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Silyl–Silylene Interplay in Cationic PSiP Pincer Complexes of Platinum

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S Supporting Information

ABSTRACT: Herein we report the synthesis and spectroscopic observation of a Pt complex featuring a P_2Si [igand containing a central silylene donor connected to phosphines via two *o*-arylene linkers. Species of the type (P_2Si)PtR undergo a net 1,2-migration of R from Pt to Si, which leads to highly unsaturated Pt cations displaying only a very distant interaction with the weakly coordinating carborane anion.

The proliferation of pincer-style ligands has led to a number of discoveries in the fundamental reactivity of transition metals and their catalytic applications. The success of pincer ligands is due in part to the feasibility of incorporating different combinations of donor atoms into these tridentate, meridionally binding frameworks.¹ Among the many options, incorporation of silylene donors (R₂Si) remains uncommon. Recent work by Hartwig and Driess explored N-heterocyclic silylenes as side arms (Chart 1, A),² while the appearance of silylene in a central

Chart 1. Pincer Complexes with Silylene and Carbene Donors



donor position of a pincer has only been documented in a 1993 report by Zybill et al. (**B**).³ We were especially interested in accessing a silylene housed within a structure where it is connected to phosphine side arms by *o*-arylene linkers. This connectivity provides for a very robust framework prearranged for meridional binding to averagely sized transition metals. Topologically similar ligands with central C, ⁴ N, ⁵ O, ⁶ P, ⁷ and Sb⁸ as well as silyl^{9–12} donors have been broadly explored. Recent work by Whited et al. implicated a silylene intermediate in some reactions of (PSiP)Rh complexes, but silylene was not directly observed (C).¹³

Our group previously reported syntheses of carbene/ bis(phosphine) complexes of Pd that were synthesized by a combination of C–H activation at Pd^{II} followed by hydride abstraction (**D**).¹⁴ Taking note of the existence of (PSi^HP)PtCl



(2), we surmised⁹ that hydride abstraction^{15,16} from the HSi–Pt group could provide access to cationic silylene/bis(phosphine) complexes of Pt. Herein we report that, while our efforts were successful, the silylene complexes proved to be rather unstable and displayed behavior indicative of substantial silylium character of these species.

Metalation of $PSi^{H2}P$ (1) with $Pt(1,5\text{-}COD)Cl_2$ in the presence of 2,6-lutidine produced a mixture of 2 and $(PSi^{Cl}P)$ -PtCl, but it was possible to isolate pure 2 in 85% yield after recrystallization. Milstein's synthesis of 2 using $(Me_2S)_2Pt(Me)$ -Cl gave 62% yield following chromatographic purification.⁹ Simple salt metathesis reactions allowed replacement of chloride in 2 with other anionic ligands to give 3–6 (Scheme 1).





Compounds **2–6** were characterized by multinuclear NMR spectroscopy and **2** by a solid-state diffraction study. The presence of a central silvl donor with an sp³-hybridized Si atom carrying a hydrogen was evident from the NMR data: the ²⁹Si NMR resonances ranged from –1.5 to 43.1 ppm ($J_{Pt-Si} = 608-1192$ Hz), while in the ¹H NMR spectrum, a signal showing coupling to ²⁹Si (${}^{1}J_{Si-H}$ between 166 and 193 Hz) and ¹⁹⁵Pt (${}^{2}J_{Pt-H}$ between 20 and 60 Hz) was observed in the 5.5–6.5 ppm range.

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Hydride abstraction reactions from the central Si–H were carried out by the treatment of **2**, **3**, **5**, and **6** with Ph_3C^+ salts of $[HCB_{11}Cl_{11}]^-$ or $[EtCB_{11}Cl_{11}]^-$ anions^{17,18} in C_6H_5F (Scheme 2). The two different carborane anions can be viewed as

Scheme 2. Abstraction Reactions of (PSi^HP)PtR



equivalent in their coordinating ability and simply offered a way to alter the solubility and crystallinity of the salts of cations of interest. Abstraction of the hydride proceeded rapidly in all cases and resulted in the formation of Ph₃CH. In the reaction of 2, immediate formation of the major Pt-containing product was evident. The NMR spectroscopic data (²⁹Si NMR, δ 32.7 ppm) were inconsistent with the silylene formulation, for which a chemical shift of >200 ppm is expected.^{15,19} Instead, the NMR data pointed to the isomeric structure **2b** and were corroborated by an XRD structural study (Figure 1). Isomerization of the



