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Reactions of some Simple Silanes and Germanes with the Hydridotris(triethylphosphine)platinum(II) Cation

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Treatment of solutions of $[PtH(PEt_3)_3]^+BPh_4^-$*, (I), with* MH_3Q *(M = Si or Ge; Q = H, F. Cl, Br or I) gives products that depend on M and Q. When M = Ge and Q = F, Cl or I, tris-phosphine cations of 6-coordinated Pt(II) have been identified as the initial products at 213 K by NMR spectroscopy; these decompose on warming, eliminating* $Et_3PH^+BPh_4^-$ *and forming* trans-$PtH(PEt_3)_2(MH_2Q)$*, the only product identified when Q = Br and M = Ge or Si. With* SiH_4 *or* SiH_3Cl*, the only products detected were* $[Pt(PEt_3)_3SiH_2Q]^+$*. There was no reaction between (I) and* GeH_4 *or* SiH_3F*. None of the products could be isolated; all were characterised by* ^{31}P*,* ^1H *and (where appropriate)* ^{19}F *NMR spectroscopy.*

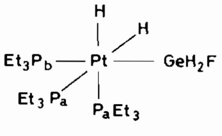
Introduction

Over the past few years we have made an extensive study of the oxidative addition of hydrides of silicon and germanium to four-coordinated d^8 complexes of platinum and iridium [1]. So far, all of our work has used neutral platinum complexes as starting-complexes; here we report a study of the interaction between some simple derivatives of monosilane and monogermane and the hydridotris(triethylphosphine)-platinum(II) cation. Although some of the products formed were stable in solution at room temperature, we have failed to isolate any of them; even the most stable decomposed on removal of solvent, giving intractable residues. Nonetheless, the NMR spectra of the solutions recorded both on initial reaction at low temperatures and on warming to room temperature have given us a good deal of information about the course of the reactions involved.

Results and Discussion

Reaction with GeH_3F

Reaction between (I) and GeH_3F began at 213 K. At this temperature we believe that the product was a complex of 6-coordinated Pt(IV) of type A below; our reasons are as follows.



(A)

The $^{31}P\{H\}$ spectrum showed two resonances, each with Pt satellites. The stronger was a doublet of narrow doublets. The weaker appeared as a quintet of relative intensities 1:2:2:2:1, which we analyse as a doublet of overlapping triplets; the triplet coupling was the same as the larger doublet splitting in the stronger resonance, and we put it down to $^2J(PP)$. The stronger resonance is assigned to P_a, and the weaker to P_b. The ^{19}F resonance was also complicated by overlapping multiplets. The overall envelope was that of a quartet of triplets, with Pt satellites; the quartet pattern derives from chance near-equality of $^2J(HGeF)$ and $^3J(FGePtP_b)$, and the triplet splitting corresponds with the doublet splitting in P_a. Unfortunately we have not been able to observe the GeH resonance directly because it is overlapped by resonances from the anion, but $^2J(HGeF)$ is always about 40 Hz in complexes like these [2]. The small triplet splitting on each line is due to $^3J(FGePtH_\delta)$. While we were unable to observe the Ge*H* resonance in the proton spectrum, the Pt*H* resonance was recorded as a wide doublet of triplets with Pt satellites. The wide doublet coupling is due to $^2J(HP_a)$; the spectrum should be second-order because of the magnetic non-equivalence of the protons, but we must suppose that $^2J(HPtH)$ and $^2J(P_aPtP_a)$ are small enough to leave second-order features unresolved within the rather broad lines.

When the solution was allowed to warm slowly the concentration of this species decreased and at 243 K it was no longer present. The solution turned black and a white solid, identified by analysis as Et_3PH^+-BPh_4^-, was precipitated. The complex initially found appears to decompose by elimination of phosphonium ion, but the product is too unstable to be detected even at 243 K.

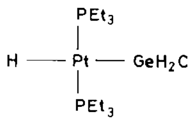
With GeH_3Cl

The reaction between (I) and GeH_3Cl gave a product of type A at 213 K. The $^{31}P\{H\}$ spectrum showed a strong doublet and a weaker triplet, assigned respectively to P_a and P_b. In the ^1H spectrum we were able to resolve the Ge*H* resonance as a doublet [due to $^3J(HGePtP_b)$] of triplets [due to $^3J(HGePtP_a)$] with Pt satellites. The Pt*H* resonance was similar to that of the analogous adduct formed by GeH_3F, but in this spectrum the lines were sharper and second-order effects were more obvious. The NMR parameters are given in Table I. As the solution was allowed to warm to room temperature, $Et_3PH^+BPh_4^-$ was eliminated, and identified by analysis and by its ^{31}P NMR spectrum. A germyl complex of 4-coordinated Pt remained in solution. The $^{31}P\{H\}$ spectrum consisted of a single line with Pt satellites. The Ge*H* resonance appeared as a triplet with Pt satellites, and the Pt*H* resonance showed a similar pattern. It is surprising that we were unable to resolve $^3J(HGePtH)$. The NMR parameters for this species are given in Table II.

