Some Silyl and Germyl Compounds of Six-co-ordinated Rhodium(III) Carbonyl Halides

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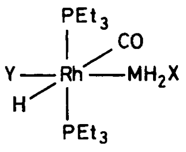
Reaction between *trans*-[Rh(CO)Cl(PEt$_3$)$_2$] (1) and MH$_3$Cl (M = Si or Ge) at low temperatures gives equimolar adducts characterised by ^{1}H and ^{31}P n.m.r. spectra as [RhH(CO)Cl(PEt$_3$)$_2$(MH$_2$Cl)] with mutually *trans* phosphine ligands and M *trans* to H. Similar reactions occur between *trans*-[Rh(CO)I(PEt$_3$)$_2$] (2) and MH$_3$I. Some of the adducts have been isolated by evaporating solvent at low temperature. Both (1) and (2) give similar adducts with MH$_4$, MH$_3$Me, SiH$_3$CH$_2$CH=CH$_2$, and SiH$_2$MeX (X = Cl or I); these dissociate reversibly between 200 K and 280 K, and thermodynamic parameters for dissociation of some of them have been determined from the n.m.r. spectra. Dissociation of the adducts of (2) with organosilanes and with methylgermane is fast on the n.m.r. time-scale, whereas dissociation of the adducts of (1) is slow. The reaction between (1) and MH$_3$I gives adducts with Cl bound to M and I bound to Rh as the thermodynamically stable products; no halogen exchange was observed in the reaction between (2) and MH$_3$Cl.

REACTION between silanes or germanes and four-co-ordinated complexes of iridium(I) gives adducts [1,2] that can be isolated without difficulty and contain six-co-ordinated Ir^{III}. Much less is known about silyl or germyl complexes of rhodium. A few have been described,[3,4] but their readiness to dissociate at or below room temperature has made them hard to characterise,[5] and little is known of them. As part of our study of the compounds formed by silanes or germanes with the platinum metals, we have explored reactions between *trans*-[Rh(CO)Y(PEt$_3$)$_2$] (Y = Cl or I) and some simple silyl and germyl compounds.

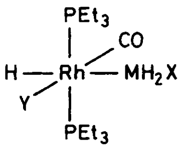
RESULTS

Reaction of trans-[Rh(CO)Cl(PEt$_3$)$_2$] (1) *with* SiH$_3$Cl.—Reaction between equimolar amounts of (1) and SiH$_3$Cl in toluene began at 203 K and was complete after a few minutes at 233 K. The n.m.r. spectra of the resulting solution were initially recorded at 213 K to avoid possible decomposition of the products. The ^{31}P-{^{1}H} spectrum showed that all complex (1) had been consumed, and that a single phosphorus–rhodium complex had been formed, in which δ(P) and ^1J(PRh) were more consistent with six-co-ordinated Rh^{III} than with four-co-ordinated Rh^I. We believe that the product was a complex of type (B) (X = Y = Cl).

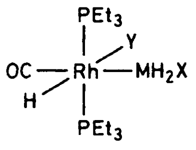
The ^{31}P-{^{1}H} spectrum gave a doublet, showing that the phosphine ligands were mutually *trans*. When only those protons with $\delta > 0$ p.p.m. were decoupled, the ^{31}P spectrum showed a narrow additional doublet coupling, indicating the presence of a single hydride ligand bound to Rh. The ^{1}H spectra contained resonances at δ *ca.* 5 p.p.m. (relative intensity 2, assigned to SiH), at δ *ca.* 2 p.p.m. (30 H, assigned to PEt$_3$ protons), and at δ *ca.* -9 p.p.m. (1 H, assigned to RhH). The SiH resonance appeared as a 1 : 2 : 3 : 4 : 3 : 2 : 1 septet. When the ^{31}P frequency was irradiated this multiplet was simplified to a 1 : 2 : 1 triplet, and when the RhH resonance was simultaneously irradiated the SiH resonance appeared as a 1 : 1 doublet with the same splitting as the triplet. These observations show that the SiH protons were coupled to Rh, to the RhH proton, and equally to two P nuclei, with ^2J(HSiRh) and ^3J(HSiRhH) roughly equal and ^3J(HSiRhP) about twice ^2J(HSiRh). The RhH resonance appeared as a 1 : 2 : 4 : 6 : 6 : 6 : 4 : 2 : 1 nonet, simplified by decoupling ^{31}P to a 1 : 2 : 2 : 2 : 1 quintet with the same splitting as in the nonet, and by simultaneous decoupling of SiH to a 1 : 1 doublet with twice the splitting observed in the absence of double irradiation. These observations show that the hydride ligand was coupled to Rh, to two equivalent SiH protons, and equally to two P nuclei, with coupling constants in the ratio 1 : 2 : 1. The chemical shift of the hydride resonance was not consistent with a structure in which H is *trans* to halogen,[6] and so the structure of the complex formed must be (A) or (B). We believe that the species is of type (B) because the magnitude of ^3J(HSiRhH) is more in keeping with a species in which H and SiH are mutually *trans*.[7] The n.m.r. parameters are included in Table 1. The n.m.r. spectra of this complex were not significantly different at room temperature, although irradiation of the SiH protons caused substantial transfer of saturation to the RhH resonance and *vice versa*. This effect was not observed at low temperatures; it implies that SiH and RhH protons exchange at room temperature at a rate which, although slow on the n.m.r. time scale, is fairly fast in relation to relaxation times, probably by dissociation and recombination. Attempts to isolate the complex by removal of solvent at room temperature led to recovery of the starting material. On prolonged standing at room temperature, the solution turned brown and there were irreversible changes in the n.m.r. spectra.



