3994 *Organometallics* **2000,** *19,* 3994−3996

Synthesis and Structural Characterization of the Mono(silyl)platinum(II) Complex *cis*-(2,6-$Mes_2C_6H_3(H)_2Si)Pt(H)(PPr_3)_2$

Richard S. Simons, Lee M. Sanow, Kevin J. Galat, Claire A. Tessier,* and
Wiley J. Youngs*

Department of Chemistry, University of Akron, Akron, Ohio 44325

Received May 12, 2000

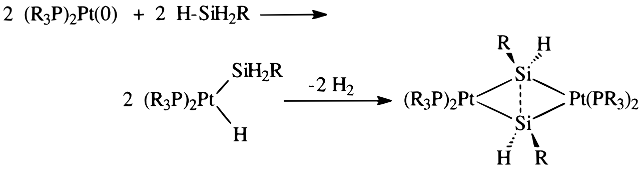
*Summary: The synthesis and structural characterization of cis-(2,6-$Mes_2C_6H_3(H)_2Si)Pt(H)(PPr_3)_2$ (**1**), a mono(silyl)platinum(II) complex, are described.*

Introduction

The most common method of synthesizing transition-metal silyl complexes involves the oxidative addition of a Si−H bond in a hydrosilane to a transition-metal center with open coordination sites.[1] Several researchers, including our group, have been investigating the reaction chemistry of primary silanes with 14-electron $(R_3P)_2Pt^0$ complexes generated in situ from $(R_3P)_3PtCl_2$ and sodium metal,[2] $(R_3P)_3Pt$ (R = Et, Pr),[3] or $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$.[4] Primary silanes bearing a ligand of moderate steric bulk afford Pt_2Si_2 dinuclear complexes. The formation of the dinuclear rings has been proposed to involve the oxidative addition of the silane to the metal to give $(R_3P)_2Pt(SiR'H_2)H$ (Scheme 1). This reaction has been observed for a number of tertiary silanes and a few secondary silanes, but rarely has such a step been observed for primary silanes.[5]

Transition-metal complexes containing terminal silylene ligands have been proposed as intermediates in transition-metal-mediated reactions.[6] It has been a major synthetic goal for many researchers to isolate stable base-free transition-metal silylenes. Because of this surge of interest, these reactive species have been isolated and characterized recently.[7] We desired to synthesize a mono(silyl)platinum(II) complex which might be used as a precursor for neutral or cationic platinum metal silylene complexes. We have employed the sterically hindered 2,6-$Mes_2C_6H_3$ (Mes = 2,4,6-$Me_3C_6H_2$) ligand for this purpose. We rationalized that the steric bulk would prevent the formation of a Pt_2Si_2 dinuclear complex and also provide kinetic stabilization of low-valent platinum silicon complexes. We report herein the synthesis and characterization of the mono(silyl)platinum(II) complex *cis*-(2,6-$Mes_2C_6H_3(H)_2Si)Pt(H)(PPr_3)_2$ (**1**).

Scheme 1



Experimental Section

General Considerations. All manipulations were carried out under anaerobic conditions under an atmosphere of nitrogen or argon. The compounds $(Pr_3P)_3Pt^{3c}$ and 2,6-$Mes_2C_6H_3$-SiH_3[8] were prepared according to literature procedures. Hexane was freshly distilled from sodium benzophenone ketyl. ^1H, ^{13}C, and ^{31}P NMR data were recorded on a Gemini 300 MHz instrument and referenced to C_6D_6 for ^1H and ^{13}C and H_3PO_4 for ^{31}P. ^{29}Si NMR data were recorded on a Varian 300 MHz instrument and referenced to Me_4Si. IR data were recorded on a Bomen FTIR instrument.

---

(1) For recent reviews of silicon−transition metal chemistry: (a) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175−292. (b) Eisen, M. S. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Part 3; Chapter 35.

(2) (a) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1988**, *110*, 4068−4070. (b) Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1989**, 577−578. (c) Anderson, A. B.; Shiller, P.; Zarate, E. A.; Tessier-Youngs, C. A.; Youngs, W. J. *Organometallics* **1989**, *8*, 2320−2322.

