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Square planar platinum(II) complexes. Crystal structures of *cis*-bis(triphenylphosphine)hydro(triphenylstannyl)platinum(II) and *cis*-bis(triphenylphosphine)hydro(triphenylsilyl)platinum(II)

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Abstract

The complexes *cis*-[PtH(SnPh$_3$)(PPh$_3$)$_2$], *cis*-[PtH{Sn(C$_6$H$_4$Me-*p*)$_3$}(PPh$_3$)$_2$], *cis*-[PtH{Sn(C$_6$H$_4$Me-*p*)$_3$}(DIOP)], and *cis*-[PtH(SiPh$_3$)(PPh$_3$)$_2$] have been prepared, and the crystal structures of *cis*-[PtH(SnPh$_3$)(PPh$_3$)$_2$] and *cis*-[PtH(SiPh$_3$)(PPh$_3$)$_2$] have been determined. Both of these complexes exhibit distorted square-planar geometry at platinum. In the tin complex, the Pt–P bonds are almost equal in length, but in the silicon complex, the Pt–P bond *trans* to silicon is significantly longer than that *cis* to silicon, in accord with the larger *trans* influence of silyl ligands.

Key words: Platinum; Tin; Silicon; Crystal structure

1. Introduction

We describe below the preparation of three new complexes, *cis*-[PtH(SnPh$_3$)(PPh$_3$)$_2$], *cis*-[PtH{Sn(C$_6$H$_4$Me-*p*)$_3$}(PPh$_3$)$_2$], *cis*-[PtH{Sn(C$_6$H$_4$Me-*p*)$_3$}(DIOP)] and the results of an X-ray diffraction study of the first of these. The structure of the corresponding silicon-containing compound, *cis*-[PtH(SiPh$_3$)(PPh$_3$)$_2$] has also been determined for comparison. A search of the Cambridge Crystallographic Data Base has revealed only one other compound containing a triarylstannyl-platinum bond, and that is a *trans*-species, *viz. trans*-[PtH(SnPh$_3$)(PCy$_3$)$_2$] [1].

2. Experimental details

2.1. Synthesis of triarylstannyl-platinum (II) complexes

The [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] complex was prepared by the standard procedure [2] and [*p*-(MeC$_6$H$_4$)$_3$SnH] by the method used for the synthesis of (C$_6$H$_5$)$_3$SnH [3]. Other reagents were purchased from commercial sources. Manipulations were carried out under nitrogen by standard vacuum and Schlenk techniques.

2.1.1. *cis-[PtH(SnPh$_3$)(PPh$_3$)$_2$]*

Equimolar amounts of [Pt(C$_2$H$_4$)(PPh$_3$)$_2$] and Ph$_3$SnH were dissolved in *ca.* 10 ml of ether. When evolution of ethylene had ceased, the pale yellow solid was filtered off and recrystallized from dichloromethane-ether mixture to afford the pure product (0.9 g, 60%), m.p. 147–149°C. (Found: C, 62.2; H, 5.0. Calc. for C$_{54}$H$_{46}$P$_2$SnPt: C, 60.6; H, 4.3%). IR (KBr): 2040 cm^{-1} (Pt–H). ^{1}H NMR (90 MHz, CDCl$_3$) at −30°C: −3.16 [2 doublets, $^{2}J(^{31}\text{P}'\text{–Pt–}^{1}\text{H})$ 154.1 Hz, $^{2}J(^{31}\text{P}''\text{–Pt–}^{1}\text{H})$ 15.5 Hz, $^{1}J(^{195}\text{Pt–}^{1}\text{H})$ 767.2 Hz] ppm relative to Me$_4$Si. ^{31}P-{^{1}H} (32.4 MHz, CDCl$_3$) at −30°C): δ(P′) −109.8 [$^{1}J(^{195}\text{Pt–}^{31}\text{P})$ 2621.9 Hz, $^{2}J(^{119}\text{Sn–Pt–}^{31}\text{P})$ 137.5 Hz, $^{2}J(^{117}\text{Sn–Pt–}^{31}\text{P})$ 131.5 Hz)], δ(P″) −107.7 [$^{1}J(^{195}\text{Pt–}^{31}\text{P})$ 2613.3 Hz, $^{2}J(^{119}\text{Sn–Pt–}^{31}\text{P})$ 1687.1 Hz, $^{2}J(^{117}\text{Sn–Pt–}^{31}\text{P})$ 1612.3 Hz, $^{2}J(^{31}\text{P–Pt–}^{31}\text{P})$ 8.6 Hz] ppm relative to P(OMe)$_3$ (P′ refers to the phosphorus *trans* to H and P″ to that *cis* to H). ^{119}Sn-{^{1}H} NMR

