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

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The title complex, $[IrH(CO)(PPh_3)_3]$ (1), reacts with MH_3Q (M = Si or Ge when Q = H, F, Cl, Br, or I; M = Si when Q = SiH_3 or CH_3) to give $[IrH_2(CO)(PPh_3)_2(MH_2Q)]$. The products have been characterised by ^1H, ^{31}P, and (where appropriate) ^{19}F 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 Q = 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 or Ge and X = F, Cl, Br, or I) with *trans*-carbonylchlorobis(triphenylphosphine)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 silyl 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, CH_3, or SiH_3; 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 ^{31}P n.m.r. spectrum shows that PPh_3 has been evolved; the overall reaction is expressed by the equation. So far we have not succeeded in separating the

$$MH_3Q + [IrH(CO)(PPh_3)_3] \longrightarrow PPh_3 + [IrH_2(CO)(PPh_3)_2(MH_2Q)]$$

iridium complexes formed from PPh_3, so we have no analytical or crystallographic information. However, the ^1H and ^{31}P 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 $[IrH_2(CO)(PPh_3)_2(MH_2Q)]$ 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 ^{31}P-{^1H} resonances; similarly, the phosphines in isomer (VI) are equivalent when protons are decoupled. On the other hand, ^{31}P-{^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 ^{31}P-{^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.

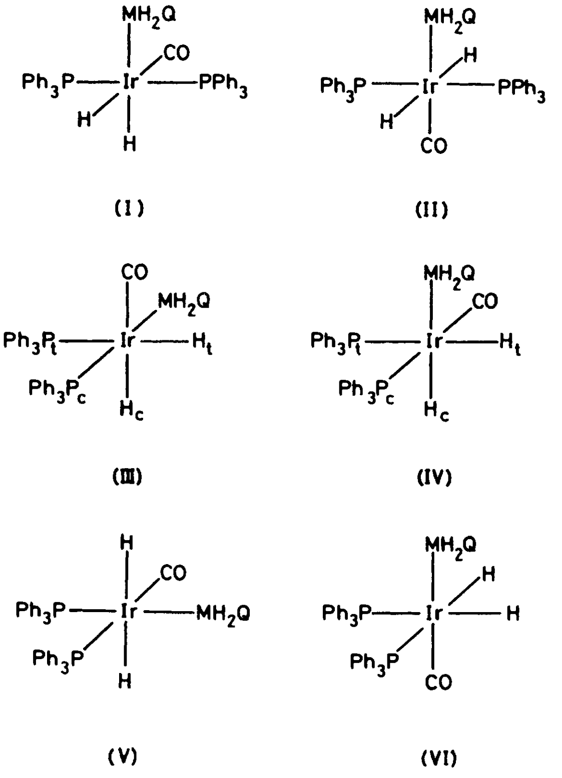

FIGURE 1 Possible isomers of adducts formed by (1) with MH_3Q

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

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

between (1) and GeH_3I shows a single peak in the ^{31}P-{^1H} spectra, besides the resonance due to PPh_3 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 $SiMeH_3$ gives a product where ^{31}P-{^1H} spectra consist of an AB quartet; here, too, the product is mono-isomeric, but of type (III), (IV), or (V). The product of the reaction of (1) with SiH_3F gives a ^{31}P-{^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 ^{31}P-{^1H} spectra, showing that isomers with both non-equivalent (AB pattern) and equivalent (singlet) phosphines were present; with all the germyl compounds the predominant product had equivalent phosphines, whereas with all the silyl compounds the main product had *cis* phosphines.

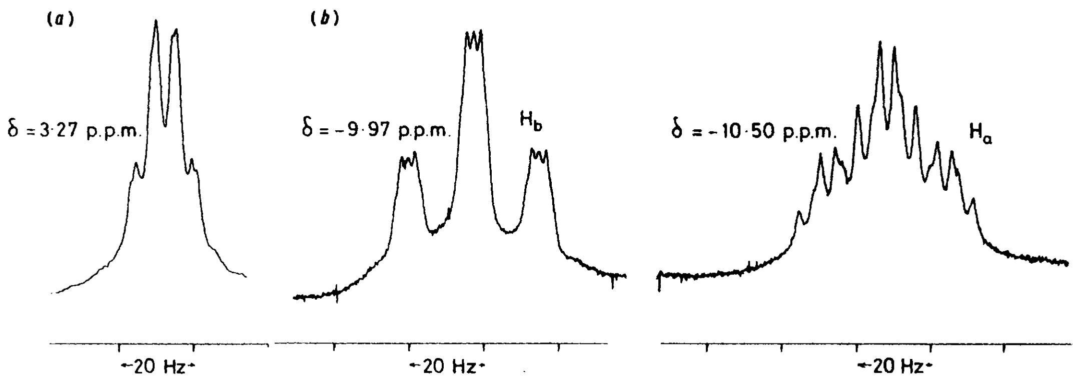

FIGURE 2 Proton n.m.r. spectra of the Ge*H* (*a*) and Ir*H* (*b*) peaks of the adduct of (1) with GeH_3I