(A)



(B)



(C)

M = Si or Ge

Reaction of trans-[Rh(CO)I(PEt_3)$_2$] (2) *with* SiH_3I.—Reaction between equimolar proportions of (2) and SiH_3I in toluene was complete in a few minutes at 198 K. The results were very like those described above, although the n.m.r. parameters, and in consequence the pattern observed in the RhH multiplet, were rather different. We conclude that here too a single species of type (B) (X = Y = I) was formed by oxidative addition of SiH to Rh^I. In this system, transfer of saturation between SiH and RhH proton resonances by double irradiation at room temperature was very marked, indicating faster dissociation and recombination, and the peaks in the ^1H spectrum recorded at 298 K were broad. Evaporation of solvent at room temperature led to recovery of (2), but careful evaporation at low temperatures gave a yellow solid whose analysis was consistent with a 1 : 1 adduct. The n.m.r. parameters are included in Table 1 and analytical data are in the Experimental section.

TABLE 1

N.m.r. parameters for [RhH(CO)Y(PEt_3)$_2$(SiH_2X)] *

Y	Cl	Cl	Cl	I	I	I
X	H	Cl	I	H	Cl	I
δ(P)/p.p.m.	28.4(1)	26.8(1)		24.3(1)	19.4(1)	17.3(1)
δ(Si*H*)/p.p.m.	3.54(2)	5.2(2)	4.1(4)	3.69(1)	5.38(2)	4.31(2)
δ(Rh*H*)/p.p.m.	−7.95(2)	−8.6(2)	−8.21(1)	−9.07(1)	−9.63(2)	−9.54(2)
^1J(HRh)/Hz	10.8(2)	12.4(2)	n.r.	8.4(1)	10.6(3)	10.0(5)
^1J(PRh)/Hz	88.7(2)	87.8(2)	n.r.	89.1(1)	85.9(2)	85.0(2)
^2J(HSiRh)/Hz	⩽0.3	5.5(5)	n.r.	⩽0.3	5.0(5)	5.0(5)
^2J(HRhP)/Hz	12.8(2)	12.4(2)	n.r.	13.3(2)	13.1(3)	11.0(5)
^3J(HSiRhH)/Hz	2.0(2)	5.1(2)	n.r.	2.0(2)	5.7(3)	5.0(5)
^3J(HSiRhP)/Hz	6.5(2)	11.0(5)	n·r.	6.65(1)	10.0(5)	10.5(5)

* All isomers are of type B. Parameters recorded at 233 K for solutions in toluene; chemical shifts taken as positive to high frequency of $SiMe_4$ (for ^1H) or 85% H_3PO_4 (for ^{31}P); n.r. = not resolved.

Reaction of Complex (2) *with* SiH_3Cl.—Reaction between SiH_3Cl and (2) was complete after a few minutes at 193 K, and the n.m.r. spectra of the single product showed that it was analogous to those described above. The values of δ(P) and ^1J(RhP) imply that iodine was bound to Rh, and the chemical shift of the SiH protons was consistent with Cl bound to Si; we formulate the product as [RhH(CO)I(PEt_3)$_2$(SiH_2Cl)]. Such a halogen distribution is in keeping with our results for work with analogous derivatives of Pt and Ir.[8] The complex was isolated by careful evaporation of the solvent at low temperatures, and its composition confirmed by analysis (see Experimental section). The n.m.r. parameters are given in Table 1. No transient resonances due to intermediates were observed.