Figure 1. ORTEP²² drawings (50% probability ellipsoids) of **2b** (top) and **7b** (bottom). H atoms and methyl groups of isopropyl are omitted for clarity. Selected distances (Å) and angles (deg) are as follows. For **2b**: Pt1–Si1, 2.2452(12); Si1–Cl1, 2.0785(15); Pt1–Cl2, 2.9206(13); P1–Pt1–P2, 163.30(4); Cl2–Pt1–Si1, 177.38(3). For **7b**: Pt1–Si1, 2.2756(10); Si1–Cl3, 1.901(4); Pt1–Cl12, 2.902(1); P1–Pt1–P2, 153.99(4); Si1–Pt1–Cl12, 167.62(4).

putative **2a** into **2b** can be viewed as a net migration of chloride from Pt to Si. Similarly, abstraction of hydride from **3** and **5** led to **3b** and **5b** (²⁹Si NMR, δ 50.1 and 20.7 ppm, respectively). On the other hand, abstraction of hydride from **6** proceeded to **6b** via an intermediate (**6a**) that appeared to be associated with the development and then disappearance of the red color. **6a** was observed by ³¹P NMR spectroscopy in C₆H₅F at 65.5 ppm (¹J_{Pt-P} = 2828 Hz), but it was not long-lived enough to isolate or collect ²⁹Si NMR data. We surmised that a bulkier aryl may retard the rate of migration and prepared the mesityl derivative 7 via reaction of **2** with Mes₂Mg. Treatment of 7 with Ph₃C-[HCB₁₁Cl₁₁] resulted in the development of a deep red color presumed to correspond to the proposed silylene species 7**a**. At room temperature, this species was observed as a broad resonance at 69.2 ppm in the ³¹P NMR spectrum. This signal became sharper at 243 K, and the coupling to ¹⁹⁵Pt (¹J_{Pt-P} = 2526 Hz) was further resolved. The diagnostic^{15,19} silylene downfield signal at 323.1 ppm (¹J_{Pt-Si} = 879 Hz) was observed in the ²⁹Si NMR spectrum.

In solution at ambient temperature, the silylene complex 7a did undergo isomerization to its silyl isomer 7b, whose structure was confirmed by a single-crystal XRD study (Figure 1). Loss of the silylene character in 7b arising from formal migration of mesityl from Pt to Si was apparent from ²⁹Si NMR data, with a new signal observed at 6.84 ppm (${}^{1}J_{Pt-Si} = 1267$ Hz). The rate of isomerization of 7a to 7b proved to be poorly reproducible: it had been observed to take place over 16 h or after as little as 30 min at ambient temperature. It is possible that the rate of isomerization is affected by the presence of varying amounts of impurities. Unfortunately, this ultimately prevented us from obtaining X-ray-quality crystals or consistently pure batches of 7a in the solid form.

DFT calculations were used to examine the isomerization of cations of 2a', 5a', and 6a' into 2b', 5b', and 6b' (where ' indicates the gas-phase cation, Table 1). In accord with the

Table 1. Calculated Energies for Silylene to Silyl Isomerization



^{*a*}Gas-phase calculations for cationic species without $[HCB_{11}Cl_{11}]^-$ (denoted with ') were performed at the B3LYP level.²⁰ Calculated energies are given in kcal/mol.

experiment, the migration of Cl/Me/Ph from Pt to Si was calculated to be favorable by -18.2, -34.5, and -31.4 kcal/mol, respectively. Relative energies for the isomers 8a'/8b' and 9a'/9b' involving -SPh and -TePh substituents were also calculated, under the notion that migration of the softer Lewis bases thiolate and tellurolate from soft Pt to hard Si may be less favorable. The computed reaction free energies were less negative (-20.1 and -11.3 kcal/mol, respectively), but because the isomerization was still predicted to be favorable, the synthesis of 8 and 9 was not attempted.

The ²⁹Si NMR chemical shifts for 7a and **6b** (including a $[HCB_{11}Cl_{11}]^-$ anion in the gas phase, M06/SDD/6-31G(d))²⁰ were calculated to be 302.8 and 53.5 ppm. While these do not reproduce the experimental values (323 ppm for 7a and 33.0 ppm for **6b**) precisely, they are consistent with the highly downfield chemical shift for the silylene species. The calculated Pt–Si distances in the silylene complexes are only marginally (0.02–0.08 Å) shorter than those in their silyl isomers.

