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THE PREPARATION OF HYDRIDO(SILYL)BIS(TRIPHENYLPHOSPHINE)-PLATINUM(II) COMPLEXES FROM BIS(TRIPHENYLPHOSPHINE)PLATINUM-ETHYLENE AND SILICON HYDRIDES

C. EABORN, B. RATCLIFF and A. PIDCOCK
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ (Great Britain)
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Summary

The reaction between $[PtL_2(C_2H_4)]$ ($L = PPh_3$) and a variety of organosilicon hydrides, R_3SiH, has given the complexes $[PtH(SiR_3)L_2]$, (I), where R_3Si = Ph_3Si, Ph_2MeSi, Ph_2HSi, $PhMe(CH_2{=}CH)Si$, Et_3Si, $(EtO)_3Si$, and $(Me_3SiO)_2MeSi$; the hydride Me_2ClSiH, however, gives the bis(silyl) complex $[Pt(SiMe_2Cl)_2L_2]$. The acetylene complexes $[PtL_2(PhC{\equiv}CX)]$ (X = H or Ph) also react, though less readily, with Ph_2MeSiH to give $[PtH(SiMePh_2)L_2]$; this complex reacts with an excess of $PhC{\equiv}CX$ to regenerate the $[PtL_2(PhC{\equiv}CX)]$. The complexes of type (I), which are thought to have *cis* configurations, are stable in the air as solids, but unstable in benzene solution.

The hydrides Cl_3SiH and $MeCl_2SiH$ react with $[Pt(PPh_2Me)_4]$ to give $[Pt(SiCl_3)_2(PPh_2Me)_2]$ and $[Pt(SiMeCl_2)_2(PPh_2Me)_2]$, respectively.

Introduction

The reactions of silicon hydrides with the tetrakis(triorganophosphine)platinum(0) species have been used in the preparation of some compounds containing silicon—platinum bonds [1,2]. Akhtar and Clark have shown that the zerovalent platinum complex $[PtL_2(C_2H_4)]$ ($L = PPh_3$) very readily undergoes oxidative additions with elimination of ethylene [3], and we describe below a useful general method of preparing $[PtH(SiR_3)L_2]$ species by treatment of the $[PtL_2(C_2H_4)]$ complex with hydrides R_3SiH*. Kumada and his colleagues previously isolated $[PtH(SiMeCl_2)L_2]$ from the reaction between methyldichlorosilane and $[PtL_2(C_2H_4)]$ in benzene in the presence of 1-hexene, but in the absence of 1-hexene they obtained only $[Pt(SiMeCl_2)_2L_2]$ from methyldichlorosilane, and $[Pt(SiCl_3)_2L_2]$ from trichlorosilane, and could not isolate any silicon—platinum complexes from several other silicon hydrides under such conditions [5].

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* For a preliminary account, see ref. 4.

Results and discussion

Treatment of $[PtL_2(C_2H_4)]$ with an excess of a variety of silicon hydrides, R_3SiH, has been found normally to give the hydrido(silyl)platinum complexes $[PtH(SiR_3)L_2]$, (I), according to eqn. (1). The reaction proceeds in this way

$$[PtL_2(C_2H_4)] + R_3SiH \rightarrow [PtH(SiR_3)L_2] + C_2H_4 \qquad (1)$$

with the R_3SiH compounds in which $R_3Si = Ph_3Si$, Ph_2MeSi, Ph_2HSi, $PhMe(CH_2{=}CH)Si$, $(EtO)_3Si$, and $(Me_3SiO)_2MeSi$; in some cases the reactions occur readily at room temperature, but in others some heating is necessary to complete the reaction in a convenient time (see Table 1).

