

## Four-Coordinate, Trigonal Pyramidal Pt(II) and Pd(II) Complexes

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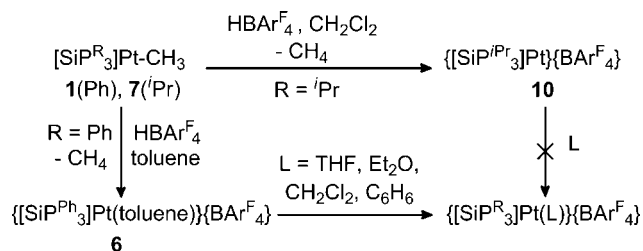
**Abstract:** We report herein the characterization of electrophilic, trigonal bipyramidal  $\{[\text{SiP}_3^{\text{R}}]\text{Pt}(\text{L})\}^+$  cations ( $[\text{SiP}_3^{\text{R}}] = [(2\text{-R}_2\text{PC}_6\text{H}_4)_3\text{Si}]$ ;  $\text{R} = \text{Ph}, ^i\text{Pr}$ ) that feature weakly coordinated ligands including  $\text{CH}_2\text{Cl}_2$ ,  $\text{Et}_2\text{O}$ , toluene, and  $\text{H}_2$ . A cationic toluene adduct that shows a close platinum aryl C–H  $\sigma$ -contact is perhaps most noteworthy in this context. For the isopropyl-substituted ligand,  $[\text{SiP}_3^{\text{Pr}}]$ , it has proven possible to exclude the fifth axial donor to afford the rigorously four-coordinate, trigonal pyramidal (TP) complex  $\{[\text{SiP}_3^{\text{Pr}}]\text{Pt}\}^+$ . An isostructural TP palladium complex  $\{[\text{SiP}_3^{\text{Pr}}]\text{Pd}\}^+$  is also accessible. Prototypical four-coordinate  $d^8$  platinum and palladium complexes are square planar. The TP  $d^8$  cations described herein are hence geometrically distinct.

Electrophilic platinum(II) compounds have been studied extensively due to their ability to activate C–H bonds such as those in methane and other cheap hydrocarbons.<sup>1,2</sup> As these species are almost always square planar, it is of interest to consider how other geometries might impact the electrophilicity and reactivity of Pt(II) centers. Using the tris(phosphino)silyl scaffold  $[\text{SiP}_3^{\text{R}}]^-$  ( $[\text{SiP}_3^{\text{R}}]^- = [(2\text{-R}_2\text{PC}_6\text{H}_4)_3\text{Si}]^-$ ;  $\text{R} = \text{Ph}, ^i\text{Pr}$ )<sup>3</sup> we sought to access trigonal bipyramidal (TBP) platinum(II) cations featuring weakly coordinated ligands in the axial site. We report herein the characterization of TBP  $[\text{SiP}_3^{\text{R}}]\text{Pt}-\text{L}$  cations, including a toluene adduct that presents a close aryl C–H contact to the platinum center. We moreover establish that it is possible to completely exclude the weak axial donor to afford a rigorously four-coordinate, trigonal pyramidal (TP) Pt(II) species. An isostructural complex is accessible for Pd(II). These species expand the small number of isolable  $d^8$  complexes that populate a TP geometry.<sup>4,5</sup>