TABLE 1

N.m.r. parameters [a] for products of type (I) from (1) and MH_3Q

	SiH_4	SiH_3Cl	SiH_3Br	SiH_3I	SiH_3-(SiH_3) [b]	GeH_4	GeH_3F [c]	GeH_3Cl	GeH_3Br	GeH_3I
δH_a/p.p.m.	−8.59	−8.73	−8.89	−8.19	−8.39	−9.21	−9.97	−9.87	−10.24	−10.50
δH_b/p.p.m.	−10.42	*ca.* −10.21	−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
$^2J(H_aH_b)$/Hz	4.2	4.2	4.0	4.0	4.3	4.1	4.0	4.0	n.m.	3.9
$^2J(H_aP)$/Hz	17.0	17.8	17.7	17.1	16.9	15.9	15.9	15.8	16.0	15.7
$^2J(H_bP)$/Hz	17.9	17.3	16	17.1	17.5	18.1	17.8	17.7	17.7	17.5
^3J(HMP)/Hz	4.7	5.5	5.5	6.1	n.m.	4.2	2.8	5.4	5.2	5.4
$^3J(HMH_a)$/Hz	<0.4	2.4	2.8	3.8	<0.4	1.5	5.3	5.6	5.5	5.9
$^3J(HMH_b)$/Hz	2.0	1.8	1.8	2.1	2.2	1.8	1.6	1.5	1.5	1.5

[a] 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] $\delta(SiH_3)$ = 3.50 p.p.m.; ^3J(HH) = 3.2 Hz. [c] δF = −224.8 p.p.m.; ^2J(HF) = 41.3, $^3J(FH_a)$ = 9.4, $^3J(FH_b)$ = 4.0 Hz.

The ^1H *Spectra.—Product from* (*a*) GeH_3I. The proton resonance spectrum (see Figure 2) shows that this compound is of type (I). There are two Ir*H* resonances of equal intensity in the low-frequency region. The Ge*H* resonance is twice as strong as either, and appears as a 1 : 3 : 3 : 1 quartet of narrow doublets. Irradiation at the lower frequency of the two Ir*H* resonances reduces the Ge*H* resonance to a 1 : 2 : 1 triplet of narrow doublets, while irradiation at the other Ir*H* resonance collapses the narrow doublet coupling. The quartet pattern is therefore due to a coincidence: coupling to the lower-frequency Ir*H*, which we call H_a, happens to be equal to a triplet coupling which is not associated with Ir*H* and which we assign to ^3J(HGeIrP). The narrow doublet is due to coupling to the higher-frequency Ir*H*, which we label H_b. Each Ir*H* resonance can be analysed as a set of overlapping triplets [^2J(HIrP)] of triplets [^3J(HIrGeH)] of doublets [^2J(HIrH)]; irradiation of the Ge*H* resonance simplifies each to a triplet of doublets, the doublet couplings being equal. The only question is as to which Ir*H* 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*) GeH_4. The ^{31}P-{^1H} 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 ^{31}P-{^1H} spectrum was an AB quartet. The ^1H spectra established that the former was an isomer of type (I), and the latter of type (III) or (IV) (see Figure 3).

The Ge*H* 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 ^3J(HGeIrH); the larger triplet coupling is assigned to ^3J(HGeIrP). In the low-frequency region two very similar resonances of equal intensity were observed, each one-third the intensity of the Ge*H* resonance. Their apparently complicated patterns were easily analysed with the help of homonuclear double 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 ${}^2J$(HIrH), when GeH protons were decoupled, and a quartet splitting [due to ${}^3J$(HIrGeH)] when the other Ir*H* resonance was irradiated. Each peak therefore consisted of a pair of overlapping quartets. The overall appearance of the spectrum was that of two triplets of sextets or septets, since ${}^2J$(HIrH) is between two and three times as large as ${}^3J$(HGeIrH).