Reaction of Complex (1) *with* SiH_3I.—The ^{31}P-{^1H} n.m.r. spectra of a solution in toluene containing equimolar proportions of (1) and SiH_3I, after a few minutes at 198 K, showed the presence of much (1), with signals corresponding to small amounts of two Rh^{III} species, (3) and (4), in roughly equimolar proportions. At 223 K, no signal due to (1) was observed, and (3) and (4) were present in roughly 1 : 3 mol ratio. At 243 K, the sole product was (4). The ^{31}P and ^1H n.m.r. spectra of (4) were the same as those of the product formed from (2) and SiH_3Cl, indicating that the thermodynamically stable product of this reaction contained iodine bound to Rh and chlorine bound to silicon. The ^1H resonance spectrum of a different sample at 190 K showed four SiH and four RhH resonances; on gradual warming, it became clear that each SiH resonance was associated with one of the RhH peaks. The resolution was too poor to allow resolution of multiplet structures, but the chemical shifts of SiH and RhH resonances allowed us to identify three of the compounds as [RhH(CO)Cl(PEt_3)$_2$(SiH_2Cl)], [RhH(CO)I(PEt_3)$_2$(SiH_2Cl)] (4), and [RhH(CO)I(PEt_3)$_2$(SiH_2I)]. The chemical shifts associated with the fourth species were consistent with its formulation as [RhH(CO)Cl(PEt_3)$_2$(SiH_2I)], and we assign the ^{31}P resonance of (3) to the same species. When this tube was warmed to 240 K, the only SiH species remaining was (4).

Reaction of Complex (1) *with* SiH_4.—The yellow colour of an equimolar solution of (1) and SiH_4 in toluene disappeared slowly at 203 K. At this temperature the ^{31}P-{^1H} and ^1H n.m.r. spectra showed the presence of a single rhodium(III)-silyl complex. As the temperature of the solution was raised, the peaks due to (1) reappeared, and became relatively stronger as the temperature increased, until at 298 K the only peaks observed in the ^{31}P-{^1H} spectra were due to (1). This behaviour was reversible.

The ^{31}P spectra were very like those of the products described above. In the ^1H spectrum, the SiH resonance appeared as a simple triplet, but under the highest resolution a further small doublet splitting was observed on each line. Double resonance showed that the triplet arose from coupling to two equivalent P nuclei, and the doublet from coupling to the RhH proton. Coupling to Rh was not resolved. The RhH resonance appeared as a quartet, simplified by decoupling ^{31}P to a doublet; the quartet pattern must arise from almost equal values of ^1J(HRh) and ^2J(HRhP). Under the highest resolution, each line showed a further small quartet coupling due to ^3J(HRhSiH). On the basis of the chemical shifts and the resolution of ^3J(HRhSiH), we believe that this complex has structure (B) (X = H, Y = Cl). Its n.m.r. parameters are included in Table 1.

Reaction of Complex (2) *with* SiH_4.—The reaction between (2) and SiH_4 was similar to that between (1) and SiH_4 in toluene; the most significant difference was that dissociation began at a higher temperature, and at 260 K the ^{31}P resonances were broad. The n.m.r. parameters of the product are included in Table 1.

Reaction of Complex (1) *with* GeH_3Cl.—Reaction between equimolar proportions of (1) and GeH_3Cl was complete within minutes at 233 K, giving a pale brown solution. At 203 K the ^{31}P-{^1H} spectrum showed peaks due to two species, each, on the basis of δ(P) and ^1J(RhP), a Rh^{III} derivative. When only those protons with δ > 0 p.p.m. were decoupled, the ^{31}P peaks all showed additional doublet splittings, and so each species contained a single hydride ligand. In the ^1H spectra, the GeH and RhH resonances of the more abundant species were clearly resolved, and were shown by double resonance to be consistent with a complex of type (B). The RhH resonance of the less abundant species was at δ −15.0 p.p.m., implying that H was *trans* to Cl and that the structure was therefore of type (C). The GeH resonance was overlapped by that of the more abundant product, but could still be distinguished. Initially, about 20% of the product at 230 K was of type (C); if the solution was allowed to warm to above 240 K, the proportion of type (C) decreased to below 10% and did not change significantly on further warming or recooling. The material was isolated as a pale brown solid by evaporating the solvent at 250 K, and its constitution was confirmed by analysis. The n.m.r. parameters are given in Table 2.

Reaction between Complex (2) *and* GeH_3I.—At 203 K a solution of equimolar proportions of (2) and GeH_3I in toluene showed that two phosphine complexes of Rh^{III} had been formed, in roughly 2 : 1 mol ratio. Each was shown by partial decoupling to contain a single hydride ligand. In the proton resonance spectrum, two sets of GeH and two sets of RhH resonances were observed. The stronger of the GeH resonances was to lower frequency, and was shown by double resonance to be associated with the stronger RhH (to higher frequency) and the stronger ^{31}P resonance. The observation of ^3J(HGeRhH) suggests that this species was of type (B) and all the parameters measured are consistent with this interpretation.