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(360 MHz, $CDCl_3$) at −20°C: δ −24.4 [2 doublets, $^1J(^{119}Sn-^{195}Pt)$ 10818.9, $^2J(^{119}Sn-Pt-P')$ 135.0, $^2J(^{119}Sn-Pt-P'')$ 1685.3 Hz] ppm relative to Me_4Sn.

2.1.2. *cis-[PtH{Sn(C$_6$H$_4$Me-p)$_3$}(PPh$_3$)$_2$]*

An analogous procedure but with $(p\text{-}MeC_6H_4)_3SnH$ gave this complex, m.p. 147–148°C, in 60% yield. (Found: C, 62.1; H, 5.0. Calc. for $C_{57}H_{52}P_2SnPt$: C, 61.5; H, 4.7%). IR (KBr): 2030 cm^{-1} (Pt–H). $^{31}P\text{-}\{^1H\}$ at −55°C: $\delta(P')$ −109.5 [$^1J(^{195}Pt-^{31}P)$ 2619.6 Hz], $\delta(P'')$ −107.8 [$^1J(^{195}Pt-^{31}P)$ 2596.4 Hz, $^2J(^{119}Sn-Pt-^{31}P)$ 1589 Hz, $^2J(^{117}Sn-Pt-^{31}P)$ 119 Hz, $^2J(^{31}P-Pt-^{31}P)$ 8.5 Hz] ppm (P′ refers to the phosphorus *trans* to H and P″ to that *cis* to H). $^{119}Sn\text{-}\{^1H\}$ NMR (360 MHz, $CDCl_3$) at 25°C: δ −37.5 [2 doublets, $^1J(^{119}Sn-^{195}Pt)$ 10781.9, $^2J(^{119}Sn-Pt-P')$ 130.6, $^2J(^{119}Sn-Pt-P'')$ 1674.5 Hz] ppm relative to Me_4Sn.

2.1.3. *[Pt(CO$_3$)(DIOP)]*

A mixture in CH_2Cl_2 of a large excess of freshly prepared Ag_2CO_3 with [$PtCl_2$(DIOP)] [prepared by treating platinum dichloride 1,5-cyclooctadiene with 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP) in CH_2Cl_2] was stirred for several hours. The solution mixture was filtered through Celite, the filtrate concentrated, and hexane added to precipitate the product, m.p. 216–218°C, in 90% yield. (Found: C, 49.7; H, 4.5. Calc. for $C_{32}H_{32}O_5P_2Pt$: C, 50.9; 4.3%). $^{31}P\text{-}\{^1H\}$ in CH_2Cl_2: $\delta(P)$ −147.6 [$^1J(^{195}Pt-^{31}P)$ 3413.1 Hz] ppm.