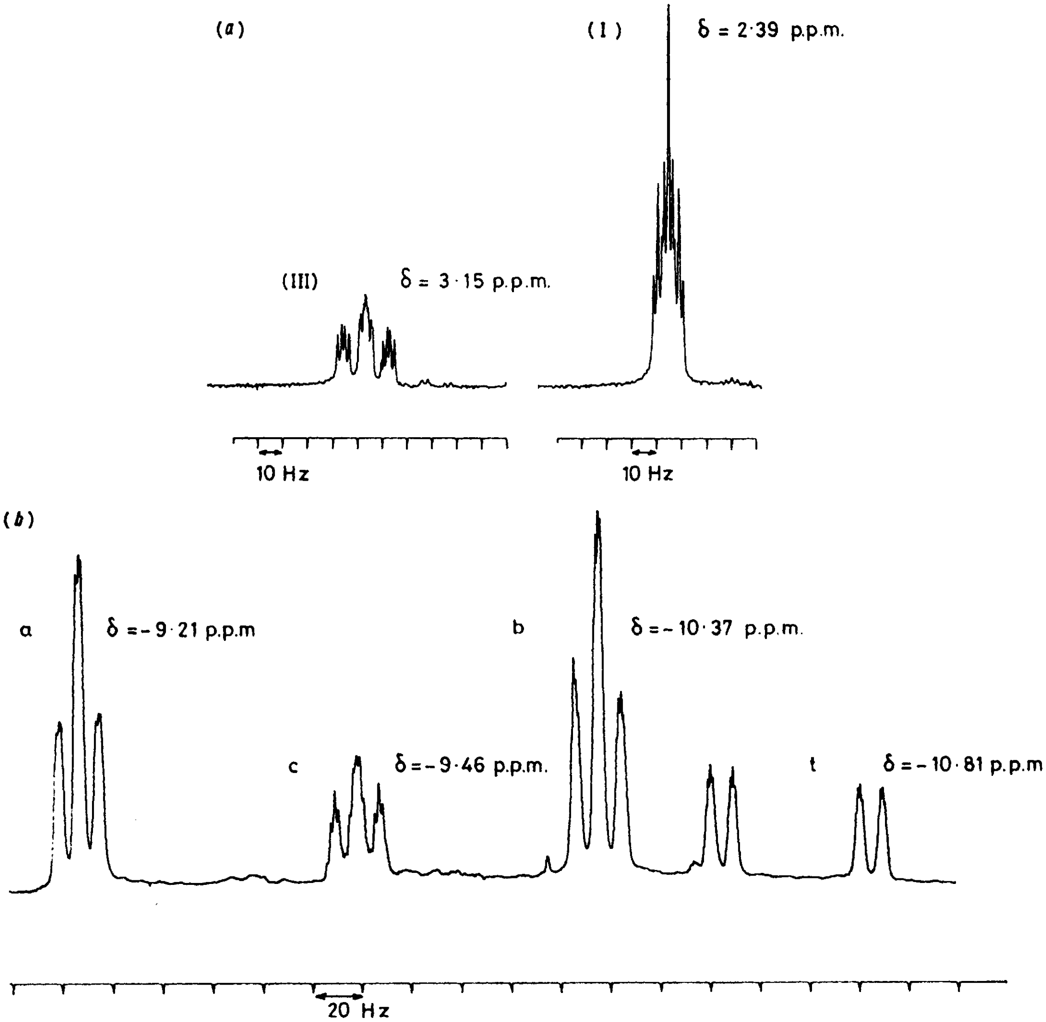

FIGURE 3 Proton n.m.r. spectra of the Ge*H* (*a*) and Ir*H* (*b*) peaks of the adduct of (1) with GeH_4. The Ge*H* peaks marked (I) and (III) are due to isomers of types (I) and (III) respectively. The IrH peaks marked a and b are due respectively to H_a and H_b in the isomer of type (I), while those marked c and t are due to H_c and H_t in the isomer of type (III)

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 Ir*H* resonances showed a large coupling (121 Hz) that we assign to ${}^2J(H_tIrP_t)$ [for notation see Figure 1 (III)]; there is a smaller doublet coupling that is unaffected by homonuclear double resonance and that we assign to ${}^2J(H_tIrP_c)$. Each line appears as a sextet, but decoupling the Ge*H* resonance reduces this to a doublet, which we assign to ${}^2J$(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 Ge*H* protons to a doublet [${}^2J(H_cP_c)$] of doublets [${}^2J(H_cP_t)$] of doublets [${}^2J(H_cH_t)$]; the couplings are easily associated with particular P nuclei by selective irradiation of the H_t peaks. Restoration of coupling to the Ge*H* protons introduces a further quartet splitting on each line that is not very well resolved because of overlap. The Ge*H* resonance appears under even the highest resolution as a triplet of doublets of doublets; each of the doublet couplings can be collapsed by decoupling on one of the Ir*H* protons, but the triplet pattern remains unaffected. We conclude that in this species the two values of ${}^3J$(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 Si*H* resonance associated with this species.

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

(IV), were generally similar to those of its germyl analogue. Here, $^3J(H_tIrSiH)$ is about half $^2J(H_cIrH_t)$; moreover, the two values of $^3J(HSiIrP)$ are substantially different, so that the appearance of the Si*H* resonance is somewhat different from that of the Ge*H* resonance in the spectrum of the germyl complex. The n.m.r. data are collected in Table 2.

