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THE INTERACTION OF ORGANOSILICON HYDRIDES AND DIMETHYLBIS(PHOSPHINE)PLATINUM(II) COMPLEXES

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Summary

The silicon hydrides Ph_3SiH and $(p\text{-}FC_6H_4)_3SiH$ react with *cis*-$[PtMe_2(PMe_2Ph)_2]$ to give the hydridosilyl complexes *cis*-$[PtH(SiR_3)(PMe_2Ph)_2]$, where R = Ph or $p\text{-}FC_6H_4$, while an excess of methyldiphenylsilane reacts to give the bis(silyl) complex, *cis*-$[Pt(SiMePh_2)_2(PMe_2Ph)_2]$. The silicon dihydride Ph_2SiH_2 reacts more readily, to give *cis*-$[Pt(SiPh_2H)_2(PMe_2Ph)_2]$ and some methyldiphenylsilane. With $[PtMe_2(PMePh_2)_2]$, diphenylsilane gives the bis(silyl) compound only on heating.

Introduction

We describe below a new method of making silyl—platinum complexes, involving the interaction of organosilicon hydrides and $[PtMe_2L_2]$ complexes, where L = PMe_2Ph or $PMePh_2$.

Results and discussion

We have found that $[PtMe_2L_2]$ complexes, where L is a phosphine, react fairly readily with some organosilicon hydrides. Depending on the nature of the hydride, the relative proportions of hydride to complex, and the reaction temperature, the product can be a hydridosilyl or a bis(silyl) complex, $[PtH(SiR_3)L_2]$ or $[Pt(SiR_3)_2L_2]$.

The results are summarized in Table 1, and the main features are as follows.

(1) The complex $[PtMe_2(PMe_2Ph)_2]$ reacts with triphenyl- and tris(*p*-fluorophenyl)silane to give the hydrido complexes *cis*-$[PtH(SiPh_3)(PMe_2Ph)_2]$ and *cis*-$[PtH\{Si(C_6H_4F\text{-}p)_3\}(PMe_2Ph)_2]$, respectively. The markedly higher yield in the latter case can be partly attributed to use of a 3/1 silane/Pt ratio compared with only a 1/1 ratio for the triphenylsilane, although it should also be noted that different solvents were used. The *cis*-configurations are indicated

TABLE 1

INTERACTION OF SILICON HYDRIDES AND $[PtMe_2L_2]$

L	Silane	Mole ratio Si/Pt	Products	M.p. (°C)	Yield (%)	ν(M—H) (cm^{-1})[a]
PMe_2Ph	Ph_2SiH_2	excess	*cis*-$[Pt(SiHPh_2)_2L_2]$	125	67	ν (Si—H), 2095(s), 2050(s), 2038(s)[b]
PMe_2Ph	Ph_2MeSiH	excess	*cis*-$[Pt(SiMe_2Ph)_2L_2]$	130—134	21	
PMe_2Ph	Ph_3SiH	1/1	*cis*-$[PtH(SiPh_3)L_2]$	113—115	18	ν (Pt—H), 2045
PMe_2Ph	$(p\text{-}FC_6H_4)_3SiH$	3/1	*cis*-$[PtH\{Si(C_6H_4F\text{-}p)_3\}L_2]$	117—120[c]	64	ν (Pt—H), 2040
$PMePh_2$	Ph_2SiH_2	excess	*cis*-$[PtH(SiPh_2H)L_2]$ (?)	110—112	80	ν (M—H), 2070 (very br)
			cis-$[Pt(SiPh_2H)_2L_2]$[d] (?)	128	10	ν (Si—H), 2080 (m)

[a] Nujol mull. [b] In benzene there was a single broad peak at 2065 cm^{-1}. [c] With decomposition. [d] After heating.

by the values of ν(Pt—H), which lie at 2045 and 2040 cm^{-1} respectively for the triphenyl- and tris(*p*-fluorophenyl) complexes; frequencies below about 1990 cm^{-1} would be expected for *trans*-complexes [1].

(2) Treatment of [$PtMe_2(PMe_2Ph)_2$] with an excess of methyldiphenylsilane, $MePh_2SiH$, gave the bis(silyl) complex, *cis*-[$Pt(SiMePh_2)_2(PMe_2Ph)_2$], which has been prepared previously by another method [2].

(3) The silicon dihydride Ph_2SiH_2, used in excess, reacted much more readily with [$PtMe_2(PMe_2Ph)_2$] to give the bis(silyl) complex *cis*-[$Pt(SiHPh_2)_2(PMe_2Ph)_2$] in good yield; the *cis*-configuration was confirmed by the NMR spectrum, which had the following features: (a) the Si—H resonances centred at δ 6.66 are not in the peak height ratios of 1/2/1, there being broadening of the central line; this can only be associated with a *cis*-configuration. (b) The PMe resonances indicate that although there is a significant amount of coupling between the two phosphorus atoms, this cannot be associated with a *trans*-configuration.