2.1.4. *[PtH{Sn(C$_6$H$_4$-Me)$_3$}(DIOP)]*

Equimolar amounts of [$Pt(CO_3)$(DIOP)] and $(p\text{-}MeC_6H_4)_3SnH$ were dissolved in *ca.* 10 ml of methanol in a Schlenk tube. When carbon dioxide evolution had ceased, the solution was concentrated to give a yellow solid. Its ^{31}P NMR spectrum showed peaks at −133.6 [$^1J(^{31}P-^{195}Pt)$ 2567.4 Hz], −135.3 [doublet, $^1J(^{31}P-^{195}Pt)$ 2019.0 Hz] and −134.1 [$^1J(^{31}P-^{195}Pt)$ 2161.1, $^2J(^{31}P-Pt-^{31}P)$ 13.6 Hz] ppm. The single peak – at −133.6 ppm was assigned to the $[Pt(DIOP)_2]^{2+}$ cationic species. The pair of peaks at −135.5, −134.1 ppm was assigned to [PtH{Sn(C_6H_4-*p*-Me)$_3$}(DIOP)] by comparison with the spectrum of *cis*-[PtH($SnPh_3$)(PPh_3)$_2$]. $^{119}Sn\text{-}\{^1H\}$ NMR for [PtH{Sn(C_6H_4-*p*-Me)$_3$}(DIOP)] (360 MHz, $C_6D_5CD_3$) at 25°C: δ −78.2 [$^1J(^{119}Sn-^{195}Pt)$ 9094.2, $^2J(^{119}Sn-Pt-P')$ 26.7, $^2J(^{119}Sn-Pt-P'')$ 1414.2 Hz] ppm relative to Me_4Sn.

2.1.5. *cis-[PtH(SiPh$_3$)(PPh$_3$)$_2$]*

A solution of Ph_3SiH and [$Pt(C_6H_4(PPh_3)_2$] in degassed C_6H_6 (3 ml) was stirred under argon at room temperature for *ca.* 48 h. When evolution of gas had ceased, most of the solvent was evaporated off and

TABLE 1. Atomic coordinates for [PtH($SnPh_3$)(PPh_3)$_2$]

Atom	x	y	z
Pt	0.05290(2)	0.28133(2)	0.27744(2)
Sn	0.24023(3)	0.32268(3)	0.24230(3)
P1	0.13780(1)	0.15850(1)	0.17660(1)
P2	−0.13160(1)	0.28260(1)	0.36010(1)
C1	0.2738(5)	0.0629(4)	0.2052(4)
C2	0.2770(5)	0.0350(5)	0.3060(5)
C3	0.3735(6)	−0.0433(6)	0.3364(6)
C4	0.4670(6)	−0.0945(6)	0.2671(6)
C5	0.4654(6)	−0.0659(5)	0.1674(5)
C6	0.3695(5)	0.0129(5)	0.1370(5)
C7	0.0663(5)	0.0737(4)	0.1673(4)
C8	0.1094(6)	−0.0325(5)	0.1920(5)
C9	0.0520(7)	−0.0925(6)	0.1805(6)
C10	−0.0465(7)	−0.0470(6)	0.1447(6)
C11	−0.0902(7)	0.0599(6)	0.1212(6)
C12	−0.0351(6)	0.1205(5)	0.1326(5)
C13	0.1642(5)	0.2240(4)	0.0465(4)
C14	0.1312(5)	0.3323(5)	0.0267(5)
C15	0.1452(6)	0.3863(6)	−0.0722(6)
C16	0.1906(6)	0.3330(6)	−0.1482(6)
C17	0.2204(6)	0.2264(6)	−0.1302(6)
C18	0.2076(5)	0.1706(5)	−0.0333(5)
C19	−0.2502(5)	0.3871(5)	0.3095(5)
C20	−0.3433(6)	0.4531(6)	0.3658(6)
C21	−0.4337(7)	0.5298(6)	0.3232(6)
C22	−0.4312(7)	0.5378(6)	0.2255(6)
C23	−0.3378(7)	0.4743(6)	0.1681(6)
C24	−0.2463(6)	0.4008(5)	0.2091(5)
C25	−0.1710(5)	0.1682(5)	0.3757(5)
C26	−0.2763(6)	0.1722(5)	0.3660(5)
C27	−0.3026(7)	0.0806(6)	0.3839(6)
C28	−0.2212(7)	−0.0136(6)	0.4089(6)
C29	−0.1149(7)	−0.0209(6)	0.4178(6)
C30	−0.0892(6)	0.0706(5)	0.4019(5)
C31	−0.1701(5)	0.3018(5)	0.4899(5)
C32	−0.2333(6)	0.2491(5)	0.5652(5)
C33	−0.2677(7)	0.2705(6)	0.6626(6)
C34	−0.2360(7)	0.3427(6)	0.6810(6)
C35	−0.1735(7)	0.3962(7)	0.6070(7)
C36	−0.1395(6)	0.3756(6)	0.5103(6)
C37	0.2783(5)	0.3145(5)	0.3783(5)
C38	0.1982(7)	0.3016(6)	0.4674(6)
C39	0.2189(8)	0.3044(7)	0.5562(7)
C40	0.3166(7)	0.3188(7)	0.5580(6)
C41	0.3963(8)	0.3318(7)	0.4706(7)
C42	0.3781(7)	0.3303(6)	0.3807(6)
C43	0.2326(5)	0.4746(4)	0.1606(4)
C44	0.1276(6)	0.5518(5)	0.1474(5)
C45	0.1244(7)	0.6499(6)	0.0906(6)
C46	0.2255(7)	0.6711(6)	0.0486(6)
C47	0.3305(6)	0.5972(5)	0.0611(5)
C48	0.3336(5)	0.4990(5)	0.1164(5)
C49	0.4039(5)	0.2388(5)	0.1581(5)
C50	0.4896(6)	0.1617(5)	0.2046(5)
C51	0.5982(6)	0.1105(6)	0.1485(6)
C52	0.6194(6)	0.1328(6)	0.0468(6)
C53	0.5353(6)	0.2072(5)	−0.0017(5)
C54	0.4277(5)	0.2592(5)	0.0551(5)