Calculations indicate that the LUMO of 7a (Figure 2) is primarily based on the Si p orbital, with some delocalization into



Figure 2. Depiction of the LUMO (isovalue 0.03) of structure 7a with $[HCB_{11}Cl_{11}]^-$, calculated by M06/SDD/6-31G(d). Hydrogen atoms are omitted for clarity.

the aromatic rings and only a modest contribution from a d orbital of Pt. The Wiberg bond indices for Si–Pt were calculated to be 0.68 in **6b** and 0.74 in **7a**. Thus, although the Si center in **7a** is planar (i.e., sp² hybridized), the modest extent of π bonding between Pt and Si suggests that **7a** may be analyzed as a platinyl-substituted silylium cation.²¹ On the other hand, any shortening of the Si–Pt bond in **7a** vs **7b** owing to an increase in the Pt–Si bond order should be attenuated since the silyl Si is trans to an empty site, while the silylene Si is not. Not surprisingly, the difference between the Pt–Si bond lengths in silylene vs silyl is greatest in **2b**, where the chloride ligand has a weaker trans influence than alkyls or aryls. This analysis also explains why the experimentally observed ¹J_{Pt–Si} coupling constant in **7a** (879 Hz) is actually smaller than that in its **7b** isomer (1267 Hz) and is closer to that in the neutral complex **7** (608 Hz).

We observed that solutions of 7b upon standing for 26 h evolved to generate the new product 10, resonating at 85.6 ppm in the ³¹P NMR spectrum. An XRD study on a single crystal (Figure 3) surprisingly revealed that 10 is a product of the apparent protodesilylation of mesitylene,²³ resulting in two Pt



Figure 3. ORTEP²² drawing (50% probability ellipsoids) of 10. H atoms and *o*-difluorobenzene cocrystallized solvent are omitted for clarity. Selected distances (Å) and angles (deg) are as follows: Pt1–Si1, 2.2499(18); Si1–O1, 1.639(2); Pt1–Cl11, 2.8753(16); P1–Pt1–P2, 162.88(7); Si1–Pt1–Cl11, 141.97(6); O1–Si1–Pt1, 113.91(19); Si1–O1–Si1#1, 149.8(4).

cationic units linked together by a siloxane bridge (Scheme 3). Dissolution of crystals from the same batch gave the same ³¹P



NMR resonance at 85.6 ppm, and the formulation of the solid was supported by elemental analysis. The siloxane-bridged PSiP ligand has been previously described by Milstein,⁹ but in a saturated complex (Scheme 3) in which the Si–O bond had been formed by Si–H oxidation. Tilley's disiloxane, also a saturated system, was derived from a silylene complex by the apparent addition of O–H across the Si=Ir bond.²⁴ In contrast, 7b reacts by hydrolysis of the Si–C(mesityl) bond with retention of unsaturation at Pt. Protolysis of a Si–C(mesityl) bond under highly acidic conditions was productively exploited by Siegel et al. in studies of catalytic C–F activation of aromatic C–F bonds.²⁵

In the solid-state structures of each of the complexes 2b and 7b (Figure 1) and 10 (Figure 3), one of the chlorines of the carborane anion approaches the Pt center trans to the silvl donor. While the Si-Pt-Cl angles vary from ca. 142 to ca. 178°, the Pt… Cl distances are quite similar at ca. 2.9 Å.²⁶ They are much longer than the distances between Pt and the anionic Cl ligand in 2 (2.4524(14) Å) or PSi^{Me}P-Pt-Cl (2.437(2) Å),¹⁰ but they are also considerably longer than the previously reported Pt-Cl distances in Pt(II) dichloromethane complexes $(2.49-2.62 \text{ Å})^{27}$ or in the AlCl₄ adduct of $[PSi^{Me}P-Pt]^+$ (2.5640(9) Å).^{11,28} The X-ray structures of 2b, 7b, and 10 are also in good agreement with the calculated anion-free structures, as can be illustrated by the similarity of calculated and XRD values for the Pt-Si distance (2.284 Å for 2b' vs 2.2452(12) Å for 2b). All in all, the Pt…Cl distances in 2b, 7b, and 10 are likely indicative of a close cationanion approach rather than a proper dative $Cl \rightarrow Pt$ bond. It is reflective of the stabilization of the empty site at Pt(II) by a strongly trans influencing silyl ligand and the steric clash between the bulky carborane and the PSi^XP ligand. The various degrees of weak stabilization of empty sites in otherwise three-coordinate Pt(II) complexes have recently been reviewed.²⁹

In summary, we have been able to access a silylene-containing pincer ligand in the coordination sphere of Pt. The silylene has proven to be an observable but short-lived species that isomerizes by abstraction of the anionic ligand from the position trans to it. DFT analysis suggests that the cationic silylene complex has only a modest degree of π bonding with Pt and may be viewed as a silylium cation with a platinyl substituent. From this perspective, it is not surprising that it readily engages in the abstraction of anionic ligands. The products of such abstraction are effectively three-coordinate cationic Pt complexes with only distant approach of the carborane anion to a position trans to the silyl donor. One of these complexes underwent an unexpected apparent hydrolysis by adventitious water with preservation of the highly unsaturated character at Pt.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.5b00596.

Details of experimental and computational procedures and characterization (PDF)

Structures of all compounds studied (ZIP) Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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