TABLE 2

N.m.r. parameters [a] for products of type (III) from (1) and MH_3Q

	SiH_4	SiH_3F [b]	SiH_3Cl	SiH_3Br	SiH_3I	SiH_3CH_3 [c]	SiH_3-(SiH_3) [d]	GeH_4	GeH_3F [e]	GeH_3Cl	GeH_3Br
δH_t/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
δH_c/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
δH_l/p.p.m.	} 3.76	6.64	6.15	5.68	5.14	4.42	3.47	} 3.15	} 6.68	6.14	5.60
δH_q/p.p.m.		($\delta < 0.1$)	5.47	4.89	4.08	4.29	3.20			5.33	4.57
δP_t/p.p.m.	5.68(4)	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)	1.74	2.77(4)	2.77(4)	1.12(4)	3.04	3.49	5.91	5.29	5.82	5.15
$^2J(H_tH_c)$/Hz	4.0	4.4	4.2	4.0	4.1	3.7	4.0	3.8	3.8	3.9	4.0
$^2J(H_tP_t)$/Hz	115.7	109.9	112.4	112.6	113.1	114.8	115.4	121.0	115.0	117.5	118.3
$^2J(H_cP_t)$/Hz	15.0	14.8	14.7	14.5	14.5	15.3	14.9	15.2	14.6	14.9	15.1
$^2J(H_tP_c)$/Hz	18.7	19.3	19.5	19.4	19.6	19.1	19.3	18.3	17.7	18.8	17.6
$^2J(H_cP_c)$/Hz	20.8	20.9	20.3	20.2	19.7	21.7	20.9	20.4	19.6	19.3	19.3
$^2J(H_qH_l)$/Hz	n.o.	15.3	12.6	12.4	12.7	7.8	n.m.	n.o.	24.5(5)	18.9	22.0
$^2J(P_tP_c)$/Hz	15.9	18.0	17.4	17.4	16.7	16.3	15.4	13.7	14.7	14.8	1.7
$^3J(H_lP_c)$/Hz	} 9.0	(10)	12.9	11.2	14.0	n.m.	n.m.	} 9.2	n.m.	23.6	21.6
$^3J(H_qP_c)$/Hz		(11)	13.7	14.0	*ca.* 12	7.8	n.m.		n.m.	24.2	22.0
$^3J(H_lP_t)$/Hz	} 5.7	(10)	8.5	8.6	8.0	n.m.	n.m.	} 9.2	n.m.	7.3	6.8
$^3J(H_qP_t)$/Hz		(11)	9.8	10.6	*ca.* 12	5.3	n.m.		n.m.	8.8	9.7
$^3J(H_lH_c)$/Hz	} 3.1	4.2	5.8	5.0	7.6	4.2	4.4	} 2.9	5.1	6.1	5.9
$^3J(H_qH_c)$/Hz		1.0	1.3	1.3	<0.4	<0.4	<0.4		<0.4	<0.4	<0.4
$^3J(H_lH_t)$/Hz	} 1.8	} 2.0	4.4	6.1	4.1	<0.4	<0.4	} 1.8	<4.0	4.3	4.2
$^3J(H_qH_t)$/Hz			0.4	0.6	<0.4	<0.4	<0.4		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.

[b] $\delta F = -173.5$ p.p.m.; $^2J(HF) = 49.9$, $^3J(FP_t) = 13.6$, $^3J(FP_c) = 24.3$, $^3J(FH_c) = 12.2$, $^3J(FH_t) = 16.4$ Hz. [c] $\delta(CH_3) = 0.7$ p.p.m.; $^3J(HH) = 4.2$, $^4J(HP_t) = 4.2$ Hz. $\delta(Si) = 62.5$ p.p.m. relative to $SiMe_4$; $^2J(SiP_t) = 99$ Hz. $\delta(^{13}CH_3) = 1.3$, $\delta(^{13}CO) = 181.2$ p.p.m.; $^2J(CP) < 5$ Hz. [d] $\delta(SiH_3) = 4.06$ p.p.m.; $^3J(HH) = 3.8$, $^4J(HP_t) = 2.8$ Hz. [e] $\delta F = -211.5$ p.p.m.; $^2J(HF) = 41.5$, $^3J(FP_t) = 12.5$, $^3J(FP_c) = 22.5$, $^3J(FH_t) = 12.3$, $^3J(FH_c) = 9.0$ Hz.

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 between the Si*H* protons and the other Ir*H* proton is not resolved. However, the relationships between the peaks were easily established by irradiating across the lower-frequency hydride resonance. The parameters for this isomer are given in Table 1, and rough relative abundances in Table 3.