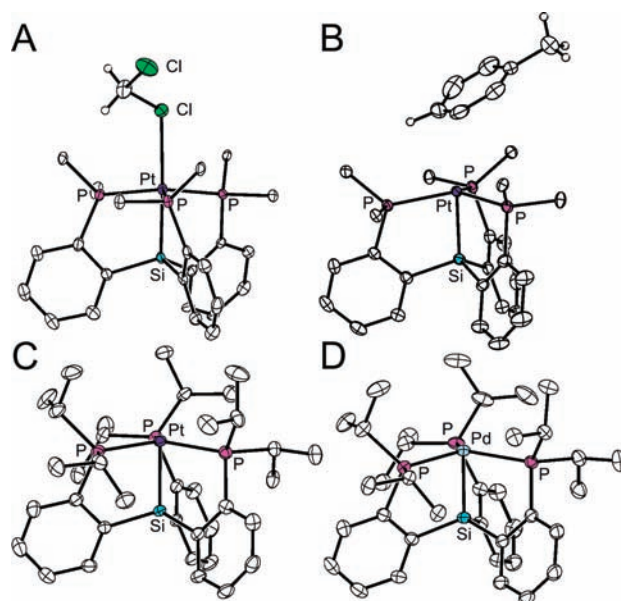
The neutral Pt(II) complexes  $[\text{SiP}_3^{\text{Ph}}]\text{Pt}-\text{CH}_3$  (**1**),  $[\text{SiP}_3^{\text{Ph}}]\text{Pt}-\text{Cl}$  (**2**), and  $[\text{SiP}_3^{\text{Ph}}]\text{Pt}-\text{H}$  (**3**) are readily accessible by Si–H activation of the phenyl-substituted ligand  $[\text{SiP}_3^{\text{Ph}}]\text{H}$  with  $(\text{COD})\text{PtMe}_2$ ,  $(\text{COD})\text{PtCl}_2$ , and  $\text{Pt}(\text{PPh}_3)_4$ , respectively. These yellow complexes exhibit 3-fold symmetry in solution at room temperature and have TBP geometries in the solid state with an average  $\tau_5 = 0.88$  (see Supporting Information for all crystallographic details).<sup>6</sup> Protonation of **1** in  $\text{CH}_2\text{Cl}_2$  at room temperature with  $\text{H}(\text{OEt}_2)_2\text{BAR}^{\text{F}_4}$  ( $\text{BAR}^{\text{F}_4} = \text{B}[3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3]_4$ ) provides access to a series of cationic solvento adducts (Scheme 1). The crystallographically characterized diethyl ether  $\{[\text{SiP}_3^{\text{Ph}}]\text{Pt}(\text{OEt}_2)\}\{\text{BAR}^{\text{F}_4}\}$  (**4**) and dichloromethane  $\{[\text{SiP}_3^{\text{Ph}}]\text{Pt}(\text{Cl}_2\text{CH}_2)\}\{\text{BAR}^{\text{F}_4}\}$  (**5**) adducts are yellow-orange while the toluene adduct  $\{[\text{SiP}_3^{\text{Ph}}]\text{Pt}(\text{toluene})\}\{\text{BAR}^{\text{F}_4}\}$  (**6**) is red-brown, consistent with d–d transitions from a  $d_{xy}/d_{x^2-y^2}$  HOMO to a  $d_z$  LUMO.

The solid-state structure of **6** (Figure 1) suggests possible coordination of the toluene to the cationic Pt center through the *para* aryl C–H bond rather than the  $\pi$ -cloud of the aryl ring. Such an interaction is of particular interest for an electrophilic platinum species as studies have suggested that aryl C–H bond activations proceed via an initial aryl C–H  $\sigma$ -complex that isomerizes to more stable, and in certain cases observable,  $\pi$ -arene adduct species.<sup>7</sup>

### Scheme 1

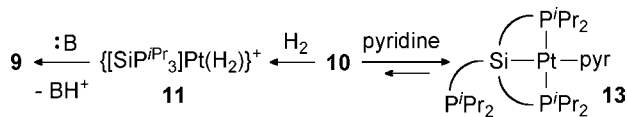


C–H  $\sigma$ -complexes have mostly been detected transiently or indirectly, with a notable exception being a Rh(I)  $\sigma$ -methane complex characterized by NMR at low temperatures.<sup>8,9</sup> The *para* hydrogen of **6** was located in the difference map at 1.02 Å from the *para* carbon atom, in contrast with three of the other aromatic hydrogens, which were located at an average of 0.96 Å from their respective carbon atoms.<sup>10</sup> The *para* hydrogen was refined freely to a distance of 2.672 Å from the Pt center while the *para* carbon is 2.766 Å from Pt; the Pt–H<sub>*para*</sub>–C<sub>*para*</sub> angle is 84.0°. These values fall slightly outside the normal range for intramolecular agostic interactions.<sup>11</sup> The closest contacts between the toluene molecule and the ligand phenyl rings range from 2.301 to 3.336 Å, suggesting that host–guest interactions may play a role in stabilizing the observed toluene adduct structure, as has been proposed for certain structurally characterized metal–alkane adducts.<sup>12</sup> Solvents in which **6** is soluble, for example  $\text{CD}_2\text{Cl}_2$  and  $\text{CDCl}_2\text{F}$ , appear to



**Figure 1.** Solid-state structures of (A) **5**, (B) **6**, (C) **10**, and (D) **16**. Thermal ellipsoids drawn at 50% probability. Hydrogen atoms and  $\text{BAR}^{\text{F}_4}$  anions omitted for clarity. Ligand phenyl rings abbreviated in A and B.

