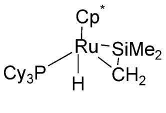
Silene–Organometallic Complexes

The Direct Synthesis of a Silene–Organometallic Complex**

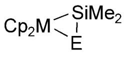
Dmitry Bravo-Zhivotovskii, Hanan Peleg-Vasserman, Monica Kosa, Gregory Molev, Mark Botoshanskii, and Yitzhak Apeloig**

Dedicated to Professor Henry F. Schaefer III
on the occasion of his 60th birthday

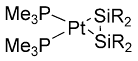
The first stable compounds with doubly bonded silicon atoms were reported in 1981 and since then vast progress has been made in this field,[1] including the synthesis of several transition-metal complexes of silenes and disilenes such as compounds **1**–**4**.[2–6] However, while numerous olefin–organometallic complexes were synthesized directly from the corresponding olefins, all known silene complexes were synthesized by indirect processes. For example, **1**,[3] **2a**,[4] **2b**,[5] **3**,[6] **4a** and **4b**[7a,b] were all obtained by cyclization reactions. Only **4c** was synthesized by a direct reaction of a disilene with an organometallic reagent, but its molecular structure was not determined by X-ray crystallography (Mes = $C_6H_2Me_3$).[7b]



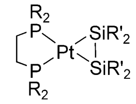
1



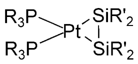
2a, E = CH_2, M = W,
2b, E = $SiMe_2$, M = W, Mo



3, R = $SiMe_2tBu$

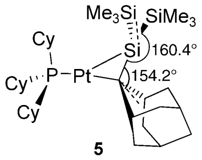


4a, R = Ph, R' = *i*Pr;
4b, R = cyclohexyl, R' = Ph

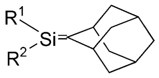


4c, R = Ph, Et, R' = Mes;

We report herein the synthesis and the molecular and electronic structure of a novel platinum η^2-silene complex, **5**, the first silene complex synthesized by a direct reaction of a silene (**6**) and an organometallic reagent $Pt(PCy_3)_2$.



5
Cy = cyclohexyl



6, $R^1=R^2=Me_3Si$
7, $R^1 = Me_3Si$, $R^2 = tBuMe_2Si$
8, $R^1 = R^2 = Me_3SiMe_2Si$

Our initial attempts to obtain a silene–platinum complex by a reaction of $Pt(PCy_3)_2$[8] and the stable silenes **7**[9] and **8**[10] failed, thus leading to a complex mixture of products. Molecular models reveal that the double bond in **7** and **8** is so effectively protected by the very bulky R^1 and R^2 substituents that the desired complex cannot be formed. A less heavily substituted silene was required and we chose **6**, which is obtained as a short lived intermediate.[11] Reaction of $(Me_3Si)_3SiLi{\cdot}3THF$ with 2-adamantanone in toluene at −70 °C yields the isolable addition adduct **9**.[12] On warming of the reaction mixture (or warming of **9** directly) to −30 °C the transient silene **6** was formed and its formation was monitored by ^{29}Si NMR (the NMR chemical shifts of **6** are very similar to those of the stable **7**[9]).[12] The warming of this reaction mixture to room temperature yielded dimer **10**, thus supporting the presence of silene **6**. Warming of the toluene reaction mixture from −30 °C to room tempretature in the presence of $Pt(PCy_3)_2$ led to the formation of **5** (31 %). A

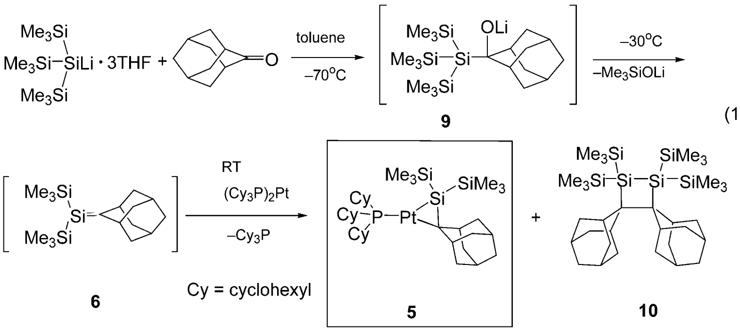
---

[*] D. Bravo-Zhivotovskii, H. Peleg-Vasserman, M. Kosa, G. Molev, M. Botoshanskii, Y. Apeloig
Department of Chemistry and
the Lise Meitner-Minerva Center for Computational Quantum Chemistry
Technion-Israel Institute of Technology
Haifa 32000 (Israel)
Fax: (+972) 4823-3735
E-mail: chrbrzh@tx.technion.ac.il
chrapel@tx.technion.ac.il

[**] This research was supported by the Israel Science Foundation administrated by the Israel Academy of Sciences and Humanities. We are grateful to Dr. Miriam Karni and Dr. Thomas Müller for helpful discussions. D.B.-Z. is grateful to the Ministry of Immigrant Absorption, State of Israel, for a Kamea scholarship.