(3) (a) Shimada, S.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc.* **1995**, *117*, 8289−8290. (b) Heyn, R. H.; Tilley, T. D. *J. Am. Chem Soc.* **1992**, *114*, 1917−1919. (c) Sanow, L. M.; Chai, M.; McConnville, D. B.; Galat, K. J.; Simons, R. S.; Rinaldi, P. L.; Youngs, W. J.; Tessier, C. A. *Organometallics* **2000**, *19*, 192−205.

(4) Levchinsky, Y.; Rath, N. P.; Braddock-Wilking, J. *Organometallics* **1999**, *18*, 2583−2586.

(5) For examples, see ref 1a.

(6) (a) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapter 9, pp 245−307. (b) Zybill, C. *Top. Curr. Chem.* **1992**, *160*, 1−45. (c) Pannell, K. H.; Sharma, H. K. *Chem. Rev.* **1995**, *95*, 1351−1374. (d) Tilley, T. D. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989. (e) Lickiss, P. D. *Chem. Soc. Rev.* **1992**, 271−279. (f) Corey, J. In *Advances in Silicon Chemistry*; Larson, G., Ed.; JAI: Greenwich, CT, 1991; Vol. 1, pp 327−387. (g) Tilley, T. D. *Comments Inorg. Chem.* **1990**, *10*, 37−51. (h) Gauvin, F.; Harrod, J. F.; Woo, H. G. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1998; Vol. 42, pp 363−405.

(7) (a) Mitchell, G. P.; Tilley, T. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2524−2526. (b) Denk, M.; Hayashi, R. K.; West, R. *J. Chem. Soc., Chem. Commun.* **1994**, 33−34. (c) Grumbine, S. K.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 5495−5496. (d) Grumbine, S. K.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 358−360. (e) Grumbine, S. K.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 7884−7885. (f) Straus, D. A.; Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801−7802. (g) Feldman, J. D.; Mitchell, G. P.; Nolte, J.-T.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 11184−11185. (h) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 7635−7636. (i) Okazaki, M.; Tobita, H.; Ogino, H. *Chem. Lett.* **1996**, 447−478. (j) Okazaki, M.; Tobita, H.; Kawano, Y.; Inomato, S.; Ogino, H. *J. Organomet. Chem.* **1998**, *553*, 1−13. (k) Okazaki, M.; Tobita, H.; Ogino, H. *Chem. Lett.* **1997**, 437−438. (l) Wanandi, P. W.; Glaser, P. B.; Tilley, T. D. *J. Am. Chem. Soc.* **2000**, *122*, 972−973. (m) Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871−9872. (n) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122* 1816−1817.

(8) Simons, R. S.; Haubrich, S. T.; Mork, B. V.; Niemeyer, M.; Power, P. P. *Main Group Chem.* **1998**, *2*, 275−283.

10.1021/om0004038 CCC: $19.00

Table 1. Experimental Details for Data Collection, Reduction, and Refinement for 1·PPr$_3$O

formula	$C_{51}H_{90}OP_3PtSi$
fw	1035.32
cryst dimens (nm)	0.5 × 0.3 × 0.3
color	colorless
cryst syst	monoclinic
space group	$P2_1/n$
a (Å)	11.900(8)
b (Å)	34.671(11)
c (Å)	13.442(6)
α (deg)	90
β (deg)	103.20(4)
γ (deg)	90
V (Å^3)	5399(4)
Z	4
d_{calcd} (Mg/m^3)	1.274
μ (mm^{-1})	2.742
GOF	1.024
R1 (obsd data)	0.0380
wR2 (all data)	0.0659
largest diff peak (e Å^{-3})	1.597