TABLE 3

Rough percentages [a] of isomers of type (I) and type (III) formed by reaction between (1) and MH_3Q at room temperature

MH_3Q	% of type (I)	% of type (III)
SiH_4	8	92
$SiH_3(CH_3)$	0	100
SiH_3F	0	100
SiH_3Cl	10	90
SiH_3Br	12	88
SiH_3I	25	75
$SiH_3(SiH_3)$	10	90
GeH_4	65	35
GeH_3F [b]	major (*ca.* 80%)	minor (*ca.* 20%)
GeH_3Cl	85	15
GeH_3Br	90	10
GeH_3I	100	0

[a] The smaller values in each case are probably accurate to at least ±2. [b] For GeH_3F, the resonances overlapped so much that satisfactory integration was not possible.

(*d*) SiH_3Br. The ^{31}P-$\{^1H\}$ 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 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 Si*H* and two Ir*H* 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 Si*H*, and C and T in the Ir*H* 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 SiH_2 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 Si*H* protons (H_l) are nearly equal, while coupling to the other Si*H* proton (H_q) 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

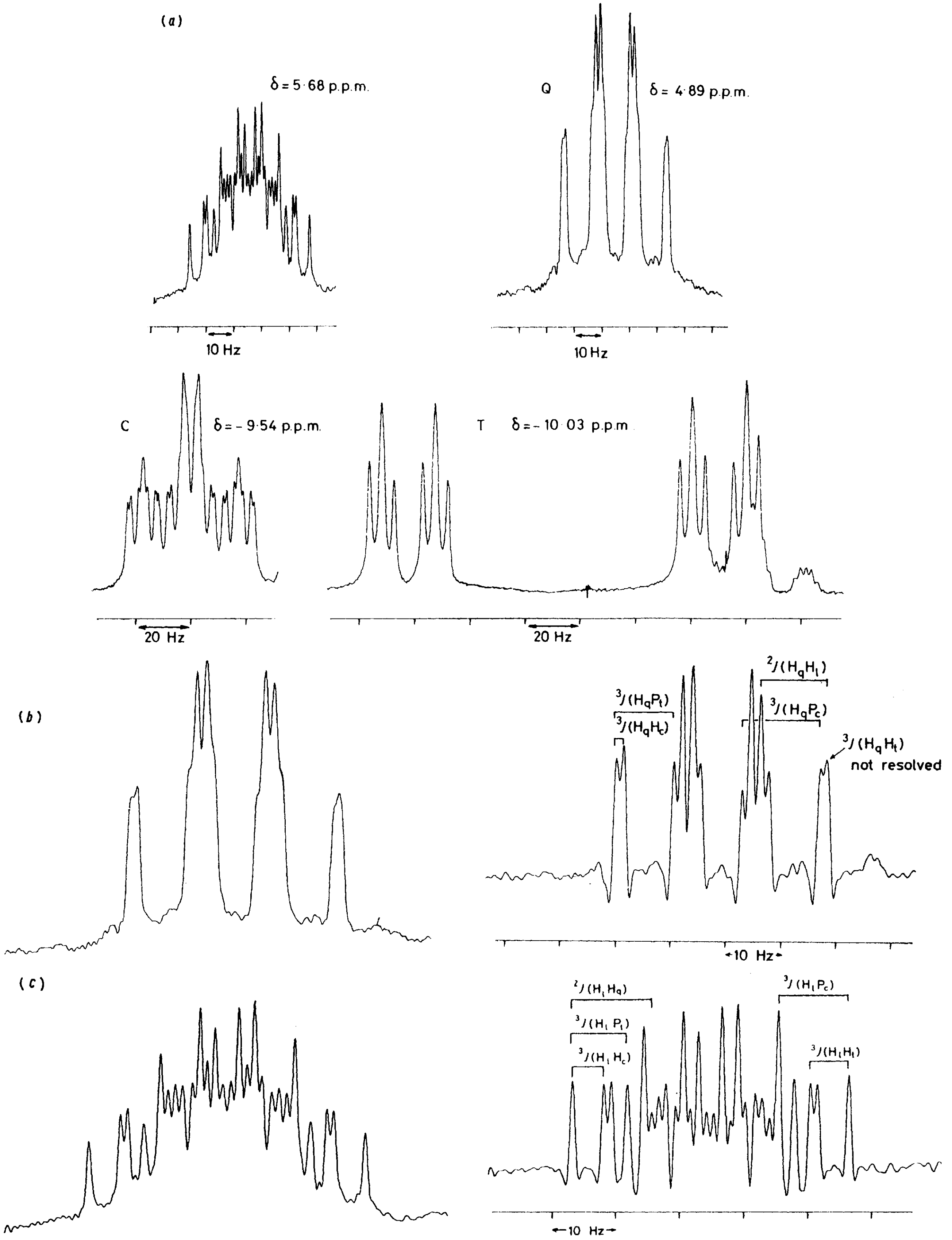

FIGURE 4 Proton resonance spectra of the isomer of type (III) formed by (I) and SiH$_3$Br. (*a*) Peaks L, Q, C, and T. The weak multiplet at the low frequency end of the diagram is due to H$_b$ in the isomer of type (I); (*b*) Q under higher resolution showing (second spectrum) the effects of line narrowing; 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 Si*H* resonances, H_l 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*)] 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.