TABLE I. NMR Parameters for Complexes of Type A Formed by (I) with GeH_3F, GeH_3Cl and GeH_3I[a].

Parameter	GeH_3F[b]	GeH_3Cl	GeH_3I
$\delta(H_a)$/ppm	-10.78	-11.25	-13.11
δ(Ge*H*)/ppm	6.96	5.53	4.65
$\delta(P_a)$/ppm	-12.5	-10.7	-12.5
$\delta(P_b)$/ppm	-24.7	-26.7	-26.8
$^1J(PtH)$/Hz	718	710	709
$^1J(PtP_a)$/Hz	1330	1376	1412
$^1J(PtP_b)$/Hz	1446	1438	1402
$^2J(P_aP_b)$/Hz	20.0	19.5	19.0
$^2J(HP_a)$/Hz	183	184	192
$^2J(HP_b)$/Hz	7	c	8.5
$^2J(HGePt)$/Hz	216	218	223
$^3J(HGePtP_b)$/Hz	19.0	8.0	8.0

[a] Chemical shifts were measured as positive relative to 85% H_3PO_4 (for ^{31}P), Me_4Si (for ^1H), and CCl_3F (for ^{19}F). [b] $\delta(F)$ = −215.7 ppm; $^2J(PtF)$ = 118, $^2J(HGeF)$ = 38, $^3J(FGePtP_b)$ = 39.0, $^3J(FGePtP_a)$ = 6.0 Hz. [c] Second-order.



$$H-\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{Pt}}-GeH_2Cl$$

(B)

Attempts to isolate the compound as a solid were unsuccessful.

With GeH_3Br

No reaction appeared to occur between (I) and GeH_3Br until the solution had warmed to 263 K; at this temperature a species of type B had been formed, with elimination of phosphonium salt. The NMR parameters for the germyl complex are given in Table II. We were unable to detect any intermediate.

With GeH_3I

Reaction between (I) and GeH_3I was similar to reaction with GeH_3Cl. At 213 K a product of type A was formed; the NMR parameters are given in Table I. In this spectrum, as with the derivative of GeH_3F, second-order effects in the Pt*H* resonance were not well-defined. When the solution was allowed to warm to room temperature, triethylphosphonium salt was eliminated, and a species identified by its NMR spectra as of type B remained in solution; its NMR parameters are given in Table II. Attempts to isolate this species were unsuccessful, though it was stable for some hours at room temperature.

With GeH_4

The $^{31}P\{H\}$ spectrum of a solution of (I) with GeH_4 barely changed over a period of several hours at room temperature. The solution darkened perceptibly, but no new peaks were observed, though the lines were somewhat broadened. We conclude that no platinum-germyl complexes are formed under these conditions.

With SiH_3I

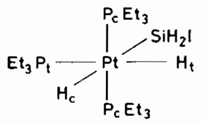
Reaction between (I) and SiH_3I at 213 K gave a product whose $^{31}P\{H\}$ spectrum showed a strong

TABLE II. NMR Parameters for Complexes of Type B Formed by (I) with Some Silyl and Germyl Halides[a].

Parameter	GeH_3Cl	GeH_3Br	GeH_3I	SiH_3Br	SiH_3I
δ(Pt*H*)/ppm	-12.10	-12.31	-13.27	-11.55	-14.10
δ(M*H*)/ppm	4.75	4.38	4.08	4.62	3.29
δ(P)/ppm	18.1	9.6	3.0	15.0	7.1
$^1J(PtH)$/Hz	915	910	906	1110	1190
$^1J(PtP)$/Hz	2354	2309	2280	2380	2354
$^2J(HPtP)$/Hz	10	8.5	10	10	9.5
$^2J(HMPt)$/Hz	226	231	231	130	132
$^3J(HMPtP)$/Hz	9.6	8.5	9.5	n.r.[b]	10.0

[a] Chemical shifts were measured as +ve to high frequency of 85% H_3PO_4 (for ^{31}P) or Me_4Si (for ^1H). Values are considered accurate to ±2 in the last figure quoted. [b] n.r. = not resolved.

doublet and a weaker triplet, with Pt satellites; the values of $^1J(PtP)$ indicated that the species contained 6-coordinated Pt, and we believe it to have been of type C below.



(C)

The Si*H* resonance was not resolved. There were two resonances in the Pt*H* region, of roughly equal intensity. The one at the higher frequency showed a large (210 Hz) coupling which we associated with a *trans*-phosphine ligand, and so we assign this resonance to H_t. Each line showed a further smaller triplet coupling, due to $^2J(HPtP_c)$, and the resonance had Pt satellites. The resonance at the lower frequency appeared as a quartet, presumably because of roughly equal coupling to P_c and P_t, again with Pt satellites. The NMR parameters for this complex are given in Table III. As the solution was allowed to warm to 253 K, the complex decomposed with elimination of Et_3PH^+-BPh_4^-, leaving a complex of type B. In this system we were able to confirm by decoupling phosphorus at a single frequency that the triplet couplings in both Pt*H* and Si*H* resonances were derived from the same species but here too $^3J(HH)$ was not resolved. The NMR parameters are given in Table II.