The weaker RhH resonance was substantially to lower frequency of that due to the other species, in a region associated with H *trans* to halogen rather than to Ge or CO, suggesting that this species was of type (C). This resonance was a five-line pattern, simplified to a doublet by decoupling ^{31}P; ^3J(HGeRhH) was not clearly resolved even under very high resolution. The GeH resonance appeared as a triplet, collapsed into a singlet by irradiating at the ^{31}P frequency that simplified the RhH resonance. Under the conditions of highest resolution, we could just distinguish a triplet splitting of *ca.* 1 Hz on each line, reduced to a doublet by decoupling the RhH proton. It appears that ^2J(HGeRh) and ^3J(HGeRhH) are small and about equal. We conclude that this species is of type (C). The n.m.r. parameters for both species are given in Table 2.

Reaction of Complex (2) *with* GeH_3Cl.—At 198 K the ^{31}P-{^1H} spectrum of an equimolar mixture of (2) and GeH_3Cl showed peaks due to two phosphine complexes of Rh^{III}; the chemical shifts imply that iodine was bound to Rh in each. At 198 K the resonance to higher frequency (J) was about twice as strong as the other (L), but when the temperature was raised to 233 K, L was found to be twice as strong as J. The ^{31}P and ^1H parameters for those species were consistent with their formulation as isomers of types (B) (resonance J) and (C) (resonance L) respectively, in which Cl was bound to Ge and I to Rh; they are given in Table 2. The relative proportions of the two isomers did not vary significantly on changing the temperature further; the change on initial warming from 198 to 233 K was irreversible.

Reaction between Complex (1) *and* GeH_3I.—Reaction between equimolar quantities of (1) and GeH_3I was fast at 198 K, and initially resonances for seven phosphorus–rhodium complexes were observed, each shown by partial decoupling to contain a single Rh–H ligand. At the same temperature we detected seven sets of GeH and eight sets of RhH resonances. The multiplet patterns suggested that four of the products were of type (B) and four of type (C); we were able to associate ^{31}P resonances with GeH and RhH multiplets by double resonance, and six of the complexes formed could then be identified as products we had obtained before: $[RhH(CO)Cl(PEt_3)_2(GeH_2Cl)]$, $[RhH(CO)I(PEt_3)_2(GeH_2I)]$, and $[RhH(CO)I(PEt_3)_2(GeH_2Cl)]$, each as isomers of type (B) and type (C). There remained two new species. The values of δ(P) and ^1J(RhP) suggested that each contained Rh^{III} with Cl bound to Rh, while the GeH chemical shifts were consistent with the presence of iodine bound to Ge. One of these products could be identified as the type (B) isomer in which iodine is bound to Ge and Cl to Rh. The other could not be identified so certainly, because we did not observe the associated GeH resonance clearly, but we believe it to be the type (C) isomer of the same species, largely because of the value of δ(RhH). Both of these complexes were very unstable; their resonances disappeared when the solution was allowed to warm to 213 K. At room temperature the major products were the two isomers of $[RhH(CO)I(PEt_3)_2(GeH_2Cl)]$, with traces of $[RhH(CO)Cl(PEt_3)_2(GeH_2Cl)]$ and $[RhH(CO)I(PEt_3)_2(GeH_2I)]$. N.m.r. parameters are given in Table 2.

Reaction between Complex (1) *and* GeH_4.—The reaction between equimolar amounts of (1) and GeH_4 at 198 K gave a product that we believe from its ^1H and ^{31}P-{^1H} n.m.r. spectra, which were very like those of the adduct of SiH_4 with (1) (see above), to have been of type (B), with *ca.* 10% of a second product for which the value of δ(RhH) implies a structure of type (C). The variation in the proportion of these two isomers was measured as a function of temperature by integrating the GeH and RhH resonances, and used to determine thermodynamic parameters for the isomerisation. As the solution was allowed to warm to room temperature, the resonances due to the products became weaker and that due to (1) became stronger, indicating dissociation of the complex. At room temperature the only RhP species present was (1). This behaviour was reversible.

Reaction between Complex (2) *and* GeH_4.—This reaction gave two products analogous to those obtained from (1) and GeH_4. The peaks in the ^{31}P-{^1H} spectrum became broad at 260 K.

