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Synthesis and Complexation of a New Tripodal Tetradentate Ligand, a Silyl Ligand Tethered with Three Thioether Moieties

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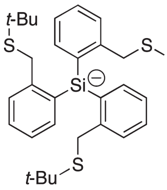
Summary: Iridium(III) and platinum(II) complexes with a new tripodal tetradentate ligand, tris[2-(tert-butylthiomethyl)-phenyl]silyl were synthesized. In addition, reaction of tris-(2-((tert-butylthio)methyl)phenyl)silane with [PdCl$_2$(PhCN)$_2$] *resulted in the cleavage of the Si−C bond to give* [{Pd[2-(t-BuSCH$_2$)C$_6$H$_4$]}$_2$(μ-Cl)$_2$].

Transition-metal complexes bearing tripodal tetradentate ligands have attracted considerable interest, due to their utility in the activation of small molecules, the stabilization of reactive species with unusual electric and geometric structures, catalytic activities, and so on.[1] Although there have been many reports on tripodal tetradentate ligands containing amine or phosphine moieties as donors, tripodal tetradentate silyl ligands tethered with three donor moieties are very rare.[2] Stobart and co-workers reported the synthesis of two types of tris(phosphino)silyl ligands, $^{-}$Si(CH$_2$CH$_2$PPh$_2$)$_3$[3] and $^{-}$Si[2-(Ph$_2$P)C$_6$H$_4$CH$_2$]$_3$,[4] and their complexation with rhodium(III) and iridium(III), respectively. Recently, Peters and co-workers reported the synthesis and properties of dinitrogen complexes with Fe, Co, and Ir supported by $^{-}$Si[2-(R$_2$P)C$_6$H$_4$]$_3$ ligands.[5] On the other hand, to the best of our knowledge, tripodal tetradentate silyl ligands tethered with three thioether moieties have not been reported. In transition-metal complexes with such ligands, it is expected that the strong trans effect of the silyl moiety results in the ready dissociation of the ligand on its trans position and thus thioether moieties, weak σ-donors, can be readily exchanged with other ligands. Such complexes are very interesting, due to not only their unique structure and reactivity but also their activity as catalysts and their ability to activate small molecules. In this paper, we present the synthesis of a new tripodal tetradentate silyl ligand, tris[2-(*tert*-butylthiomethyl)phenyl]-silane $^{-}$Si[2-(*t*-BuSCH$_2$)C$_6$H$_4$]$_3$ (**1**; Chart 1), and its coordination chemistry with iridium(III), palladium(II), and platinum(II).

Chart 1



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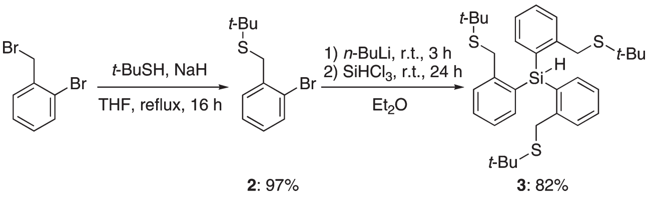
Synthesis of the precursor tris(2-((*tert*-butylthio)methyl)-phenyl)silane, [2-(*t*-BuSCH$_2$)C$_6$H$_4$]$_3$SiH (**3**), is shown in Scheme 1. The reaction of 1-bromo-2-(bromomethyl)benzene with 2-methyl-2-propanethiol and NaH yielded 1-bromo-2-(*tert*-butylthiomethyl)benzene (**2**) in good yield.[6] Lithiation of sulfide **2** with *n*-BuLi, followed by treatment with SiHCl$_3$, resulted in the formation of the silane precursor **3**.

Scheme 1. Synthesis of Silane Precursor 3



The structure of **3** was determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, elemental analysis, and X-ray structural analysis. The crystal structure of **3** showed that the three sulfur atoms were situated on the same side as the H−Si bond at the silicon atom, although the lone pairs of the sulfur atoms were not oriented to the center (Figure 1). This pre-organized structure suggests that **3** can behave as a tetradentate ligand.