n-hexane (5 ml) added to produce a pale yellow solid, which was filtered off, washed with more hexane, and dried under vacuum. Recrystallization from CH_2Cl_2/Et_2O gave the pure product (0.21 g, 80%), m.p. 118°C; IR(KBr): (PtH) 2095 cm^{-1}; (Found: C, 63.7; H, 4.9. Calc. for $C_{54}H_{46}P_2SiPt$: C, 66.7; H, 5.1%). ^1H NMR (90 MHz, $CDCl_3$) at −30°C: −2.38 [2 doublets, $^2J(^{31}P'-Pt-^1H)$ 150.0 Hz, $^2J(^{31}P''-Pt-^1H)$ 18.0 Hz, $^1J(^{195}Pt-^1H)$ 933.0 Hz] ppm relative to Me_4Si. ^{31}P-{^1H} (32.4 MHz, $CDCl_3$) at −30°C: $\delta(P')$ −107.8 [$^1J(^{195}Pt-^{31}P)$ 2621.0 Hz], $\delta(P'')$ −104.7 [$^1J(^{195}Pt-^{31}P)$ 1683.0 Hz, $^2J(^{31}P-Pt-^{31}P)$ 10.4 Hz] ppm relative to $P(OMe)_3$.

2.2. Crystallographic studies

2.2.1. cis-[PtH(SnPh$_3$)(PPh$_3$)$_2$]

Crystal data: $C_{54}H_{46}P_2SnPt$, FW 1070.7, triclinic, $P\bar{1}$ (No. 2), *a* 12.832(3), *b* 14.246(3), *c* 14.422(3) Å, α 73.46(4), β 71.83(4), γ 66.71(3)°, *V* 2261.1 Å^3, *D* 1.573 g cm^{-3}, *F*(000) 1056, μ 39.14 cm^{-1} for $Z = 2$. Diffraction measurements were made at room temperature with a crystal of $[PtH(SnPh_3)(PPh_3)_2]$ of dimensions