## Scheme 2



substitute the toluene at temperatures as low as  $-100\text{ }^{\circ}\text{C}$ , frustrating our attempts to characterize the Pt–toluene interaction in **6** by solution NMR spectroscopy.

The yellow Pt(II) complexes,  $[\text{SiP}_3^{\text{iPr}}]\text{Pt}-\text{CH}_3$  (**7**),  $[\text{SiP}_3^{\text{iPr}}]\text{Pt}-\text{Cl}$  (**8**), and  $[\text{SiP}_3^{\text{iPr}}]\text{Pt}-\text{H}$  (**9**), can be synthesized in a manner analogous to that of the phenyl ligand system. The hydride **9** has been structurally characterized, and the hydride position was found in the difference map and refined freely, providing a  $\tau_5$  value of 0.94. Protonation of **7** with  $\text{H}(\text{OEt}_2)_2\text{BAR}_4^{\text{F}}$  in dichloromethane solution results in an immediate color change to purple ( $\lambda_{\text{max}} = 494\text{ nm}$ ,  $\epsilon = 964\text{ cm}^{-1}\text{ M}^{-1}$ ), in contrast to the yellow-orange color of solvento adducts such as **5**. While the  $^1\text{H}$  NMR spectrum retains the same general characteristics as those of the other  $[\text{SiP}_3^{\text{iPr}}]\text{Pt}-\text{X}$  compounds, the  $^{31}\text{P}$  NMR resonance is dramatically shifted downfield to 102.1 ppm, in contrast to ca. 22 to 46 ppm for the five-coordinate  $[\text{SiP}_3^{\text{iPr}}]\text{Pt}-\text{X}$  complexes described above. The  $^{195}\text{Pt}$  NMR resonance was located indirectly by a  $^{195}\text{Pt}/^1\text{H}$  2D HMBC experiment at  $-2818$  ppm. For comparison, the  $^{195}\text{Pt}$  NMR resonances of TBP **7**, **8**, and **9** are at  $-6324$ ,  $-4439$ , and  $-6039$  ppm, respectively.

The solid-state structure of a single crystal grown from dichloromethane solution reveals the four-coordinate, trigonal pyramidal complex  $\{[\text{SiP}_3^{\text{iPr}}]\text{Pt}\}\{\text{BAR}_4^{\text{F}}\}$  (**10**) (Figure 1). The structure of **10** has been refined in  $P\bar{1}$  to an R1 of 0.0358 and a wR2 of 0.0767, and the only disordered positions concern the  $-\text{CF}_3$  groups on the  $\text{BAR}_4^{\text{F}}$  anion. The closest approach to the platinum center, other than the Si and three P-atoms of the immediate coordination sphere, is an isopropyl methyl hydrogen that is at  $3.344\text{ \AA}$ , larger than the sum of their van der Waals radii and well outside the range of a plausible agostic interaction. These data are consistent with the solution  $^1\text{H}$  NMR spectrum, which exhibits a single methine and two methyl resonances at RT. The platinum center deviates minimally from the plane of the phosphines, as the P–Pt–P angles sum to  $358^{\circ}$ . The  $\tau_4$  value of **10** is 0.855, where  $\tau_4$  is 0.851 for an ideal trigonal pyramid.<sup>13</sup>

