at 233 K, and so great care is needed in these experiments. We intend to make a more thorough study of the stereospecificity of formation of both types of isomer.

EXPERIMENTAL

Compounds were prepared by established synthetic routes; the purity of (1) was determined by ¹H and ³¹P n.m.r., and by i.r. spectroscopy, and confirmed by microanalysis. Volatile compounds were manipulated in vacuum apparatus fitted with conventional greased taps. Solutions for n.m.r. spectroscopy were made up in benzene or toluene or their deuteriated analogues. Proton resonance spectra were obtained using Varian HA100 continuous-wave or XL100 Fourier-transform spectrometers, both equipped for ¹H-{³¹P} experiments, or with a Brucker WH360 spectrometer that was capable of homo- but not hetero-nuclear double resonance. All spectra reported here were obtained from samples that had been allowed to react for 1 h or more at room temperature, unless otherwise stated. Phosphorus and fluorine spectra were determined by means of JEOL FX60Q or Varian XL100 spectrometers, and ¹³C using a Varian CFT20 instrument. Infrared spectra were obtained using Perkin-Elmer 577 and 225 instruments (250-4000 cm⁻¹).

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