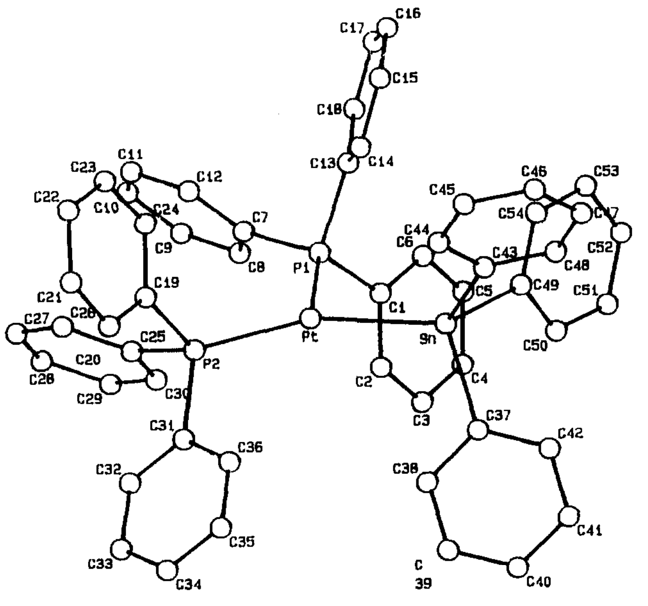

Fig. 1. Atomic labelling for $[PtH(SnPh_3)(PPh_3)_2]$. Selected bond distances and angles: Pt–Sn = 2.564(1), Pt–P1 = 2.305(1), Pt–P2 = 2.290(1), Sn–C37 = 2.126(5), Sn–C43 = 2.129(4), Sn–C49 = 2.137(4), P1–C1 = 1.882(4), P1–C7 = 1.835(4), P1–C13 = 1.834(4), P2–C19 = 1.830(5), P2–C25 = 1.826(5), P2–C31 = 1.851(5) Å; Sn–Pt–P1 = 93.27(3), Sn–Pt–P2 = 155.75(3), P1–Pt–P2 = 110.20(4), Pt–Sn–C37 = 109.9(1), Pt–Sn–C43 = 114.9(1), Pt–Sn–C49 = 123.7(1), C37–Sn–C43 = 105.1(1), C37–Sn–C49 = 103.7(2), C43–Sn–C49 = 97.6(2), Pt–P1–C1 = 112.4(1), Pt–P1–C7 = 123.9(1), Pt–P1–C13 = 109.2(1), C1–P1–C7 = 100.9(2), C1–P1–C13 = 109.8(2), C7–P1–C13 = 99.5(2), Pt–P2–C19 = 115.9(1), Pt–P2–C25 = 119.4(1), Pt–P2–C31 = 113.4(2), C19–P2–C25 = 102.0(2), C19–P2–C31 = 101.9(2), C25–P2–C31 = 101.8(2)°.

TABLE 2. Atomic coordinates for for $[PtH(SiPh_3)(PPh_3)_2]\cdot\frac{1}{2}OEt_2$