DOI: 10.1002/ange.200353048

higher yield (40%) of the desired silene–platinum complex **5** (together with **10**, 37%) was obtained when Pt(PCy$_3$)$_2$ was added to a toluene solution of **9** at $-70\,^\circ$C and the solution was warmed to room temperature [Eq. (1)]. These experiments support strongly the conclusion that **5** is obtained by a direct reaction between the transient silene **6** and Pt(PCy$_3$)$_2$ as shown in Equation (1). Compound **5** was obtained as pale pink crystals and its molecular structure was determined by X-ray crystallography.[13]



(1)

The molecular structure of **5** (Figure 1) reveals the surprising presence of a tricoordinated Pt atom. Thus, the reaction of silene **6** with Pt(PCy$_3$)$_2$ involves a ligand substitution reaction at the dicoordinated Pt center at which one of the PCy$_3$ ligands is displaced to allow coordination with the sterically bulky silene. To our best knowledge this ligand exchange reaction is unprecedented in dicoordinated Pt compounds. Another unusual feature of the structure of **5** is the near colinearity of the C25-Pt1-P1 atoms (bond angle 177.7°).

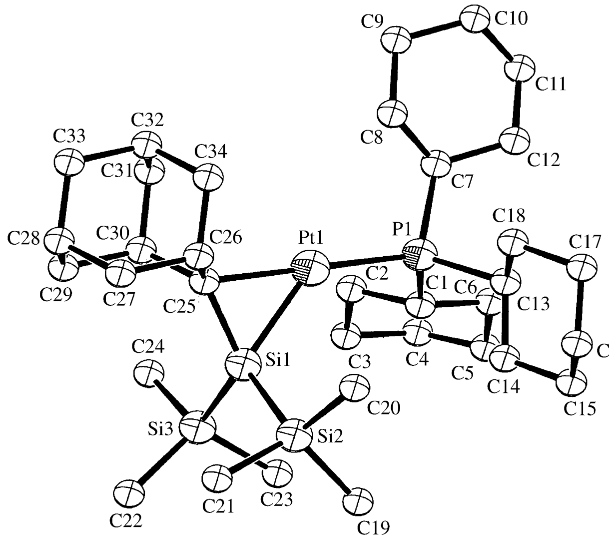
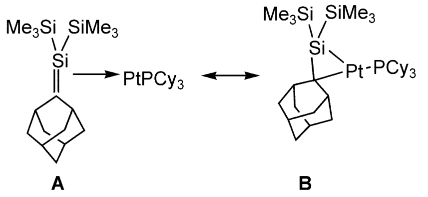


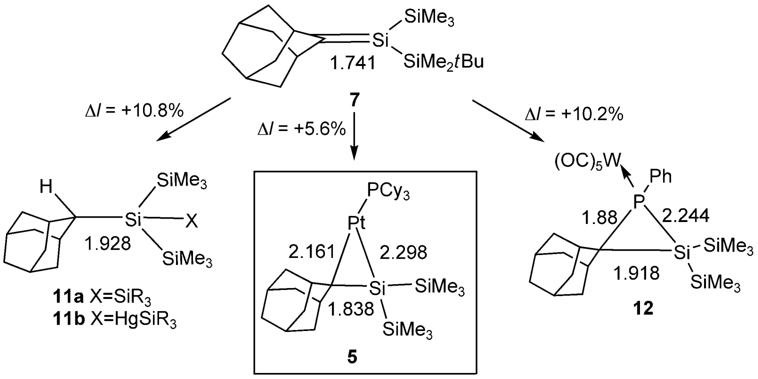
Figure 1. ORTEP diagram of the η^2-silene–platinum complex **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Si1-C25 1.838(12), Pt-Si1 2.298(3), Pt-C25 2.161(11), Pt-P 2.268(3), Si1-Si2 2.344(5), P-C7 1.861(11), C25-Pt-Si1 48.6(3), Pt-Si1-C25 61.8(3), Pt-C25-Si1 69.6(4), P-Pt-C25 177.7(3), P-Pt-Si 131.24(11), Pt-Si1-Si2 116.21(15), C25-Si1-Si2 119.5(4), C25-Si1-Si3 122.1(4), Si2-Si1-Si3 112.22(18), P-Pt-Si1-C25 177.0(4), C25-Pt-Si1-Si2 111.0(4), P-Pt-Si1-Si2 72.0(2).