(4) The complex [$PtMe_2(PMePh_2)_2$], with the slightly different phosphine, reacted less readily with diphenylsilane, in the sense that even with an excess of the latter the product in the absence of heating appeared to be the hydridosilyl complex *cis*-[$PtH(SiHPh_2)(PMePh_2)_2$], but there is some doubt about its identity since instead of the expected two ν(M—H) bands in the IR spectrum, one due to ν(Pt—H) and one to ν(Si—H), there was only a single band, at 2070 cm^{-1}; however, this band is very broad, and possibly represents an overlapping of the two bands. More prolonged reaction at higher temperature appeared to give the bis(silyl) complex, *cis*-[$Pt(SiHPh_2)_2(PMePh_2)_2$].

(5) No reaction, or only very slow reaction, occurred between [$PtMe_2(PMe_2Ph)_2$] and the hydrides Et_3SiH, $(EtO)_3SiH$, and *o*-$HMe_2SiC_6H_4CH_2SiMe_2H$, and no silyl—platinum complexes were obtained.

(6) In the reaction between [$PtMe_2(PMe_2Ph)_2$] and an excess of diphenylsilane, the compound Ph_2MeSiH was positively identified among the products, and no Ph_2SiMe_2 could be detected. Clearly products of a different type are also formed, however, since in this and in several of the other reactions studied, gas was rapidly evolved. This was presumably hydrogen or methane, or both, and possibly ethane was also formed. (It is noteworthy that Kumada and his colleagues found that hydrogen and ethyltrichlorosilane were major products in the interaction of [$NiEt_2$(dipyridyl)] and trichlorosilane to give [$Ni(SiCl_3)_2$(dipyridyl)] [3].

It is reasonable to assume that in all cases oxidative-addition of the silicon hydride occurs as the first step, to give the Pt^{IV} species [$PtHMe_2(SiR_3)L_2$], which can lose R_3SiMe (to give [$PtHMeL_2$], which would react further), or methane, or possibly ethane. Further oxidative-additions of R_3SiH and subsequent reductive eliminations would take place until stable products appeared.

Experimental

Preparation of [$PtMe_2(PMe_2Ph)_2$] and [$PtMe_2(PMePh_2)_2$]

These were made by Ruddick and Shaw's methods [4].

Interaction of diphenylsilane with $[PtMe_2(PMe_2Ph)_2]$

Immediate gas evolution occurred when an excess of diphenylsilane (ca. 1.0 ml) was added to $[PtMe_2(PMe_2Ph)_2]$ (200 mg) under dry nitrogen, and the complex dissolved to give a faintly yellow solution. The mixture was kept at 75° for 45 min, during which the solution became orange-yellow and gas evolution almost ceased. After cooling, and addition of n-hexane (5 ml), a yellow oil separated, and treatment of this with a little benzene (1 ml) produced a very pale yellow solid, which was washed with a little n-hexane and dried under vacuum to give bis(diphenylsilyl)bis(dimethylphenylphosphine)platinum(II) (225 mg, 67%), m.p. 125° (Found: C, 57.4; H, 5.3. $C_{40}H_{44}P_2PtSi_2$ calcd.: C, 57.3; H, 5.3%). The IR spectrum taken with a Nujol mull showed three ν(M—H) bands, all strong and sharp, at 2095, 2050 and 2038 cm^{-1}, but that taken with a benzene solution showed only a very broad band centred at 2065 cm^{-1}. The 100 MHz NMR spectrum showed an Si—H multiplet at τ 4.34 [^2J(PtSiH) 74 Hz], and a PMe multiplet at τ 8.92 [^3J(PtPCH) 20.0 Hz].

In a repeat experiment, but on a somewhat larger scale, after collection of the solid product the mother liquor was subjected to GLC analysis. Comparison with the retention times of authentic samples showed that unchanged diphenylsilane and methyldiphenylsilane were present, but no dimethyldiphenylsilane.

Interaction of methyldiphenylsilane and $[PtMe_2(PMe_2Ph)_2]$

When an excess of methyldiphenylsilane (ca. 1 ml) was added to $[PtMe_2(PMe_2Ph)_2]$ (300 mg) under dry nitrogen, gas evolution was not as rapid as with diphenylsilane. The solution turned pale yellow-green, and gas evolution soon ceased, and did not restart on brief heating of the mixture to 60°. The mixture was cooled and n-hexane (5 ml) was added, but no solid separated, and so most of the solvent was removed and the residue set aside. The yellow crystals which formed during several days were treated with n-hexane (5 ml), filtered off, washed with a little more n-hexane, and dried under vacuum at ca. 60° to give a solid of m.p. 120 - 126°. This was recrystallized from benzene/n-hexane to give bright-yellow crystals of bis(methyldiphenylsilyl)bis(dimethylphenylphosphine)platinum, (110 mg, 21%), m.p. 130 - 136° (Found: C, 57.4; H, 5.7. $C_{42}H_{48}P_2PtSi_2$ calcd.: C, 58.3; H, 5.6%). The IR spectrum showed no ν(Pt—H) peak, and was very similar to that of a sample of the same compound, m.p. 124 - 128°, prepared by a different route by Chatt et al. [2].