Atom	*x*	*y*	*z*
Pt	0.16214(1)	−0.02617(3)	0.07896(1)
P1	0.1506(1)	0.1434(2)	0.0949(1)
P2	0.1414(1)	−0.0529(2)	−0.0030(1)
Si	0.1853(1)	−0.0893(2)	0.1569(1)
C1	0.0966(4)	0.1607(7)	0.1323(3)
C2	0.0585(4)	0.0894(8)	0.1267(4)
C3	0.0150(4)	0.0965(9)	0.1544(4)
C4	0.0112(5)	0.174(1)	0.1861(5)
C5	0.0495(5)	0.241(1)	0.1934(4)
C6	0.0940(4)	0.239(1)	0.1656(5)
C7	0.2056(3)	0.2103(7)	0.1250(3)
C8	0.2074(4)	0.3160(8)	0.1303(4)
C9	0.2484(5)	0.3646(9)	0.1532(4)
C10	0.2895(4)	0.3098(9)	0.1699(4)
C11	0.2908(4)	0.207(1)	0.1640(4)
C12	0.2479(4)	0.1563(8)	0.1405(4)
C13	0.1369(4)	0.2324(7)	0.0443(4)
C14	0.0942(5)	0.2906(9)	0.0388(5)
C15	0.0860(5)	0.353(1)	−0.0007(5)
C16	0.1196(6)	0.3583(9)	−0.0337(4)
C17	0.1634(6)	0.3000(9)	−0.0303(4)
C18	0.1727(5)	0.2347(8)	0.0100(4)
C19	0.2573(4)	−0.1069(7)	0.1662(4)
C20	0.2830(4)	−0.1210(8)	0.2119(4)
C21	0.3354(5)	−0.139(1)	0.2159(5)
C22	0.3629(5)	−0.141(1)	0.1782(5)
C23	0.3391(5)	−0.127(1)	0.1321(5)
C24	0.2868(4)	−0.1106(8)	0.1276(4)
C25	0.1560(4)	−0.2197(9)	0.1658(4)
C26	0.1763(5)	−0.2893(9)	0.1997(4)
C27	0.1555(5)	−0.3849(9)	0.2048(4)
C28	0.1120(5)	−0.4116(9)	0.1771(5)
C29	0.0899(4)	−0.3439(9)	0.1445(4)
C30	0.1123(4)	−0.2494(8)	0.1386(4)
C31	0.1649(4)	−0.0218(7)	0.2123(3)
C32	0.1169(4)	−0.0383(8)	0.2280(4)
C33	0.1002(4)	0.0108(9)	0.2682(4)
C34	0.1310(5)	0.0769(9)	0.2944(4)
C35	0.1783(5)	0.0962(9)	0.2794(4)
C36	0.1951(4)	0.0486(8)	0.2388(4)
C37	0.1991(3)	−0.0668(7)	−0.0344(3)
C38	0.2421(4)	−0.0129(8)	−0.0179(4)
C39	0.2867(4)	−0.0195(8)	−0.0407(4)
C40	0.2900(4)	−0.0821(8)	−0.0795(4)
C41	0.2478(4)	−0.1390(9)	−0.0955(4)
C42	0.2025(4)	−0.1331(8)	−0.0738(3)
C43	0.1019(3)	0.0361(7)	−0.0411(3)
C44	0.0560(4)	0.0691(8)	−0.0233(4)
C45	0.0226(4)	0.1289(8)	−0.0514(4)
C46	0.0337(4)	0.1578(8)	−0.0967(4)
C47	0.0793(4)	0.1265(8)	−0.1130(4)
C48	0.1142(4)	0.0659(8)	−0.0851(4)
C49	0.1068(4)	−0.1729(7)	−0.0172(3)
C50	0.1187(4)	−0.2590(8)	0.0095(4)
C51	0.0931(5)	−0.3488(9)	0.0001(5)
C52	0.0563(4)	−0.3564(9)	−0.0375(5)
C53	0.0448(4)	−0.2711(9)	−0.0641(5)
C54	0.0689(4)	−0.1805(8)	−0.0541(4)
C55	0.5576(6)	0.112(1)	0.3279(6)
C56	0.5153(8)	−0.042(2)	0.2897(8)
O57	0.5	0.298(2)	0.25

0.15 × 0.25 × 0.30 mm on an Enraf-Nonius CAD4 diffractometer (Mo Kα, 0.71069 Å radiation). The unit-cell dimensions were calculated from 25 strong reflections with $\theta \approx 15°$. Data were measured by $\theta/2\theta$ scans for $2° \leq 2\theta \leq 50°$; two standard reflections monitored hourly showed no significant variations in intensity. The data were corrected for Lorentz and polarization effects and for absorption. After averaging of equivalent reflections, 6866 reflections with $I \geq \sigma(I)$ were used in the structure solution by the heavy-atom method. The full-matrix least-squares refinements on F utilized anisotropic temperature factors for the Pt, Sn and P atoms. The refinements converged with a shift-to-error ratio of 0.02 to a final R index of 0.040; $R = 0.050$ ($w = [\sigma^2 \mid F \mid]^{-1}$); phenyl H-atoms were placed at calculated positions (C–H = 1.08 Å, $B = 8$ Å^2) in the structure factor calculations. The final difference map was featureless except for a peak of 1.34 eÅ^{-3} (0.0273, 0.3887, 0.3125) 1.63 Å from the Pt atom which is consistent with the presence of a hydride atom. Scattering factors and anomalous dispersion coefficients were taken from reference [4]. All computations were performed with the Structure Determination Package [5] on a PDP 11/34 computer. Atomic coordinates are listed in Table 1 and the numbering scheme is shown in Fig. 1. Complete lists of bond lengths and angles and tables of thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