***cis*-(2,6-Mes$_2$C$_6$H$_3$(H)$_2$Si)Pt(H)(PPr$_3$)$_2$·Pr$_3$PO (1·Pr$_3$PO).** 2,6-Mes$_2$C$_6$H$_3$SiH$_3$ (0.5 g, 1.3 mmol) in hexane (20 mL) was added by cannula to (Pr$_3$P)$_3$Pt (1.0 g, 1.3 mmol) in hexane (30 mL) with stirring at ambient temperature. This solution was stirred for an additional 16 h at 50 °C. The volume was reduced to ca. 10 mL under reduced pressure and stored at ca. −60 °C for 24 h to give *cis*-(2,6-Mes$_2$C$_6$H$_3$(H)$_2$Si)Pt(H)(PPr$_3$)$_2$·Pr$_3$PO (**1**·Pr$_3$PO) as colorless crystals. Yield: 0.5 g, 0.5 mmol, 38%. Mp: 69−71 °C. Anal. Calcd for $C_{51}H_{90}OP_3PtSi$: C, 59.11; H, 8.85. Found: C, 58.01; H, 10.07. ^{1}H NMR (C$_6$D$_6$): δ −3.40 ppm (dd, 1 H, J_{H-P}(cis) = 23.0 Hz, J_{H-P}(trans)$_s$ = 154 Hz, J_{Pt-H} = 891 Hz) 0.85 (m, 36 H, P(CH$_2$CH$_2$C*H*$_3$)$_3$ and O(PCH$_2$CH$_2$C*H*$_3$)$_3$), 1.24 (m, 24 H, P(CH$_2$C*H*$_2$CH$_3$)$_3$ and OP(CH$_2$C*H*$_2$CH$_3$)$_3$), 1.40 (m, 24 H, P(C*H*$_2$CH$_2$CH$_3$)$_3$ and OP(C*H*$_2$CH$_2$CH$_3$)$_3$), 2.28 (s, 6 H, *p*-Mes), 2.41 (s, 12 H, *o*-Mes), 4.58 (dd, 2 H, J_{H-P}(trans) = 7.2 Hz, J_{H-P}(cis) = 3.0 Hz, Si−H), 6.93 (s, 4 H, *m*-Mes), 7.07 (d, 2 H, J = 9.0 Hz, *m*-C$_6$H$_3$), 7.30 (tr, 1 H, J = 7.8 Hz, *p*-C$_6$H$_3$). ^{13}C NMR (C$_6$D$_6$): δ 16.05 (d, J_{C-P} = 4.9 Hz, PCH$_2$CH$_2$*C*H$_3$), 16.05 (d, J_{C-P} = 3.8 Hz, OP(CH$_2$CH$_2$*C*H$_3$)$_3$), 16.17 (d, J_{C-P} = 14.8 Hz, OP(CH$_2$*C*H$_2$CH$_3$)$_3$), 16.18 (d, J_{C-P} = 13.8 Hz, P(CH$_2$*C*H$_2$CH$_3$)$_3$), 18.37 (s, *p*-Mes), 18.73 (s, *p*-Mes), 21.57 (*o*-Mes), 22.17 (*p*-Mes), 31.00 (dd, J_{C-P} = 296 Hz, $J_{C-P-Pt-P}$ = 65 Hz, P(*C*H$_2$CH$_2$CH$_3$)$_3$), 31.21 (d, J_{C-P} = 65 Hz, O=P(*C*H$_2$CH$_2$CH$_3$)$_3$), 127.65, 128.18, 128.25, 128.46, 135.39, 136.85, 143.11, 148.72 (Ar). ^{31}P NMR (C$_6$D$_6$): δ 4.9 (d, J_{P-P} = 16.2 Hz, J_{P-Pt} = 2231 Hz), 14.1 (d, J_{P-P} = 16.2 Hz, J_{P-Pt} = 1715 Hz). ^{29}Si NMR (C$_6$D$_6$): δ −54.9 (dd, J_{Si-P}(trans) = 166 Hz, J_{Si-P}(cis) = 14.7 Hz, J_{Si-Pt} = 1132 Hz). IR (Nujol, cm^{-1}): 2915 (vs), 2067 (s), 2049 (s), 1662 (w), 1609 (w), 1455 (s), 1341 (s), 1237 (m), 1163 (s), 1060 (m), 933 (m), 836 (m), 730 (m).

X-ray Crystallography. A colorless crystal of **1**·PPr$_3$O with dimensions 0.5 × 0.3 × 0.3 mm was coated in paraffin oil, mounted on a glass fiber, and placed under a stream of nitrogen.[9] All manipulations were carried out at 143 K using Mo Kα (0.710 73 Å) radiation. Unit cell parameters were obtained by a least-squares analysis of 20 well-centered reflections with 20° ≥ 2θ ≥ 30°. Additional experimental details are given in Table 1. The structure of **1** was solved by direct methods.[10] Phenyl and alkyl hydrogen atoms were placed in idealized positions using a riding model and C−H distances of 0.96 and 0.97 Å, respectively. An absorption correction was applied using the method of ψ scans. Compound **1** was refined to convergence using anisotropic thermal parameters for all non-hydrogen atoms.