Reactions of Organo-silanes and -germanes with (1) *and* (2).—The compounds SiH_3Me, GeH_3Me, and $SiH_3CH_2CH{=}CH_2$ were found to react with (1) and with (2) to give products of type (B) at low temperatures; SiH_2MeCl reacted similarly with (1), and SiH_2MeI with (2). These dissociated reversibly as the systems were allowed to warm, and none was stable to dissociation at room temperature. The systems with Cl bound to Rh gave ^{31}P-{^1H} spectra over the range of temperature from 203 K upwards that showed separate resonances for the Rh^{III} and the Rh^I species, showing that dissociation and recombination are slow on the n.m.r. time-scale. The spectra of organo-silanes and -germanes with (2) were rather different. At every temperature only two lines were observed. At 203 K, both lines were sharp, and ^1J(RhP) corresponded to the value expected for a derivative of Rh^{III}. As the temperature was raised, one line remained sharp; the other broadened markedly, and the separation between the lines increased. As the temperature was further increased, the line that had become broad sharpened again, and the doublet separation became equal to that for (2). At room temperature the chemical shift and coupling constant corresponded to those of (2). We believe that these observations are due to a coincidence. The systems we have studied involve an equilibrium between Rh^I, an organo-silane or -germane, and the silyl or germyl adduct of Rh^{III}. The equilibrium constant favours the adduct at low temperatures, and the products of dissoci-

TABLE 2

N.m.r. parameters for [RhH(CO)Y(PEt$_3$)$_2$(GeH$_2$X)] [a]

	Isomer of type (B)						Isomer of type (C)					
Y	Cl [b]	Cl	Cl	I [c]	I	I	Cl [b]	Cl	Cl	I [c]	I	I
X	H	Cl	I	H	Cl	I	H	Cl	I	H	Cl	I
δ(P)/p.p.m.	27.8(1)	26.1(2)	24.9(2)	21.1(1)	19.1(2)	17.3(2)	22.1(1)	20.7(1)	18.8(1)	16.8(1)	14.3(1)	12.1(1)
δ(Ge*H*)/p.p.m.	3.09(2)	5.45(2)	3.88(1)	3.27(2)	5.68(3)	4.03(2)	3.36(2)	5.58(2)	3.9(1)	3.82(2)	5.8(1)	4.39(2)
δ(Rh*H*)/p.p.m.	−8.30(2)	−9.09(2)	−8.75(2)	−9.41(2)	−10.10(3)	−9.79(2)	−15.60(2)	−15.01(2)	−14.84(2)	−13.07(2)	−12.4(1)	−12.00(2)
^1J(RhH)/Hz	6.0(2)	5.9(3)	5.9(3)	4.4(2)	6.1(3)	5.5(3)	20.7(2)	20.0(3)	18.5(5)	23.4(2)	22.0(5)	21.3(1)
^1J(RhP)/Hz	88.5(2)	84.5(2)	84.7(2)	87.8(2)	84.3(2)	83.4(2)	88.2(2)	88.1(2)	86.9(3)	88.2(1)	85.8(2)	85.3(2)
^2J(HRhP)/Hz	12.7(2)	12.0(5)	12.6(3)	13.6(2)	13.1(3)	13.2(2)	10.5(2)	11.6(2)	11.5(5)	12.2(2)	11.5(3)	10.7(2)
^2J(HGeRh)/Hz	1.5(2)	6.0(5)	6.0(5)	1.8(2)	6.0(5)	9.8(2)	⩽0.3	⩽0.5	n.r.	⩽0.3	n.r.	1.0(5)
^3J(HGeRhH)/Hz	2.0(2)	6.7(3)	6.0(2)	2.1(2)	6.7(3)	6.6(2)	⩽0.3	⩽0.5	n.r.	⩽0.3	n.r.	1.0(5)
^3J(HGeRhP)/Hz	5.8(2)	9.5(5)	9.6(3)	6.0(2)	10.0(5)	9.8(1)	7.8(2)	10.1(2)	n.r.	7.8(2)	9.9(2)	4.9(2)

[a] Parameters recorded at 233 K for solutions in toluene; chemical shifts taken as positive to high frequency of SiMe$_4$ (for ^{1}H) or 85% H$_3$PO$_4$ (for ^{31}P); n.r. = not resolved. [b] Ratio of isomers (C) : (B) = 1.6(±1) : 1 at 238 K and 1.5(±5) : 1 at 288 K. [c] Ratio of isomers (C) : (B) = 14(±2) : 1 at 217 K and 14(±2) : 1 at 257 K.

ation at room temperature. At intermediate temperatures, the rates of formation and of dissociation of the adducts are fast on the n.m.r. time-scale, and so we observe a weighted average for ^1J(PRh) (see Figure). By chance, one line in the spectrum of each adduct coincides fairly exactly with the corresponding line in the spectrum of (2); therefore exchange does not affect the position of this line, which remains sharp. The position of the other line changes with temperature, because of the averaging effect of the fast-exchange process. Selected n.m.r. parameters for all these complexes are given in Table 3.