With the chlorosilicon hydride Me_2ClSiH, however, the product, which is yellow, is not of type (I), but is the bis(silyl) complex $[Pt(SiMe_2Cl)_2L_2]$ (probably *cis*), formed by reaction of the initially produced $[PtH(SiMe_2Cl)L_2]$ with further silicon hydride according to eqn. (2), which represents a well established type of reaction [6,7]. The behaviour is consistent with the obser-

$$[PtH(SiMe_2Cl)L_2] + Me_2ClSiH \rightarrow [Pt(SiMe_2Cl)_2L_2] + H_2 \qquad (2)$$

vation by Kumada and his colleagues that $[Pt(SiCl_3)_2L_2]$ is formed from $[PtL_2(C_2H_4)]$ and trichlorosilane in benzene [5]. Their failure to isolate any complexes from other silicon hydrides under their conditions may possibly be attributable to their use of solvent benzene, since we have found that some complexes of type (I) decompose slowly in benzene.

The platinum—alkyne complexes $[PtL_2(PhC{\equiv}CH)]$ and $[PtL_2(PhC{\equiv}CPh)]$ react similarly with an excess of methyldiphenylsilane to give $[PtH(SiMePh_2)L_2]$, according to eqn. (3), and there is no reason to doubt that this reaction would occur with other silicon hydrides. The diphenylacetylene is

$$[PtL_2(PhC{\equiv}CX)] + Ph_2MeSiH \rightarrow [PtH(SiPh_2Me)L_2] + PhC{\equiv}CX \qquad (3)$$

(X = H or Ph)

displaced from its complex less readily than phenylacetylene, and both are displaced much less readily than ethylene. The reaction represented in eqn. (3) is easily reversed, the complexes $[PtL_2(PhC{\equiv}CX)]$ being reformed on treatment of $[PtH(SiPh_2Me)L_2]$ with an excess of phenyl- or diphenyl-acetylene at room temperature. This is probably a general reaction for complexes of type (I), and proved valuable in regenerating (+)-MePh(l-$C_{10}H_7$)SiH from the optically-active (—)-*cis*-$[PtH\{SiMePh(l\text{-}C_{10}H_7)\}L_2]$ [7].

Reaction conditions, yields, analytical data, and some physical constants for the complexes of type (I) are listed in Table 1; ν(Si—H) frequencies for the initial R_3SiH compounds are shown for comparison with the corresponding ν(Pt—H) frequencies, but there is no apparent correlation between the two sets of bands. The complexes are off-white to cream, and are stable in the air as solids, but their solutions in benzene decompose slowly even under nitrogen; some complexes of type (I) are known to undergo reversible dissociation to

TABLE 1

YIELDS, M.P.'S, ANALYSES, AND ν(Pt—H) FREQUENCIES FOR *cis*-$[PtH(SiR_3)(PPh_3)_2]$ COMPLEXES, WITH ν(Si—H) FOR THE CORRESPONDING R_3SiH COMPOUNDS

R_3Si	Yield (%)	M.p. (°C)	Analysis found (calcd.) (%)		ν(Pt—H)[a] (cm^{-1})	ν(Si—H)[b] (cm^{-1})
			C	H		
Ph_3Si	46	118 - 120	66.3 (66.2)	5.1 (4.7)	2090 m	2125 s
Ph_2MeSi	98	122 - 126	64.7 (64.1)	5.0 (4.8)	2095 m	2121 s
Ph_2HSi	73	108 - 110	63.5 (63.8)	4.9 (4.7)	2075 m, 2055(sh)[c]	2142 vs
$PhMe(CH_2{=}CH)Si$	65	109 - 112	62.2 (62.3)	4.9 (4.9)	2144 w, 2043 m	2125 vs
Et_3Si	45	103 - 104	60.3 (60.3)	5.2 (5.6)	2105 m	2105 vs
$(EtO)_3Si$	80	110 - 111	56.7 (57.1)	5.3 (5.3)	2090 m	2198 s
$(Me_3SiO)_2MeSi$	72	110 - 112	54.5 (54.8)	5.6 (5.6)	2080 m	2150 s

[a] Nujol mull. [b] Liquid smear. [c] One frequency must be assigned to ν(Si—H)

reform the hydride R_3SiH and a Pt^0 species [7,8], and this may be the initial process in the observed decompositions. The complex $[PtH(SiMePh_2)L_2]$ was found to react with triphenylphosphine in benzene, with disappearance of the ν(Pt—H) absorption and formation of a bright yellow complex, which was probably $[PtL_3]$.