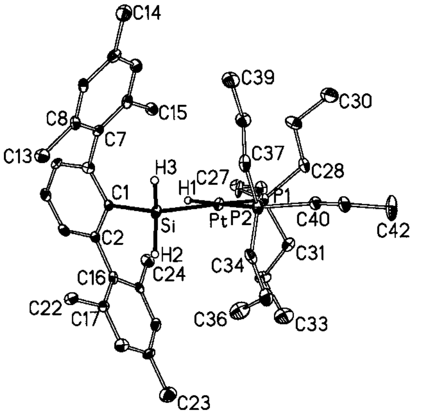
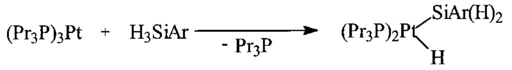


Figure 1. Molecular structure of *cis*-(2,6-Mes$_2$C$_6$H$_3$(H)$_2$Si)Pt(H)(PPr$_3$)$_2$ with thermal ellipsoids drawn at 30% probability. Phenyl and alkyl hydrogen atoms have been omitted for clarity.

Results and Discussion

cis-(2,6-Mes$_2$C$_6$H$_3$(H)$_2$Si)Pt(H)(PPr$_3$)$_2$ (**1**) is prepared by the reaction of (Pr$_3$P)$_3$Pt and 2,6-Mes$_2$C$_6$H$_3$SiH$_3$ and is isolated with the cocrystallate Pr$_3$PO as colorless crystals (mp 69−72 °C) (eq 1). The source of the Pr$_3$PO is the (Pr$_3$P)$_3$Pt reagent. As reported in the literature,[3c] (Pr$_3$P)$_3$Pt could not be isolated free of Pr$_3$PO. The structure of **1** is consistent with the ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR and IR spectroscopic data. The IR spectrum for **1** shows two absorbances in the Pt−H and Si−H region at 2067 and 2049 cm^{-1}. Assignment of these stretching frequencies is difficult due to the overlapping regions assigned for Pt−H and Si−H stretching bands.[11] The most notable features in the ^{1}H NMR spectrum are the Si−H (4.58 ppm, dd, J_{H-P}(trans) = 7.2 Hz and J_{H-P}(cis) = 3.0 Hz, J_{H-Si} = 166 Hz) and the Pt−H (−3.40 ppm, dd, J_{H-P}(cis) = 23.0 Hz and J_{H-P}(trans) = 154 Hz, J_{Pt-H} = 891 Hz) chemical shifts. In the ^{31}P NMR, the two chemically inequivalent phosphorus atoms give rise to two doublets centered at 14.1 ppm (J_{P-P} = 16.2 Hz, J_{P-Pt} = 1715 Hz). and 4.9 ppm (J_{P-P} = 16.2 Hz, J_{P-Pt} = 2231 Hz). The proton-decoupled ^{29}Si NMR shows a doublet of doublets centered at −54.9 ppm (J_{Si-P}(trans) = 166 Hz and J_{Si-P}(cis) = 14.7 Hz.) with satellite peaks (J_{Si-Pt} = 1132 Hz).[12]



$$(Pr_3P)_3Pt + H_3SiAr \xrightarrow[- Pr_3P]{} (Pr_3P)_2Pt\begin{matrix}SiAr(H)_2\\ H\end{matrix} \quad (1)$$

1

Ar = C$_6$H$_3$Mes$_2$-2,6

A crystal of **1**·Pr$_3$PO was studied by X-ray diffraction, and its structure is shown in Figure 1. Selected bond distances and angles are given in Table 2. Compound **1** cocrystallizes in the monoclinic space group $P2_1/n$ as two discrete molecules, Pr$_3$PO and *cis*-(2,6-Mes$_2$C$_6$H$_3$(H)$_2$Si)-Pt(H)(PPr$_3$)$_2$. The structural description will be limited to the mono(silyl)platinum(II) molecule, which exists as a distorted-square-planar Pt(II) complex with P1−Pt−

---

[9] Hope, H. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; Chapter 10.