We have been able to use the n.m.r. spectra to determine equilibrium constants and associated thermodynamic parameters for these systems. For the chlorides, we have integrated the MH, RhH, and PEt_3 proton resonances at several temperatures between 237 K and 280 K. These integrals give measures of the concentrations of each species present, and so enable us to calculate equilibrium constants at each temperature; from these, knowing the volumes of the solutions and the weights of reagents taken, we can determine $\Delta G_T^{\ominus}$, and so estimate $\Delta H_T^{\ominus}$ and $\Delta S_T^{\ominus}$. The integrals also give an estimate of the internal consistency of the measurements. In some cases we have used integrals of $^{31}P-\{^1H\}$ spectra to give ratios of the concentrations of Rh^I and Rh^{III} species, and we have combined these values with integrals of the ^1H spectra.

The faster exchanges observed for the adducts formed by complex (2) with organo-silanes and -germanes makes it impossible for us to study the variation in equilibrium constants with temperature in these systems using integration. Provided, however, that we know the volumes of the solutions and the starting quantities of silane or germane and of (2), and can estimate the variation of ^1J(RhP) with temperature both in (2) and in each adduct, we can use the

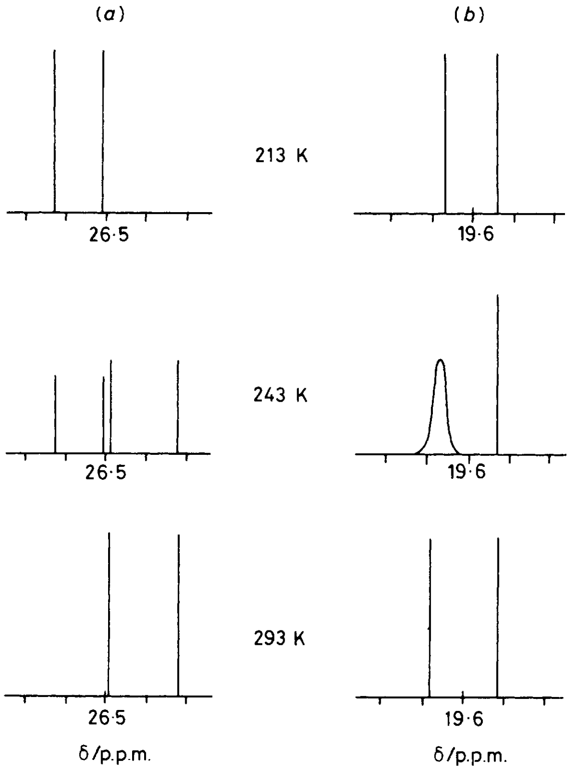


FIGURE $^{31}P-\{H\}$ spectra of the reaction systems SiH_3Me/[Rh(CO)Cl$(PEt_3)_2$] (*a*) and SiH_3Me/[Rh(CO)I$(PEt_3)_2$] (*b*) at the stated temperatures, recorded at 24 MHz. The scale markings are in 70 Hz separations, with the centre reference shown in p.p.m.

TABLE 3

Selected n.m.r. parameters for [RhH(CO)Y$(PEt_3)_2$(MHRX)] *

Y	M	R	X	δ(P)/p.p.m.	δ(M*H*)/ p.p.m.	δ(Rh*H*)/p.p.m.	^1J(RhP)/Hz	^1J(RhH)/Hz	^2J(PH)/Hz
Cl	Si	CH_3	H	27.1(1)	3.7(1)	−8.1(1)	90.3(2)	12.0(5)	12.0(5)
Cl	Si	CH_3	Cl	27.3(1)	5.3(1)	−8.0(1)	90.0(2)	12.0(5)	12.0(5)
Cl	Si	CH_2CHCH_2	H	27.4(1)	3.6(1)	−8.1(1)	90.0(2)	12.0(5)	12.0(5)
Cl	Ge	CH_3	H	27.4(1)	3.3(1)	−8.4(1)	90.9(2)	6.0(5)	13.0(5)
I	Si	CH_3	H	18.6(1)	3.9(1)	−9.1(1)	86.6(2)	10.0(5)	10.0(5)
I	Si	CH_3	Cl	20.6(1)	5.3(1)	−9.2(1)	89.6(2)	12.0(5)	12.0(5)
I	Si	CH_3	I	20.3(1)	3.9(1)	−9.3(1)	90.1(2)	11.0(5)	11.0(5)
I	Si	CH_2CHCH_2	H	20.6(1)	3.8(1)	−9.3(1)	89.8(2)	9.3(5)	11.3(5)
I	Ge	CH_3	H	20.2(1)	3.5(1)	−9.6(1)	89.6(2)	6.0(5)	14.0(5)

* Measurements made in C_7D_8 at 203 K; chemical shifts are taken as positive to high frequency of $SiMe_4$ (for ^1H) or 85% H_3PO_4 (for ^{31}P).