The NMR spectrum is consistent with the molecular structure of **5**. The NMR signals of ^{29}Si1 ($\delta = 6.8$ ppm) and of ^{13}C25 ($\delta = 137.8$ ppm) of **5** are shifted upfield, as expected, compared to silenes (e.g., $\delta(^{29}\mathrm{Si}) = 51.7$ ppm, $\delta(^{13}\mathrm{C}) = 196.8$ ppm in **7**). The ^{31}P signal in **5** of $\delta = 21.5$ ppm is similar to that in Pt(PMe$_3$)$_3$.

Is **5** better described as a π-complex (**A**) or as a σ-bonded cyclopropane-type compound (**B**)?



One criterion to answer this question is the structure of **5**, most importantly the Si−C bond length and the degree of bending around the complexed Si=C bond.[14] Structural data for comparison with model compounds is given in Scheme 1.



Scheme 1. A comparison of Si−C bond lengths (Å) in several organosilicon compounds.

The Si=C bond of silene **7** (a close model for **6**) is elongated (Δ*l*) by 5.6%, from 1.741 Å in **7** to 1.838 Å in **5**. This bond elongation is similar to that found in **1**, **2a**, and **3**, compared to the corresponding Si=E bonds (Δ*l* = +5.8%, +6.4% and +5.4%, respectively). However, the *l*(Si−C) bond in **5** is significantly shorter than in related singly bonded compounds; e.g., 1.928 Å in **11a** and **11b**; [10b] thus Δ*l* in **11a** and **11b** is almost twice as large as in **5** (Scheme 1). The closest available comparison is between **5** and **12**,[15] as both have a three-membered ring; *l*(Si−C) in **5** is 0.08 Å shorter than in **12.**[16] The bending angles in **5** at Si1 and C25 of 160.4° and 154.2°, respectively, are larger than those of analogous angles in **3** (150.7°[6]). The sum of the angles around Si1 and C25 are 353.8° and 353.1° respectively. In conclusion, the geometrical parameters indicate that **5** is best described as a hybrid between π complex (**A**) and σ-bonded compound (**B**),as **5** has a higher π-complex character than the disilene complex **3**.[6]

The difference Fourier (DF) electronic map of **5** was studied experimentally at $-70\,^\circ$C and a cut through the main molecular plane is shown in Figure 2. Three main regions of accumulation of nonnuclear electron density are observed: (a) between Pt and the Si1 and C25 atoms, with significant density overlap at the center of the PtSiC ring and being polarized towards the Pt–C internuclear region (b) between the Si1 and C25 atoms—a maximum which is shifted outwards of the three-membered ring and towards the C atom, and (c) along the Pt–P bond, corresponding to a Pt–P σ bond.

Natural bond orbital (NBO)[17] calculations[18–20] for the model complex **13** reveal that on complexation 0.15 electrons are transferred from the organometallic fragment to the silene. In the complex, the π orbital of the silene ((H$_3$Si)$_2$Si=C(CH$_3$)$_2$), is depopulated to 1.64 electrons while the π*(C=Si) orbital is populated by 0.42 electrons. The σ* (Pt–P) antibonding orbital, which is located mainly on Pt, is populated with 0.31 electrons. According to the calculated second-order perturbation interaction energies[18b] the strongest orbital interaction in complex **13** (and thus in **5**) is interaction **14a**, between the polarized π(Si=C) orbital and the σ*(Pt–P) orbital. This interaction is also evident in the observed (Si–C), (Pt–Si) and (Pt–C) electron-density peaks. The strong polarization of π(Si=C) towards C and the good acceptor ability of phosphorous dictates the near linearity of the P-Pt-C angle. The energy difference between optimized **13** ($\sphericalangle$ P-Pt-Si = 129.6°, P–Pt–C = 180°) and its constrained isomer, in which $\sphericalangle$ P-Pt-Si = 180° is 15.9 kcal mol^{-1}. The second strongest interaction is **14b** between the filled Pt(d$_{xy}$) orbital and the empty π*(Si=C) orbital, which is polarized towards the Si atom. In general, the NBO calculations produce the classical Dewar–Chatt–Duncanson model.[21]