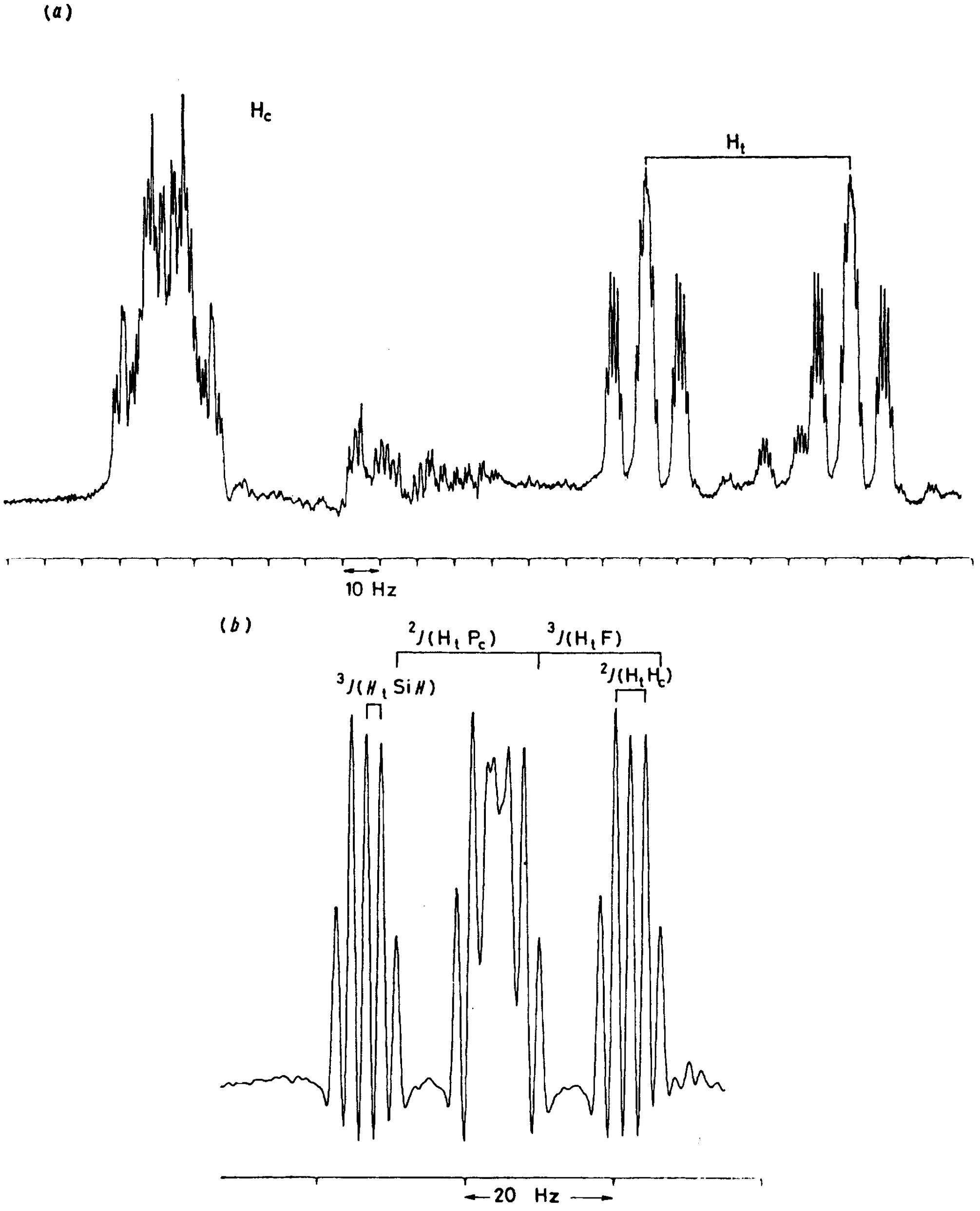

FIGURE 5 Ir*H* resonances of the adduct of (1) with SiH_3F. (*a*) Resonances due to H_c and H_t; (*b*) half of one of the multiplets due to H_t, with line narrowing; couplings are assigned as indicated

(*e*) SiH_3Cl. The reaction between (1) and SiH_3Cl is not clean, even in toluene at −30 °C: the products include the adduct of SiH_4 and the ^1H spectrum shows peaks that can easily be assigned to a complex of type (III) or (IV) with $SiHCl_2$ as ligand. However, ^{31}P-{^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 SiH_3Br. Some of the details were different: for example, $^2J(H_cIrH_t)$ could not be distinguished from $^3J(H_lSiIrH_t)$, and $^3J(H_qSiIrH_t)$ was not resolved, while the differences in the couplings to H_l made the appearance of H_l 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.