TABLE 4

Some thermodynamic data for the reaction

$$[Rh(CO)Y(PEt_3)_2] + MH_2RX \rightleftharpoons [RhH(CO)Y(PEt_3)_2(MHRX)] \ *$$

Y	M	X	R	$\Delta H_T^{\ominus}$/kJ mol^{-1}	$\Delta G_T^{\ominus}$/kJ mol^{-1}	$\Delta S_T^{\ominus}$/J K^{-1} mol^{-1}
Cl	Si	H	CH_3	−30(2)	2.4(2)	−140(10)
Cl	Si	Cl	CH_3	−34(2)	−3.4(2)	−130(10)
Cl	Si	H	CH_2CHCH_2	−60(2)	0.40(5)	−260(10)
Cl	Si	H	H	−34(2)	−7.3(3)	−115(10)
Cl	Ge	H	H	−44(2)	−8.3(3)	−150(10)
Cl	Ge	H	CH_3	−43(2)	−0.80(5)	−180(10)
I	Si	H	CH_3	−47(3)	1.4(2)	−180(10)
I	Si	I	CH_3	−55(3)	−8.2(4)	−180(10)
I	Si	H	CH_2CHCH_2	−66(3)	−4.6(3)	−230(10)
I	Ge	H	CH_3	−61(3)	−7.6(3)	−200(10)

* *T* = 233 K for Y = Cl. *T* = 263 K for Y = I.

observed average values of ^1J(RhP) in the exchanging systems to determine the ratio [Rh^{III}] : [Rh^I] and hence the equilibrium constants. We have determined ^1J(RhP) in (2) as a function of temperature (T). We cannot measure d[^1J(RhP)]/dT for any of those adducts whose dissociation is significant at temperatures above about 230 K, because of this dissociation. We have, however, prepared other adducts, such as [$RhH(CO)I(PEt_3)_2(SiH_2I)$], that do not dissociate appreciably below room temperature. We have measured ^1J(RhP) for this complex as a function of temperature, and have assumed that the variation with temperature of ^1J(RhP) in other adducts will be similar. Since d[^1J(RhP)]/dT is small, any inaccuracy in this assumption is unlikely to have a large effect on the equilibrium constants or thermodynamic parameters calculated. The results of our calculations are given in Table 4. Unfortunately, dissociation of the adducts of (2) with GeH_4 or SiH_4 was too small to allow either the use of integration at low temperatures, or the use of the method based on peak separations near 270 K, to measure equilibrium constants.

DISCUSSION

The reactions of (1) and (2) with all the silyl or germyl compounds studied here occur smoothly and rapidly at low temperatures to give the expected molecular patterns. The stereochemistry of these products can be deduced from the n.m.r. spectra. All the SiH_3 compounds gave a single isomer of type (B); we detected no silyl product of type (C). Similar results have been obtained previously from reactions with analogous iridium complexes. The GeH_3 compounds reacted to give mixtures of isomers of types (B) and (C); in each case the more abundant product was of type (B), but in the reaction with germyl iodide the proportion of the product of type (C) was comparable. The proportion of isomer of type (C) was substantially higher in initial reactions at low temperatures than after the systems had been allowed to warm, and after warming any subsequent cooling had only a small effect on the ratio of isomers. These results are consistent with an initial reaction in which the first product is of type (C), and that this then rearranges. We did not observe transient products of type (C) in the reactions of SiH_3 compounds.

In reactions between (1) and SiH_3I or GeH_3I,the stable product contained iodine bound to Rh and chlorine bound to Ge or Si. At very low temperatures, however, complexes were detected with the opposite halogen distribution. This shows both that oxidative addition is faster than halogen exchange at low temperatures, and that exchange of halogen between Rh and Si or Ge in Rh^{III} species is rapid at 240 K.