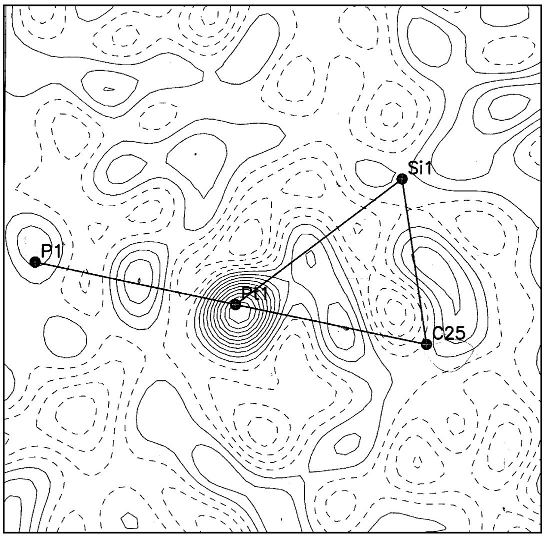
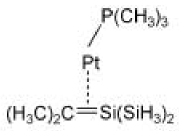
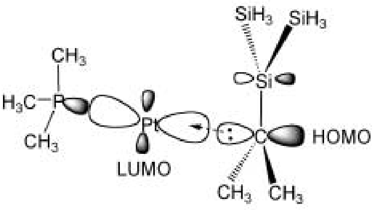


Figure 2. Difference Fourier electronic map of **5** at −70 °C, showing a cut through the main molecular plane.

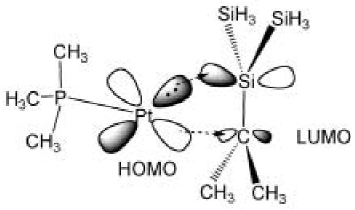
In summary, the silene—platinum complex **5** is best described as an hybrid between a π complex (**A**) and a σ-cyclopropane structure (**B**), which has a more pronounced π-complex character than the disilene complex **3**. We are currently studying the chemistry of **5** and using similar strategies to prepare other silene and disilene organometallic complexes.



13



14a



14b

Experimental Section

Standard Schlenk techniques were used for the syntheses and sample manipulations.

A toluene solution of (Me$_3$Si)$_3$SiLi·3 THF (0.123 g, 0.26 mmol; 10 mL) was added to a toluene solution of 2-adamantanone (0.038 g, 0.25 mmol; 10 mL), which was kept at −70 °C under vacuum. After the reaction mixture had been stirred for 30 min, a toluene solution of Pt(PCy$_3$)$_2$[8] (0.2 g, 0.26 mmol; 20 mL) was added and the mixture allowed to reach room temperature and maintained at this temperature overnight. The solvent was removed by evaporation and the crude product was crystallized from hexane (0.083 g, 0.1 mmol; 40 % yield), of pale pink crystals suitable for X-ray crystallization of **5** were obtained. ^{1}H NMR (C$_6$D$_6$): $\delta = 0.174$ (18 H s, SiMe$_3$), 1.2–2.4 ppm (14 H m, Ad, 33 H m, PCy$_3$); ^{13}C NMR (C$_6$D$_6$): $\delta = 137.8$ (1 C PtC(Ad)Si), 4.1 (6 C SiMe$_3$), 44.1, 43.0, 41.0, 35.9, 34.0, 32.7, 32.1, 31.9, 31.5, 29.1, 28.0, 26.9, 25.6 ppm (9 C Ad, 18 C PCy$_3$); ^{29}Si NMR (C$_6$D$_6$): $\delta = 6.8$ (1 Si PtSiAd), −14.67 ppm (2 Si SiMe$_3$); ^{31}P NMR (C$_6$D$_6$): $\delta = 21.5$ (1 P t $^1J_{\mathrm{Pt,P}} = 1475$ Hz, PCy$_3$); MS(CI) m/z 756.3 ($M-2$Me).

Received: October 9, 2003 [Z53048]
Published Online: January 8, 2004

Keywords: bond theory · platinum · Si ligands · transition metals

[1] T. Müller, W. Ziche, N. Auner, *The Chemistry of Organic Silicon Compounds*, *Vol. 2* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, chap. 16.
[2] T. D. Tilley, *The Silicon-Heteroatom Bond* (Eds.: S. Patai, Z. Rappoport) **1991**, chap. 10, p. 330.
[3] a) B. K. Campion, R. H. Heyn, T. D. Tilley, *J. Am. Chem. Soc.* **1988**, *110*, 7558; b) B. K. Campion, R. H. Heyn, T. D. Tilley, *J. Am. Chem. Soc.* **1990**, *112*, 4079.
[4] T. S. Koloski, P. J. Carroll, D. H. Berry, *J. Am. Chem. Soc.* **1990**, *112*, 6405–6406.
[5] J. H. Chey, P. J. Carroll, H. S. Zipin, D. H. Berry, *J. Am. Chem. Soc.* **1990**, *112*, 452–453.
[6] H. Hashimoto, Y. Sekiguchi, T. Iwamoto, C. Kabuto, M. Kira, *Organometallics* **2002**, *21*, 454–456.