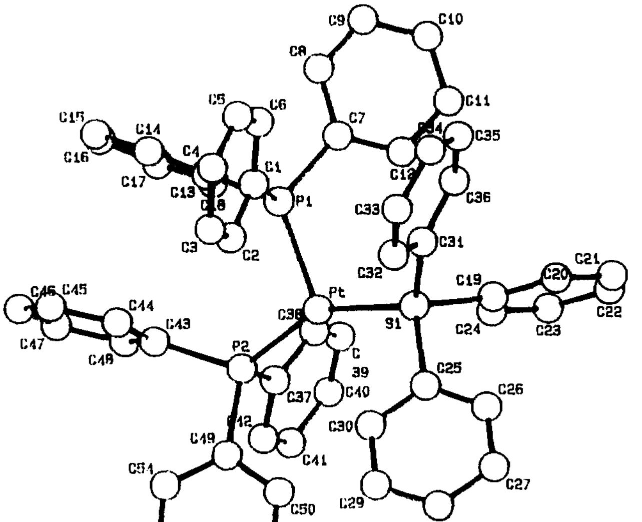

Fig. 2. Atomic labelling for $[PtH(SiPh_3)(PPh_3)_2] \cdot \frac{1}{2}OEt_2$; ether molecule not shown. Selected bond distances and angles: Pt–P1 = 2.298(3), Pt–P2 = 2.332(2), Pt–Si = 2.357(3), Si–C19 = 1.90(1), Si–C25 = 1.90(1), Si–C31 = 1.90(1), P1–C1 = 1.84(1), P1–C7 = 1.839(9), P1–C13 = 1.84(1), P2–C37 = 1.814(9), P2–C43 = 1.884(9), P2–C49 = 1.848(9) Å; P1–Pt–P2 = 108.05(9), P1–Pt–Si = 101.19(9), P2–Pt–Si = 150.61(8), Pt–Si–C19 = 110.7(3), Pt–Si–C25 = 111.0(3), Pt–Si–C31 = 120.9(3), C19–Si–C25 = 106.3(4), C19–Si–C31 = 106.7(4), C25–Si–C31 = 100.0(4), Pt–P1–C1 = 110.3(3), Pt–P1–C7 = 116.2(3), Pt–P1–C13 = 103.8(5), C1–P1–C7 = 107.33(4), C1–P1–C13 = 103.8(5), C7–P1–C13 = 98.4(4), Pt–P2–C37 = 109.9(3), Pt–P2–C43 = 104.2(4), Pt–P2–C49 = 114.3(3), C37–P2–C43 = 104.2(4), C37–P2–C49 = 103.1(4), C43-P2-C49 = 100.0(4)°.

2.2.2. *cis-[PtH(SiPh$_3$)(PPh$_3$)$_2$]*

Single crystals were grown from solution in a dichloromethane-ether mixture. The complex crystallized with half a molecule of ether, the presence of which was confirmed by the ^{1}H NMR spectrum. Crystal data: $C_{56}H_{51}O_{0.5}P_2SiPt$, FW 874.60, monoclinic, $C2/c$ (No. 15), a 26.272(3), b 13.147(1), c 27.786(3) Å, β 94.29(3)°, V 9570 Å^3, D 1.214 g cm^{-3}, $F(000)$ 3616, μ 15.43 cm^{-1} for $Z = 8$. The structure was solved by the heavy atom method and refined by full-matrix least squares procedures with anisotropic temperature factors for the non-H atoms; H-atoms were placed at calculated positions (C–H = 1.08 Å, $B = 8$ Å^2). The ether molecule, which lies on a two-fold axis, suffers from severe disorder and could not be accurately located. The refinement converged at $R = 0.042$, $R_w = 0.057$ ($w = [\sigma \mid F \mid^2]^{-1}$). The final difference map had a peak of 1.2 eÅ^{-3} near the Pt atom and a peak of 0.6 eÅ^{-3} near the solvent molecule, but was otherwise featureless. It was impossible to locate the hydride ligand atom. Atomic coordinates are listed in Table 2 and the structure and atom numbering shown in Fig. 2.