[10] SHELXTL, Version 5.11; Siemens Analytical Instruments, Madison, WI, 1997.

[11] (a) Muetterties, E. L. In *Transition Metal Hydrides*; Dekker: New York, 1971; p 88. (b) Stock, A. In *Hydrides of Boron and Silicon*; Cornell University Press: Ithaca, NY, 1957.

[12] The ^{29}Si chemical shift for *cis*-(2,6-Mes$_2$C$_6$H$_3$(H)$_2$Si)Pt(H)(PPr$_3$)$_2$ (**1**; −54.9 ppm) is shifted downfield when compared to the same value reported for the silane precursor 2,6-Mes$_2$C$_6$H$_3$SiH$_3$ (−77 ppm) in ref 8.

Table 2. Selected Bond Distances (Å) and Angles (deg) for *cis*-(2,6-$Mes_2C_6H_3(H)_2Si$)Pt(H)(PPr_3)$_2$ (1)

Pt−Si	2.357(2)	Pt−P2	2.295(2)
Pt−P1	2.312(2)	Si−C1	1.905(6)
P1−Pt−P2	105.5(7)	P1−Pt−Si	163.02(6)
P2−Pt−Si	91.26(7)	C1−Si−Pt	116.7(2)

P2 = 105.50(7)°, P1−Pt−Si = 163.02(6)°, and P2−Pt−Si = 91.26(7)° bond angles. The deviation from the P_2PtSi plane is greatest at the Pt atom (0.03 Å) and can be attributed to steric repulsion between the silyl and phosphorus ligands and the relatively small space required for the platinum hydride. The Pt−Si (2.357(2) Å) distance is similar to the values reported for the same bonds in *cis*-H(Ph_3Si)Pt[$Cy_2P(CH_2)_4PCy_2$] (2.363(4) Å),[13] *cis*-H(Ph_3Si)Pt(PPh_3)$_2$ (2.357(3) Å),[14] and *cis*-H($SiPh_3$)-Pt(PEt_3)$_2$ (2.357(3) Å)[15] and within the range (2.321−2.406 Å) of values reported for mononuclear silyl complexes.[1a] The Pt−P1 bond (2.312(2) Å) trans to the silyl ligand is slightly longer than the Pt−P2 bond (2.295(2) Å) situated cis, indicating only a slightly greater trans influence of the silyl ligand with respect to the hydride ligand. This is consistent with the J_{P-Pt} (1715 and 2231 Hz) coupling values observed in the ^{31}P NMR spectrum. The Si−C1 bond (1.905(6) Å) is quite normal; however, the geometry of the silicon atom deviates significantly from an ideal tetrahedron with a C1−Si−Pt (116.7(2)°) bond angle. The hydrides bound to platinum and silicon were located in the difference map but not refined at distances of 1.5 Å (Pt−H) and 1.4 Å (Si−H).

A notable feature of **1** is its reluctance to eliminate H_2 (16 h at 50 °C). Similar observations have been reported for *cis*-(Cy_3P)$_2$Pt(H)($SiHMes_2$), which also does not undergo reductive elimination of hydrogen.[7g]

Conclusion

The compound *cis*-(2,6-$Mes_2C_6H_3(H)_2Si$)Pt(H)(PPr_3)$_2$ (**1**) represents an example of a mono(silyl)platinum(II) complex obtained by the oxidative addition reaction of a primary arylsilane to a Pt(0) complex.

Acknowledgment. We wish to thank the National Science Foundation for financial support. We also wish to thank Joshua R. Simons and Michaele Tisevich-Sanow for their contributions.

Supporting Information Available: Tables giving X-ray crystallographic data for **1**·Pr_3PO. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0004038

---

(13) Mullica, D. F.; Sappenfield, E. L.; Hampden-Smith, M. J. *Polyhedron* **1991**, *10*, 867−872.

(14) Latif, L. A.; Eaborn, C.; Pidcock, A. P.; Weng, N. S. *J. Organomet. Chem*. **1994**, *474*, 217−221.

(15) Koizumi, T.; Osakada, K.; Yamamoto, T. *Organometallics* **1997**, *16*, 6014−6016.