[7] a) E. K. Pham, R. West, *J. Am. Chem. Soc.* **1989**, *111*, 7667–7668; b) E. K. Pham, R. West, *Organometallics* **1990**, *9*, 1517.

[8] R. Yoshida, S. Otsuka, *Inorg. Synth.* **1979**, *19*, 105.

[9] Y. Apeloig, M. Bendikov, M. Yuzefovich, M. Nakash, D. Bravo-Zhivotovskii, D. Bläser, R. Boese, *J. Am. Chem. Soc.* **1996**, *118*, 12228–12229.

[10] a) M. Bendikov, MSc thesis, Technion-Israel Institute of Technology, **1996;**b) N. Sigal, MSc thesis, Technion-Israel Institute of Technology, **2001**.

[11] D. Bravo-Zhivotovskii, V. Braude, A. Stanger, M. Kapon, Y. Apeloig, *Organometallics* **1992**, *11*, 2326.

[12] D. Bravo-Zhivotovskii, G. Korogodsky, Y. Apeloig, *J. Organomet. Chem.* **2003**, *686*, 58.

[13] X-ray structure data: Nonius Kappa CCD diffractometer; phi-scans; $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$); $T = 220$ K; semiempirical absorption correction; the structure were solved by direct methods with SHELXS-97 and refined against F^2 with SHELXL-97. The hydrogen atoms were generated with idealized geometry. Crystal structure data: Pt1 P1 Si3 C34 H65; $M_r = 784.18$; crystal size $0.14 \times 0.125 \times 0.038$ mmmonoclinic space group $P21/n$, $a = 13.455(3)$ Å, $b = 19.568(4)$ Å, $c = 14.818(3)$ Å, $\beta = 106.15(3)$, $V = 3747(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.39$, $\mu(Mo_{K\alpha}) = 3.904$ mm^{-1}, $F(000) = 1616.0$, $2\theta_{max} = 50.04$, 24189 reflections measured, 6587 unique reflections ($R_{int} = 0.098$), final $R_1 = 0.0623$ for 3782 reflections [$I > 2\sigma(I)$], $R_w = 0.1142$(all data), residual maximum electron density 1.714 e$^-$ Å^3. CCDC-220373 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[14] J. Uddin, S. Dapprich, G. Frenking, B. F. Yates, *Organometallics* **1999**, *18*, 457–465.

[15] M. J. M. Vlaar, A. W. Ehlers, F. J. J. de Kanter, M. Schakler, A. L. Spek, M. Lutz, N. Sigal, Y. Apeloig, K. Lammertsma, *Angew. Chem.* **2000**, *112*, 4296–4299; *Angew. Chem. Int. Ed.* **2000**, *39*, 4127–4129.

[16] *l*(Pt–C) in **5** of 2.161 Å is within the range found in a bisolefin platinum monophosphane complex (2.154–2.185 Å),[16a] but it is shorter than *l*(Ru–C) and *l*(W–C) in **1** and **2a** of 2.250 Å and 2.329 Å, respectively. *l*(Pt–Si) in **5** of 2.298 Å is at the shorter end of reported *l*(Pt–Si) distances (2.255–2.444 Å[16b]), but it is significantly shorter than in **3** (2.43 Å). a) G. Chandra, P. Y. Lo, P. B. Hitchcock, M. F. Lappert, *Organometallics* **1987**, *6*, 191–192; b) J. Y. Corey, J. Braddock-Wilking, *Chem. Rev.* **1999**, *99*, 175.

[17] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926.

[18] The fully optimized geometry of **13** is similar to that of **5.** All calculations were performed with the Gaussian 98 program[18a] with implementation of NBO version 5.0;[18b] a) Gaussian 98 (Revision A.11.3), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2002**.; b) NBO 5.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, **2001**; http://www.chem.wisc.edu/~nbo5.

[19] All calculation used the B3LYP/6-31G(d) level of theory for all atoms, except for Pt for which B3LYP/SDD was used.

[20] For previous theoretical studies on Pt–silene complexes see: a) T. R. Cundari, M. S. Gordon, *THEOCHEM* **1994**, 47; b) S. Sakaki, M. Ieki, *Inorg. Chem.* **1991**, *30*, 4218.

[21] a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.* **1951**, *18*, C79; b) J. Chatt, L. A. Duncanson, *J. Chem. Soc.* **1953**, 2929.