We think that the complexes of type (I) have *cis* configurations, but the evidence is not rigorously conclusive. It comes mainly from the IR spectra, which show that the ν(Pt—H) bands appear above 2040 cm^{-1}. Such ν(Pt—H) frequencies seem to be associated with *cis* rather than *trans* configurations, as the following arguments indicate:

(i). The complex *trans*-$[PtH(CH_2SiMe_3)(PEt_3)_2]$ has the ν(Pt—H) band at 1955 cm^{-1} (Nujol mull) [9]. Since R_3Si groups, such as Ph_2MeSi, are known to have markedly larger *trans* influences than the CH_2SiMe_3 group [10], the ν(Pt—H) band would be expected to be significantly below 1955 cm^{-1} in *trans*-$[PtH(SiR_3)L_2]$ complexes.

(ii). In the chelated complexes $[PtH(SiMe_3)(Diphos)]$ [11] and $[PtH(SiCl_3)(Diphos)]$ [12] (where Diphos represents $PPh_2CH_2CH_2PPh_2$), in which the hydrogen must be *cis* to silicon, the ν (Pt—H) bands appear at 2000 and 2076 cm^{-1} respectively. Clemmit and Glockling have concluded that in all *trans*-R_3M—Pt—H complexes, whether Pt^{II} or Pt^{IV}, and where M = Si, Ge, or Sn, ν(Pt—H) lies below 2000 cm^{-1} [11].

(iii). In the complex $[PtH\{Si(C_6H_4CF_3\text{-}m)_3\}L_2]$, for which there is some NMR evidence for a *cis* configuration, the ν(Pt—H) band appears at 2104 (Nujol mull) or 2092 cm^{-1} ($CHCl_3$); in the closely similar complexes $[PtH\{Si(C_6H_4F\text{-}x)_3\}L_2]$, made by the same method, and thought also to have *cis* configurations, the ν(Pt—H) band (Nujol mull) appears at 2089 cm^{-1} for $x = m$ and at 2095 cm^{-1} for $x = p$ [13].

(iv). The ν(Pt—H) frequencies in the complexes of type (I) are consistent with known values for hydrogen *trans* to a tertiary phosphine [2,11,12].

The complex $[PtH\{SiPhMe(CH{=}CH_2)\}L_2]$ shows two bands in the ν(Pt—H) region. This is probably a solid-state effect; two bands were similarly observed with $[PtH\{SiPhMe(1\text{-}C_{10}H_7)\}L_2]$ in Nujol mull, but only one band was present in the solution spectrum [7]. The IR spectra of benzene solutions of some of the complexes of type (I) were examined, and in all cases the ν(Pt—H) band was markedly broader than in Nujol.

The *cis* configuration for the complexes of type (I) is supported by their general resemblance to $[PtH(SiCl_3)(Diphos)]$ and *cis*-$[PtH\{Si(C_6H_4CF_3\text{-}m)_3\}L_2]$ [13]. The ready reversible dissociation of some other $[PtH(SiR_3)L_2]$ species prepared by oxidative additions of silicon hydrides also favours the *cis* configuration [7,8], as does the ease of displacement of the R_3SiH from the type (I) complexes by neutral ligands such as diphenylacetylene and triphenylphosphine. It seems likely that oxidative additions of silicon hydrides to Pt^0 species is normally a *cis* process (cf. ref. 7).