The bulky nature of the isopropyl-substituted  $[\text{SiP}_3^{\text{iPr}}]$  ligand precludes cationic **10** from binding solvents such as benzene, dichloromethane, diethyl ether, and THF. Indeed, XRD analysis of crystals grown from a THF solution of **10** afforded the same solid-state structure as those grown from  $\text{CH}_2\text{Cl}_2$ . The electrophilic character of **10** is manifest in its reactivity toward  $\text{H}_2$  and a series of N-donor ligands. Exposing **10** to an atmosphere of dihydrogen generates the cationic  $\text{H}_2$  adduct  $\{[\text{SiP}_3^{\text{iPr}}]\text{Pt}(\text{H}_2)\}\{\text{BAR}_4^{\text{F}}\}$  (**11**). The coordinated  $\text{H}_2$  resonance has a  $T_{1\rho}$  of 26 ms ( $-50\text{ }^{\circ}\text{C}$ , 500 MHz) and exhibits  $^{195}\text{Pt}$  satellites with  $^1J_{\text{Pt}-\text{H}} = 264\text{ Hz}$  upon cooling to  $-70\text{ }^{\circ}\text{C}$ ; the analogous HD complex has a  $^1J_{\text{H}-\text{D}}$  of 29 Hz. These values are consistent with an intact dihydrogen ligand rather than a dihydride species.<sup>14</sup> Excess 2,6-lutidine deprotonates **11** to regenerate hydride **9** (Scheme 2). The addition of acetonitrile to **10** affords the 18-electron, TBP adduct  $\{[\text{SiP}_3^{\text{iPr}}]\text{Pt}(\text{NCMe})\}\{\text{BAR}_4^{\text{F}}\}$  (**12**), whereas the addition of excess pyridine results in the dissociation of one phosphine arm to form the crystallographically characterized square planar Pt(II) species  $\{[\text{SiP}_3^{\text{iPr}}]\text{Pt}(\text{pyridine})\}\{\text{BAR}_4^{\text{F}}\}$  (**13**). The pyridine ligand in **13** is labile, and diluted samples in  $\text{CH}_2\text{Cl}_2$  also show **10**.

Compound **10** represents a bona fide divalent trigonal pyramidal platinum(II) complex. A structurally related platinaboratrane complex  $\{(2\text{-}^i\text{Pr}_2\text{PC}_6\text{H}_4)_3\text{B}\}\text{Pt}$  was recently accessed via a Pt(0) precur-

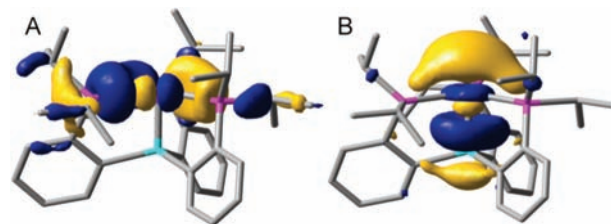


Figure 2. DFT-calculated (A) HOMO and (B) LUMO of **10**.

sor and exhibited an electronic spectrum similar to that of **10**.<sup>15</sup> While the platinaboratrane complex was formulated as Pt(0), its close electronic relationship to **10** is evident and the two systems are isoelectronic.<sup>16</sup> Minimization of cationic **10** by DFT methods affords a structure very similar to that observed in the solid state. The HOMO and LUMO orbitals obtained from single-point calculations of **10** plotted in Figure 2A,B are consistent with the  $d^8$  formulation. A high-lying LUMO of  $d_{z^2}$  parentage with a lobe protruding into the empty axial site opposite the silyl anchor is well separated from an in-plane HOMO of  $d_{xy}$  parentage. The electrophilicity of **10**, and the corresponding  $\{[\text{SiP}_3^{\text{iPr}}]\text{Pt}\}^+$  system which scavenges very weak ligands, lends further credence to the  $d^8$  formulation.

We have begun to canvass related palladium systems for comparison. In brief, the yellow complexes  $[\text{SiP}_3^{\text{iPr}}]\text{Pd}-\text{CH}_3$  (**14**) and  $[\text{SiP}_3^{\text{iPr}}]\text{Pd}-\text{Cl}$  (**15**) have been synthesized and spectroscopically characterized. Protonation of **14** with  $\text{H}(\text{OEt}_2)_2\text{BAR}_4^{\text{F}}$  in dichloromethane solution immediately affords a deep red solution ( $\lambda_{\text{max}} = 463\text{ nm}$ ) with a corresponding  $^{31}\text{P}$  NMR resonance at 53 ppm. An X-ray diffraction experiment on a single crystal of the product grown from dichloromethane confirms the identity of this species as a four-coordinate trigonal pyramidal Pd(II) species,  $\{[\text{SiP}_3^{\text{iPr}}]\text{Pd}\}\{\text{BAR}_4^{\text{F}}\}$  (**16**) (Figure 1).<sup>17,18</sup> Reactivity studies of **10** and **16**, and of related Ni(II) complexes, are presently underway.