These adducts dissociate much more readily than do their iridium analogues. Adducts of *trans*-[$Ir(CO)X(PEt_3)_2$] with silyl halides, methylsilane, allylsilane, phenylsilane, and vinylsilane have been isolated without difficulty and show no signs of dissociation at room temperature.[9] In contrast, the analogous rhodium adducts of the silyl or germyl halides dissociate sufficiently at room temperature in solution to show marked saturation transfer under Rh*H*-{M*H*} double resonance, and can only be isolated by evaporation at low temperatures, even though the n.m.r. spectra show that any dissociation at room temperature must be slight. With organogermanes the ^{31}P n.m.r. spectra show that dissociation is effectively complete at room temperature, and for some systems is extensive even at 233 K. The difference in stability between analogous derivatives of Ir and Rh is a reflection of the generally much greater stability of Ir^{III} relative to Ir^I than of Rh^{III} relative to Rh^I. The dissociation of the less stable adducts has allowed us to collect some thermodynamic data, which enables us to make an assessment of the importance of certain factors in determining the relative stabilities of these adducts. For a given silane or germane, the formation constant of the adduct with (2) is always greater at a given temperature than that of the adduct with (1). The thermodynamic data suggest that the difference is an enthalpy effect, partly offset by changes in entropy. In the reaction between MH_3R and [$Rh(CO)X(PEt_3)_2$], the enthalpy released is slightly greater when M = Ge than when M = Si, but since the enthalpy of the Ge–H bond (which has to be broken in the process of forming the adduct) is somewhat smaller than that of the Si–H bond, it is probable that Si–Rh and Ge–Rh bond enthalpies are similar.

Among the adducts formed by organosilanes, those of allylsilane with both (1) and (2) have significantly larger enthalpies of formation than any of the others. Since the allyl substituents at silicon are unlikely to have a significant direct effect on the Rh–H bond enthalpies, it seems likely that the enthalpy of the Rh–Si bond is highest when an allyl group is bound to silicon. As with so many chemical measurements, the enthalpies we have measured are all enthalpy *differences*, and without further information we cannot make firmer deductions about the absolute values of the terms involved. The thermodynamic changes associated with isomerisation were also investigated for the adducts of GeH_4 with (1) and with (2), and for the adduct of GeH_3I with (2). In all three cases the enthalpy change was very small, and the change in entropy favours the species with H *trans* to Ge, though the difference is less for the adducts of GeH_3I than for those of GeH_4.

There are some well defined patterns in the n.m.r. parameters. The ^{31}P chemical shifts are all to lower frequency for isomers of type (C) than for analogous isomers of type (B). The values of ^1J(RhP) are almost independent of the other substituents in the Rh^{III} complexes, but ^1J(RhH) changes from *ca.* 6 Hz in germyl complexes of type (B) to *ca.* 20 Hz in analogous complexes of type (C). The magnitudes of ^2J(HMRh) and ^3J(HMRhH) both depend on the substituent at M, and are similar in almost all the complexes studied. The only species of type (C) for which we were able to resolve ^3J(HGeRhH) was the derivative of GeH_3I.

EXPERIMENTAL

Volatile compounds were handled using a conventional vacuum system; air-sensitive solids were transferred between vessels in a V.A.C. model HE-493 glove-box. Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer. N.m.r. spectra were recorded using JOEL FX 60Q FT (for ^{31}P) and Varian HA100 CW spectrometers; the probe of the latter had been modified for heteronuclear double resonance. Some of the ^{31}P and ^{1}H spectra were also obtained using a Bruker WH360 FT spectrometer; the precision of the measurements made with the CW instrument is lower than with the FT spectrometers. Starting materials were prepared by established methods,[10] or purchased commercially.

In a typical experiment, (1) (0.15 mmol) was weighed into an n.m.r. tnbe, solvent distilled in, and the complex dissolved; SiH_3Cl (0.15 mmol) was then distilled in and the tube was sealed. N.m.r. spectra were run initially at 190 K, and after that at appropriate temperatures. Products were isolated after all n.m.r. spectra had been recorded by opening the tube under N_2 and evaporating solvent at *ca.* 260 K. For $[RhH(CO)Cl(PEt_3)_2(GeH_2Cl)]$ (Found: C, 30.5; H, 6.2. $C_{13}H_{33}Cl_2GeOP_2Rh$ requires C, 30.4; H, 6.5%); for $[RhH(CO)I(PEt_3)_2(SiH_2Cl)]$ (Found: C, 27.5; H, 5.6. $C_{13}H_{33}ClIOP_2RhSi$ requires C, 27.8; H, 5.9%); for $[RhH(CO)I(PEt_3)_2(SiH_2I)]$ (Found: C, 24.3; H, 5.0. $C_{13}H_{33}I_2OP_2RhSi$ requires C, 23.9; H, 5.1%).

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