We also examined the reactions of some of the silicon hydrides with $[Pt(PMePh_2)_4]$. Trichloro- and methyldichloro-silane, used with no solvent, readily gave $[Pt(SiCl_3)_2(PMePh_2)_2]$ and $[Pt(SiMeCl_2)_2(PMePh_2)_2]$, respectively, (probably *cis*; cf. ref. 6), but triphenyl- and methyldiphenyl-silane, used with benzene as solvent, reacted differently, to give a bright yellow complex which had the correct analysis for $[Pt(PMePh_2)_3(C_6H_6)]$. These latter hydrides might well give silicon—platinum complexes if used with a different solvent or in the absence of a solvent.

Experimental

General

All the reactions were carried out under dry nitrogen. Solvents were dried, and distilled before use under dry nitrogen.

The complexes $[Pt(PPh_3)_2(C_2H_4)]$, $[Pt(PPh_3)_2(PhC{\equiv}CH)]$ and $[Pt(PPh_3)_2\text{-}(PhC{\equiv}CPh)]$ were prepared as previously described [14]. The complex $[Pt(PMePh_2)_4]$ was prepared as described by Clark and Itoh [15]. The hydrides Ph_2SiH_2, Cl_3SiH, $(EtO)_3SiH$, and $PhMe(CH_2{=}CH)SiH$ were freshly distilled before use.

IR spectra were recorded as Nujol mulls on a Perkin - Elmer 457 grating spectrometer.

Preparation of cis-$[PtH(SiR_3)(PPh_3)_2]$ complexes, (I)

(*a*). In a typical procedure, $[Pt(PPh_3)_2(C_2H_4)]$ (200 mg, 0.27 mmol) was treated, with stirring under nitrogen, with an excess of methyldiphenylsilane (ca. 0.75 ml). A gas was briskly evolved as the ethylene complex dissolved to give a pale yellow solution, from which an off-white solid separated after a few minutes. The mixture was stirred for 2 h at room temperature, then n-hexane (5 ml) was added and the solid filtered off. It was washed with more n-hexane (2 × 5 ml) and dried under vacuum at 60°, to give *cis*-hydrido(methyldiphenylsilyl)bis(triphenylphosphine)-platinum(II) (240 mg, 98%), m.p. 122 - 126°.

(*b*). The other complexes of type (I) were prepared similarly, but with minor variations in some cases as follows: (i). With triphenylsilane, benzene (2 ml) was used as solvent. (ii). When ethylene evolution was slow, a longer reaction time (6 - 48 h) or warming gently at 70° for 0.5 h was used. Actual reaction temperatures and times were as follows: Ph_3SiH, 64 h, 20°; Ph_2MeSiH, 2 h, 50°; Ph_2H_2Si, 6 h, 20°; $PhMe(CH_2{=}CH)SiH$, 16 h, 20°; Et_3SiH, 3 h, 20°; $(EtO)_3SiH$, 20 min, 70°, then 20 h at 20°; $(Me_3SiO)_2MeSiH$, 0.75 h, 80°. It should be appreciated, however, that reaction may have been complete in several cases in shorter times than those used.

Details of the products are given in Table 1.

Bis(chlorodimethylsilyl)bis(triphenylphosphine)platinum(II)

Use of chlorodimethylsilane in the procedure described above gave the pale yellow $[Pt(SiClMe_2)_2(PPh_3)_2]$. m.p. 195° (dec.) in 74% yield. (Found: C, 52.9; H, 4.7; Cl, 6.5. $C_{40}H_{42}Cl_2P_2PtSi_2$ calcd.: C, 53.0; H, 4.7; Cl, 7.8%.) (The apparently low chlorine content is attributed to some hydrolysis during the preparation of the sample for analysis for this element.)