Interaction of triphenylsilane and tris(p-fluorophenyl)silane with $[PtMe_2(PMe_2Ph)_2]$

(i) Triphenylsilane (130 mg, 0.05 mmole) and $[PtMe_2(PMe_2Ph)_2]$ (250 mg, 0.05 mmole) were dissolved together in benzene (2 ml) under dry nitrogen. The mixture was kept at 70° for 3 h (during which a ν(Pt—H) band at 2045 cm^{-1} appeared in the IR), and it was then set aside at room temperature overnight. Most of the solvent was removed, n-hexane (5 ml) was added, and all the solvent was then removed under vacuum to leave a sticky yellow solid. n-Hexane (5 ml) was added and the mixture agitated for 2 h to yield cream crystals of *cis*-hydrido(triphenylsilyl)bis(dimethylphenylphosphine)platinum(II), (75 mg, 18%), m.p. 113 - 115° (Found: C, 55.6; H, 5.5. $C_{34}H_{38}P_2PtSi$ calcd.: C, 55.8; H, 5.2%). The IR spectrum (Nujol mull) showed a

ν(Pt—H) band at 2045 cm^{-1} (m). There was also a strong unassigned band at 522 cm^{-1}, and it was at first thought this might be attributable to ν(Pt—C) of a Pt—Me linkage, but the NMR spectrum (at 60 MHz) showed no Pt—Me resonances. This spectrum showed a complex multiplet centred at *ca.* τ 8.9. No resonance due to Pt—H proton could be detected.

(ii) Tris(*p*-fluorophenyl)silane (40 mg, 0.14 mmole) was added to a solution of [PtMe$_2$(PMe$_2$Ph)$_2$] (200 mg, 0.04 mmole) in anhydrous n-hexane (10 ml) under dry nitrogen. The mixture was filtered to remove a small insoluble residue, and set aside at room temperature for 24 h, during which crystals separated. These were filtered off, washed with a little n-hexane, and shown to be *cis*-hydrido{tris(*p*-fluorophenyl)silyl}bis(dimethylphenylphosphine)platinum(II), (200 mg, 64%), m.p. 117 - 120°, ν(Pt—H) 2040 cm^{-1} (Found: C, 52.6; H, 4.8. $C_{34}H_{35}F_3P_2PtSi$ calcd.: C, 51.9; H, 4.5%). The NMR spectrum showed a complex multiplet centred at ca. τ 9.0. No resonance due to Pt—H was found.

Interaction of diphenylsilane and [PtMe$_2$(PMePh$_2$)$_2$]

(i) An excess of diphenylsilane (ca. 0.5 ml) was added to [PtMe$_2$-(PMePh)$_2$] (200 mg) under dry nitrogen. Vigorous gas evolution immediately occurred, and the complex dissolved to give a pale yellow solution, from which solid separated. The mixture was stirred with n-hexane (5 ml) at room temperature overnight, and the pale yellow solid was filtered off, washed with a little n-hexane, and dried at 60° under vacuum. The product, m.p. 110 - 112° (decomp), was thought to be *cis*-hydrido(diphenylsilyl)bis(methyldiphenylphosphine)platinum(II) (200 mg, 80%) (Found: C, 58.8; H, 5.1. $C_{38}H_{36}P_2PtSi$ calcd.: C, 58.5; H, 4.9%). However, there was only a single very broad ν(M—H) band in the IR spectrum (Nujol mull) centred at 2070 cm^{-1}, and in view of this the possibility that the product was [PtMe(SiPh$_2$H)$_2$(PMePh$_2$)$_2$], which has rather similar carbon and hydrogen contents, cannot be discounted.

(ii) An excess of diphenylsilane (0.5 mol) was added to [PtMe$_2$(PMePh$_2$)$_2$] (200 mg), mixed with the product from procedure (i) (200 mg) in benzene (4 ml) under dry nitrogen. The cloudy yellow solution became clear when heated at 60°, and gas was slowly but steadily evolved. It was kept at 60° for 3 h, then most of the solvent was evaporated off under reduced pressure, and n-hexane (5 ml) was added. The mixture was set aside overnight, and the yellow solid was filtered off, washed with hexane, and dried in vacuum; this solid (210 mg) had a m.p. of 124 - 130°, and an IR spectrum rather similar to that of the product described under (i), and was assumed to be a mixture. It was extracted with benzene (4 ml), and the residue was washed with n-hexane to give a white solid (30 mg, 10%), m.p. 128°, ν(Si—H) 2080 cm^{-1} (m), thought to be bis(diphenylsilyl)bis(methyldiphenylphosphine)platinum(II). (Found: C, 61.5; H, 5.1. $C_{50}H_{48}P_2PtSi_2$ calcd.: C, 62.4; H, 5.0%). There was also a weak shoulder in the IR spectrum at 515 cm^{-1}, which could possibly have arisen from a Pt—Me bond in an impurity.

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