3. Results and discussion

The two new bis(triphenylphosphine)hydro(triarylstannyl)platinum(II) complexes *cis*-$[PtH(SnR_3)(PPh_3)_2]$, R = Ph or C_6H_4Me-4, were made by treatment of $[Pt(C_2H_4)(PPh_3)_2]$ with the appropriate hydride R_3SnH. The complex $PtH\{Sn(C_6H_4Me\text{-}4)_3\}$(DIOP) was not isolated but was characterized in solution by NMR spectroscopy. The three complexes exhibit large phosphorus couplings to both platinum (1–3 kHz) and tin (1–2 kHz). The values agree satisfactorily with those for other Pt-Sn complexes [6,7]. The coupling constants permit unambiguous assignment of the phosphorus atoms *trans* and *cis* to tin, since indirect coupling between ligand atoms in Pt^{II} complexes is known to be larger for *trans* than for *cis* ligands [8]. The three compounds studied have the phosphorus ligands in a *cis* disposition.

The NMR assignment for the triphenylstannyl derivative was confirmed by a single-crystal structure determination. The complex crystallizes as discrete molecules (Fig. 1). The hydride was not located but it is evident that the geometry at platinum is a severely distorted square-plane (sum of angles at Pt 359.2(1)°), the P1–Pt–P2 angle of 110.20(4)° being substantially larger than the 90° expected for an ideal square-planar species, the PPh_3 ligands *cis* to H presumably lying over towards the small H atom to minimize steric strain. The angle between the *cis*-related PPh_3 and the $SnPh_3$ ligand [93.27(3)] is much smaller.

The Pt–P1 [2.305(1) Å] and Pt–P2 [2.290(1) Å] bond lengths differ only slightly, and this is consistent with the fairly similar values of the coupling constants ^1J(Pt–P1) (2621.9 Hz) and ^1J(Pt–P2) (2613.3 Hz). The Ph–P–Ph angles (mean 102.1°) and the Ph–P–Ph (mean 103.4°) are closed markedly below the tetrahedral value to relieve steric strain between the three bulky ligands.

In the related silicon-containing complex, *cis*-$[PtH(SiPh_3)(PPh_3)_2]$ (the hydride is not shown in Fig. 2), the small distortion from square-planarity is of slightly different form; the P(1)–Pt–P(2) angle, 108.05(9), being smaller and the P(1)–Pt–Si angle, 101.19(9), significantly larger than the corresponding angles in the tin compound, reflecting the larger steric demand of $SiPh_3$ than of $SnPh_3$. However the means of the Ph–Si–Ph angles (104.3) and Ph–Si–Ph angle (103.2) are not significantly different from those in the tin compound. Whereas the Pt–P1 and Pt–P2 bond lengths for the Pt–Sn complex are very similar, the corresponding lengths in the Pt–Si complex differ significantly (Pt–P1 2.298(3) Å, Pt–P2 2.332(2) Å). This is in accord with the fact that a silyl ligand has a stronger *trans* influence than a hydride or the stannyl ligand [9].

Both complexes, *cis*-$[PtH(XPh_3)(PPh_3)_2]$, X = Si or Sn, show distortion of the angles around the Si or Sn and the two phosphorus atoms from the ideal tetrahedral angles of 109.5°. Similar distortions around the Si and both P atoms were previously observed in (tricyclohexylphosphine)Pt^{II}–Si complexes [10–12].

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