Reaction of $[Pt(PPh_3)_2(PhC{\equiv}CH)]$ and $[Pt(PPh_3)_2(PhC{\equiv}CPh)]$ with methyldiphenylsilane

(*a*). An excess of methyldiphenylsilane (ca. 0.75 ml) was added to a solution of $[Pt(PPh_3)_2(PhC{\equiv}CH)]$ (200 mg, 0.24 mmol) in benzene (2 ml), and the mixture was set aside at room temperature overnight. n-Hexane (5 ml) was added, and the solid filtered off, washed with n-hexane, and dried under vacuum to give *cis*-$[PtH(SiMePh_2)(PPh_3)_2]$ (105 mg, 47%), m.p. 118 - 120°; the IR spectrum was identical with that of the product obtained from $[Pt(PPh_3)_2(C_2H_4)]$. GLC examination of the filtrate showed the presence of phenylacetylene.

(*b*). A similar procedure using $[Pt(PPh_3)_2(PhC{\equiv}CPh)]$, but with a reaction time of 3 days at room temperature, gave the same product in similar yield.

Reaction of cis-$[PtH(SiMePh_2)(PPh_3)_2]$ with phenyl- or diphenyl-acetylene

A solution of the platinum hydride in benzene was treated with an excess of phenylacetylene. After 3 h at room temperature, n-hexane was added, and the solid (m.p. 133°) which separated was filtered off and shown to be $[Pt(PPh_3)_2(PhC{\equiv}CH)]$ (56%) by the identity of its IR spectrum with that of an authentic sample. GLC examination of the filtrate showed the presence of methyldiphenylsilane.

Reaction of cis-$[PtH(SiMePh_2)(PPh_3)_2]$ with triphenylphosphine

The platinum hydride (80 mg, 0.09 mmol) and triphenylphosphine (50 mg, 0.19 mol) were dissolved together in benzene (2 ml) to give a bright yellow solution. The latter was slowly concentrated and n-hexane (5 ml) was added. The bright yellow crystalline solid which separated showed no ν(Pt—H) or ν(Si—H) band in its IR, and the spectrum was very similar to that of $[Pt(PPh_3)_4]$.

Preparations from $[Pt(PMePh_2)_4]$

(*a*). An excess of trichlorosilane (ca. 1 ml) was added to $[Pt(PMePh_2)_4]$ (300 mg, 0.3 mmol). A vigorous evolution of gas (presumably hydrogen) occurred. The mixture was refluxed for 2 h, and the pale yellow solid was washed with ether and collected, and shown to be bis(trichlorosilyl)bis(methyldiphenylphosphine)platinum(II) (180 mg, 69%), m.p. 170 - 175°. (Found: C, 36.2; H, 3.0; Cl, 24.4. $C_{26}H_{26}Cl_6P_2PtSi_2$ calcd.: C, 36.1; H, 3.0; Cl, 24.7%.)

(*b*). Similarly, from methyldichlorosilane, bis(methyldichlorosilyl)bis(methyldiphenylphosphine)platinum(II), m.p. 128° (softens without giving clear liquid) was obtained in 60% yield. (Found: C, 40.4; H, 3.8; Cl, 17.4, $C_{28}H_{32}Cl_4P_2PtSi_2$ calcd.: C, 40.8; H, 3.9; Cl, 17.3%.)

Reaction of $[Pt(PMePh_2)_4]$ *with triphenyl- or methyldiphenyl-silane*

An excess of triphenylsilane was added to a solution of $[Pt(PMePh_2)_4]$ in benzene, and the mixture was kept at 70° for 3 h, then cooled. Half of the solvent was evaporated off, and n-hexane was added, to give bright yellow crystals, m.p. 95 - 101°, which were probably $[Pt(PMePh_2)_3C_6H_6]$. (Found: C, 61.9; H, 5.4; P, 10.7. $C_{45}H_{45}P_3Pt$ calcd.: C, 61.8; H, 5.2; P, 10.6%.) The IR spectrum was very similar to that of $[Pt(PMePh_2)_4]$.

Essentially identical results were obtained with methyldiphenylsilane.

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