(*f*) $SiH_3(CH_3)$. The product of this reaction was monoisomeric; the ^{31}P-$\{^1H\}$ 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 ^{31}P decoupling. This suggests that Si is *trans* to P, and so that the product is of type (III). In keeping with this, the ^{29}Si-$\{^1H\}$ spectrum showed a single large (100 Hz) doublet coupling, which we assign to $^2J(SiP_t)$; in the ^{13}C resonance due to CO there was no coupling larger than 2—3 Hz. In the Ir*H* region of the ^1H spectrum, H_t was found to couple only to the P nuclei and to H_c, but H_c showed roughly equal couplings to H_t and to one of the SiH protons. At 360 MHz the Si*H* 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 ^3J(HCSiH); the other couplings were with the two P and the other Si*H* nuclei. By analogy we suppose that ^2J(HH) is roughly equal to $^3J(HP_c)$.

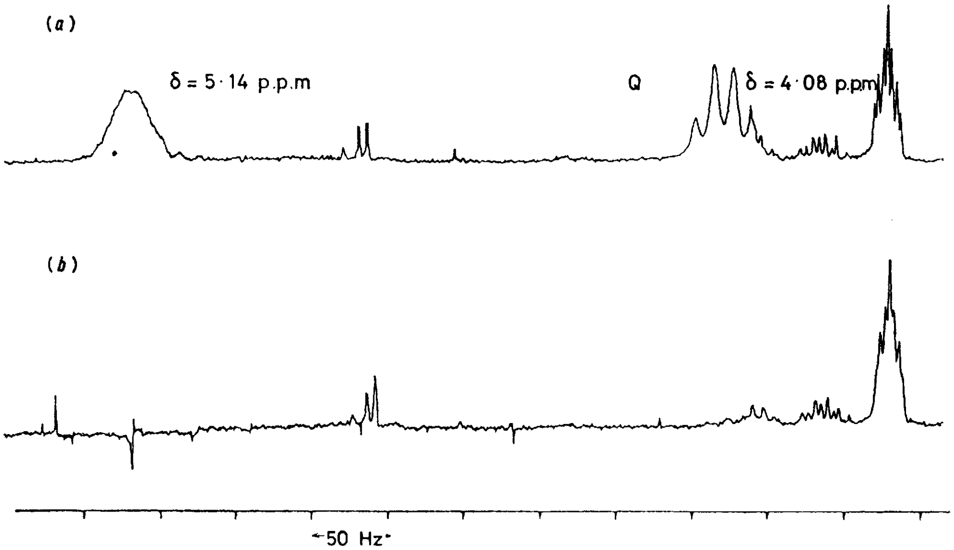

FIGURE 6 Saturation transfer in the Si*H* resonances of the isomer of type (III) formed by (1) with SiH_3I. (*a*) Peaks due to L and Q at 298 K with no double irradiation; (*b*) effect on Q of irradiation at L at room temperature with *ca.* 0.05 W power. The multiplet at the low-frequency end of the drawing is due to the Si*H* resonance of the isomer of type (I)

TABLE 4

Relative signs * of coupling constants in $[IrH_2(CO)(PPh_3)_2(SiH_2Br)]$

$^2J(H_lH_q)$	− (assumed)	$^3J(H_qH_t)$	
$^2J(H_tH_c)$	+	$^3J(H_qH_c)$	−
$^2J(H_tP_t)$	−	$^3J(H_lH_t)$	
$^2J(H_tP_c)$	+	$^3J(H_lH_c)$	
$^2J(H_cP_c)$	+	$^3J(H_qP_t)$	−
$^2J(H_cP_t)$	+	$^3J(H_qP_c)$	−
$^2J(P_cP_t)$	+	$^3J(H_lP_t)$	−
		$^3J(H_lP_c)$	−