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**Supporting Information Available:** Experimental, spectroscopic, X-ray, and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) (a) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471–2526. (b) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2181–2192. (c) Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fujii, H. *Science* **1998**, *280*, 560–564. (d) Sen, A. *Acc. Chem. Res.* **1998**, *31*, 550–557. (e) Peters, J. C.; Thomas, J. C.; Thomas, C. M.; Betley, T. A. In *Activation and Functionalization of C-H Bonds*; Goldberg, K.; Goldman, A., Eds. 2004; Vol. 885.
- (2) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Dordrecht, The Netherlands, 1984.
- (3) Mankad, N. P.; Whited, M. T.; Peters, J. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 5768–5771.
- (4) Ostendorf, D.; Landis, C.; Grützmacher, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 5169–5173.
- (5) Goodman et al. recently reported a TP transition state for intramolecular ligand exchange for distorted square planar  $d^8$   $\text{Rh}(\text{PR}_3)_3\text{CF}_3$ ; Goodman, J.; Grushin, V. V.; Larichev, R. B.; Macgregor, S. A.; Marshall, W. J.; Roe, D. C. *J. Am. Chem. Soc.* **2009**, *131*, 4236–4238.
- (6) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.
- (7) (a) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 5961–5976. (b) Heiberg, H.; Swang, O.; Ryan, O. B.; Gropen, O. *J. Phys. Chem. A* **1999**, *103*, 10004–10008. (c) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235–10236. (d) Wick, D. D.; Reynolds, K. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 3974–3983. (e) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 8870–8888.

- (8) (a) Schneider, J. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1068–1075. (b) Bengali, A. A.; Schultz, R. H.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 9585–9589. (c) Lian, T.; Bromberg, S. E.; Yang, H.; Proulx, G.; Bergman, R. G.; Harris, C. B. *J. Am. Chem. Soc.* **1996**, *118*, 3769–3770. (d) Geftakis, S.; Ball, G. E. *J. Am. Chem. Soc.* **1998**, *120*, 9953–9954.
- (9) Bernskoetter, W. H.; Schauer, C. K.; Goldberg, K. I.; Brookhart, M. *Science* **2009**, *326*, 553–556.
- (10) Three residual electron density peaks are generated near the fourth, *meta* carbon (distances to the carbon atom range from 0.88 Å to 1.49 Å), making its C–H distance ambiguous.
- (11) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6908–6914.
- (12) (a) Evans, D. R.; Drovetskaya, T.; Bau, R.; Reed, C. A.; Boyd, P. D. W. *J. Am. Chem. Soc.* **1997**, *119*, 3633–334. (b) Castro-Rodriguez, I.; Nakai, H.; Gantzel, P.; Zakharov, L. N.; Rheingold, A. L.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 15734–15735.
- (13) Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955–964.
- (14) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1998**, *37*, 2422–2431.
- (15) (a) Bontemps, S.; Bouhadir, G.; Gu, W.; Mercy, M.; Chen, C.-H.; Foxman, B. M.; Maron, L.; Ozerov, O. V.; Bourissou, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 1481–1484. (b) Sircoglou, M.; Bontemps, S.; Bouhadir, G.; Saffon, N.; Miqueu, K.; Gu, W.; Mercy, M.; Chen, C.-H.; Foxman, B. M.; Laurent, M.; Ozerov, O. V.; Bourissou, D. *J. Am. Chem. Soc.* **2008**, *130*, 16729–16738.
- (16) Parkin, G. In *Comprehensive Organometallic Chemistry*; 2007; Vol. 1, pp 1–57.
- (17) An unusual d<sup>8</sup> Pd butterfly structure type has been reported: Frech, C. M.; Shimon, L. J. W.; Milstein, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 1709–1711.
- (18) For representative Pd(II) structures significantly distorted from planarity, see: (a) Bröring, M.; Brandt, C. D. *J. Chem. Soc., Dalton Trans.* **2002**, 1391–1395. (b) Yeo, J. S. L.; Vittal, J. J.; Hor, T. S. A. *Chem. Commun.* **1999**, 1477–1478.

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