With SiH_3Br

Reaction between (I) and SiH_3Br began at 243 K, and the only products we detected were the triethylphosphonium salt and a platinum-silyl complex of type B, whose NMR parameters are given in Table II.

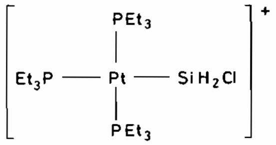
TABLE III. NMR Parameters for the Adduct of Type C Formed by (I) with SiH_3I.[a]

$\delta(H_t)$/ppm	−14.22
$\delta(H_c)$/ppm	−14.10
δ(SiH)/ppm	n.o.[b]
$\delta(P_c)$/ppm	−3.2
$\delta(P_t)$/ppm	−31.4
$^1J(H_tPt)$/Hz	1178
$^1J(H_cPt)$/Hz	698
$^1J(P_tPt)$/Hz	1534
$^1J(P_cPt)$/Hz	1610
$^2J(P_cP_t)$/Hz	18.5
$^2J(H_tP_t)$/Hz	210
$^2J(H_tP_c)$/Hz	n.r.[b]
$^2J(H_cP_c)$/Hz	6.0

[a] Chemical shifts were measured as +ve to high frequency of 85% H_3PO_4 (for ^{31}P) or Me_4Si (for ^1H) [b] n.r. = not resolved, n.o. = not observed.

With SiH_3Cl

We were unable to detect any complex of 6-coordinated Pt(IV) among the products of the reaction between (I) and SiH_3Cl. At 273 K a single product had been formed, whose $^{31}P\{H\}$ spectrum was quite different from that of the complexes of type B. It showed two resonances in rough intensity ratio 1:1, the stronger appearing as a doublet and the weaker as a triplet with the same coupling. The Si*H* resonance appeared as a narrow doublet with Pt satellites, suggesting that Si was trans to P, and no Pt*H* resonance was detected. These observations suggest that the product formed here is of type D, and that H_2 has been eliminated from the intermediate:



(D)

Even at room temperature, however, the reaction was far from complete; only about 40% of the starting-material had been converted into (D).

With SiH_4

Reaction between (I) and SiH_4 occurred slowly at room temperature. No product containing 6-coordinated Pt was detected; after four hours, some 10% of the starting-material had been converted into a product of type D, whose NMR parameters are given in Table III. The solution decomposed slowly on standing for a longer period. Only small amounts of H_2 were observed to have been evolved, in keeping with the small extent of reaction.

With SiH_3F

No reaction could be detected between (I) and SiH_3F at room temperature even after a period of weeks.

Discussion

Reactions between the cation (I) and silyl or germyl halides are in general no faster than the reactions between the same silyl or germyl species and the neutral complexes $PtH(PEt_3)_2X$; with the cation, as with the neutral complex, we have had difficulty in detecting the complexes of 6-coordinated Pt(IV) that are usually suggested as intermediates, but here we have been able to observe the NMR spectra of four such species. Each decomposed below room temperature, giving a silyl or germyl complex of four-coordinated Pt; in the other cases where complexes of four-coordinated Pt are formed, it seems reasonable to suppose that they are produced by decomposition of similar 6-coordinated species. However, the routes of decomposition are not the same. In most cases, phosphonium salt is eliminated; however, for SiH_4 and SiH_3Cl it appears that H_2 is eliminated, giving a silyl cation. Without much more knowledge of the stereochemistries of possible intermediates it is not profitable to speculate about the factors that are responsible for the differences. There are some unexpected features in the NMR spectra of the species we have detected. The absence of marked second-order features in the Pt*H* resonances of adducts of type A is a little surprising; so is our failure to detect $^3J(HMPtH_t)$, while it is also strange to observe $^3J(HSiPtP_c)$ when there is no *trans*-phosphine ligand, as in complexes of type B, yet to see no such coupling when phosphorus is also trans to Si, as in species of type D. Perhaps the positive charge on the latter makes a significant difference. It is disappointing that we have been unable to isolate any of these complexes, but the spectroscopic parameters leave little room for doubt as to their identities.

Experimental

Volatile compounds were handled using standard vacuum apparatus fitted with either greased or Sovirel teflon taps. Air-sensitive solids were handled in a glove-box under an atmosphere of dry nitrogen gas. NMR spectra were recorded by means of JEOL FX60Q (for ^{31}P), Varian XL100 (for ^{31}P or ^{19}F), and Brucker WH360 (for ^1H) FT spectrometers, and also using a Varian HA100 CW spectrometer whose probe had been double-tuned to accept a second radio-frequency for the $^1H\{P\}$ experiments. Silyl, germyl and platinum starting-materials were prepared by standard methods.

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