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

(*g*) SiH_3SiH_3. The ^{31}P-$\{^1H\}$ spectrum of the products of this reaction showed peaks due to isomers with both *cis* and *trans* phosphines. In the ^1H spectrum there were resonances of the type associated with an isomer of type (I), and in addition peaks in the Ir*H* and Si*H* regions that were qualitatively very like those given by the product obtained from (1) and $SiH_3(CH_3)$. The main difference was that the SiH_3 resonances were to high frequency of the SiH_2 peaks, so that the SiH_3 peak from the product of type (I) overlapped one of the SiH_2 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*) GeH_3Cl. The main product is of type (I). A small proportion of an isomer with *cis* phosphines is also formed: as with its silyl analogues, there is a large internal chemical shift between the two Ge*H* protons. Here the coupling between one of the Ge*H* protons, H_q, and the two Ir*H* 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 Ir*H* resonances almost coincide, giving an ABM_2X_2 pattern. We have resolved this by studying the product obtained from GeD_3Br and (1). In such a reaction, the product will contain one Ir*H* and one Ir*D* group in each molecule unless intermolecular H–D exchange occurs. The main Ir*H* 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 Ge*H* 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*) GeH_3F. The main product here contains mutually *trans* phosphines. The ^1H and ^{31}P spectra are complicated by coupling to fluorine; ^3J(HIrGeF) is small. One of the Ir*H* resonances appears somewhat unsymmetrical, because of overlap with one of the Ir*H* resonances from the species with *cis* phosphines. The ^1H resonances of the latter were not fully resolved. We were able to identify about three-quarters 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_c are not so well determined, and these values are included in brackets in Table 2. The Ge*H* 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 ^2J(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 ^3J(FSiIrP) are much bigger than for the germyl adduct, but the one to P_c 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 $^2J(H_tIrP_c)$ happens to be numerically about equal to $^3J(H_tIrSiF)$, giving a near triplet, and because ^3J(HIrSiH) is half ^2J(HIrH), giving a near quintet (see Figure 5). It should be noted that here the two Si*H* 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 Si*H* resonance is much more complicated. Values of $^3J(H_cIrSiH)$ and $^3J(H_tIrSiH)$ are obtained from the Ir*H* peaks, and of ^2J(HSiF) from the ^{19}F spectrum; patterns obtained under phosphorus decoupling, however, consist of two fairly narrow multiplets separated by ^2J(HSiF), so the internal chemical shift must be small. Weak outer lines in the SiH-{IrH} spectrum give values of ^2J(HSiH), and the proton spectra can then be simulated, leading to the values for the coupling constants given in Table 2.

(*l*) SiH_3I. 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 SiH_3Br or SiH_3Cl: the Ir*H* resonances are extremely similar to the analogous resonances in the adducts of chloride or bromide, and the two Si*H* 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 Ir*H* resonances is irradiated.

The most dramatic observation in recording this spectrum was made when we attempted to decouple one Si*H* 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 Ir*H* 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 Ir*H* resonances in the isomers of type (I). While in the spectra of the species containing MH_3 the two resonances look very similar, in all the others the Ir*H* resonance labelled H_a shows much larger coupling to M*H* than does the other. We believe that this proton is *trans* to M. In all the isomers of the species we have studied, H_t 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_c 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 Ir*H* 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 ^3J(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 silyl 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 ^{31}P 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 Ir*H* 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_l and H_q 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 SiH_3 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 ^2J(HMH) in these molecules. The most unexpected feature of the many coupling constants recorded is the very wide range of values of ^3J(HIrMH) in isomers of type (III). When the substituent at Si is F, $^3J(H_tIrSiH_q)$ and $^3J(H_tIrSiH_l)$ are effectively equal, whereas $^3J(H_cIrSiH_q)$ and $^3J(H_cIrSiH_l)$ are 1.7 and 4.4 Hz respectively; in the complex containing SiH_3,

$^3J(H_tIrSiH)$ is not detected, while of the two possible values of $^3J(H_cIrSiH)$, 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_l 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 SiH_3Br, using low-power homo- and hetero-nuclear double resonance. The signs, given in Table 4, are all related to the sign of $^2J(HSiH)$, 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 $^2J(HSiH)$, the other negative two-bond coupling involves mutually *trans* H and P.

(*d*) *The Saturation Transfer*.—The mechanism by which saturation of H_l is transferred to H_q is by no means clear. Since there is no transfer of saturation to either of the Ir*H* resonances, the process responsible cannot involve reductive elimination of SiH_3I; it must simply interchange H_q and H_l. 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 PPh_3 that is present in solution. If the co-ordination round the silicon atom were to become planar, interchange of H_l and H_q would become possible. Alternatively, co-ordination of PPh_3 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 Harrod[4] 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 equilibration 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 $Si(CH_3)D_3$ 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 ^{31}P 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 $^1H-\{^{31}P\}$ 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 ^{13}C using a Varian CFT20 instrument. Infrared spectra were obtained using Perkin-Elmer 577 and 225 instruments (250—4 000 cm^{-1}).

We are grateful to the S.R.C. for studentships (to D. M. L. and T. E. F.). We also thank Messrs. Johnson Matthey Ltd. for lending us chemicals.

[0/1220 *Received*, 1*st August*, 1980]

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