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(2) In recent years, silyl ligands tethered with two donor groups (pincer-type ligands) have been extensively studied; see: (a) Balakrishna, M. S.; Chandrasekaran, P.; George, P. P. *Coord. Chem. Rev.* **2003**, *241*, 87–117. (b) Brost, R. D.; Bruce, G. C.; Joslin, F. L.; Stobart, S. R. *Organometallics* **1997**, *16*, 5669–5680. (c) Sangtrirutnugul, P.; Stradiotto, M.; Tilley, T. D. *Organometallics* **2006**, *25*, 1607–1617. (d) MacInnis, M. C.; MacLean, D. F.; Lundgren, R. J.; McDonald, R.; Turculet, L. *Organometallics* **2007**, *26*, 6522–6525. (e) Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2008**, *130*, 15254–15255.

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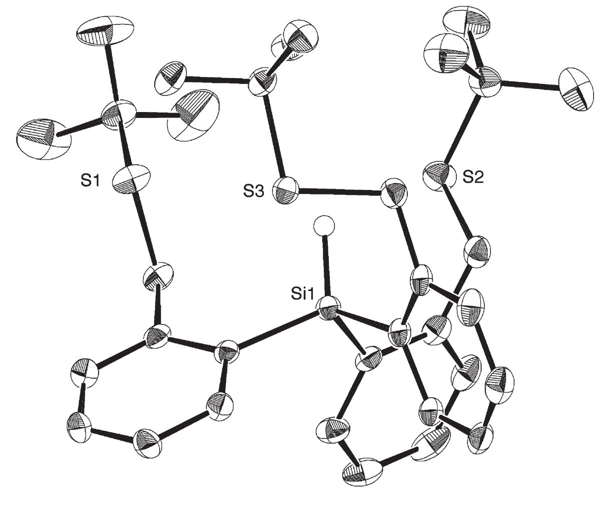
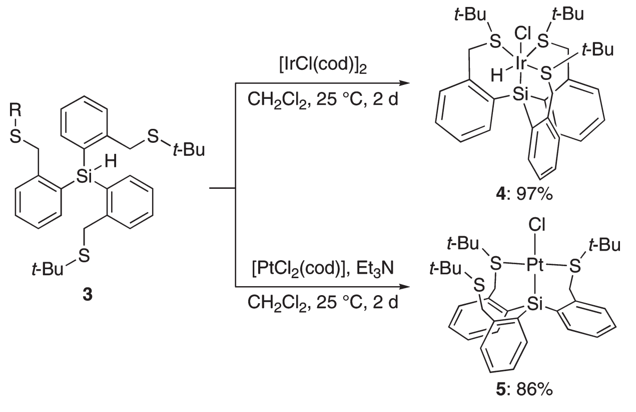


Figure 1. ORTEP drawing for one fragment of two nonidentical silanes **3** in the unit cell with 50% probability thermal ellipsoids. The other fragment has been omitted, due to the small differences between the two fragments. All H atoms, except for the hydrogen connected to Si, have been omitted for clarity.

Silane **3** reacted with $[IrCl(cod)]_2$ in dichloromethane at 25 °C for 5 h to give the corresponding six-coordinate iridium(III) complex **4** via oxidative addition of the Si−H bond to the iridium(I) metal (Scheme 2). A similar reaction has been reported in the treatment of $[2\text{-}(Ph_2P)C_6H_4CH_2]_3$-SiH with $[IrCl(cod)]_2$, giving the corresponding complex $[IrHCl\{Si[2\text{-}(Ph_2P)C_6H_4CH_2]_3\}]$.[4] The structure of **4** was determined by ^1H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray structural analysis.

Scheme 2. Synthesis of the Iridium(III) and Platinum(II) Complexes 4 and 5



The structural analysis of **4** revealed the six-coordinate octahedral structure of **4**, in which the silyl group was situated in a position trans to the chloro ligand (Figure 2). The Ir−Cl bond length (2.5278(15) Å) is close to the reported Ir−Cl bond lengths trans to a hydrido ligand (2.50−2.52 Å), and is much longer than the reported Ir−Cl bond lengths trans to a chloro (2.36−2.40 Å) or phosphine (2.42−2.45 Å) ligand.[7] This suggests that the silyl group has a trans influence almost similar to that of hydrido ligands. The Ir−S2 distance (2.4693(15) Å) is longer than the other two Ir−S distances (2.3383(14) and 2.3439(13) Å), probably due to the greater trans influence of the hydrido ligand.

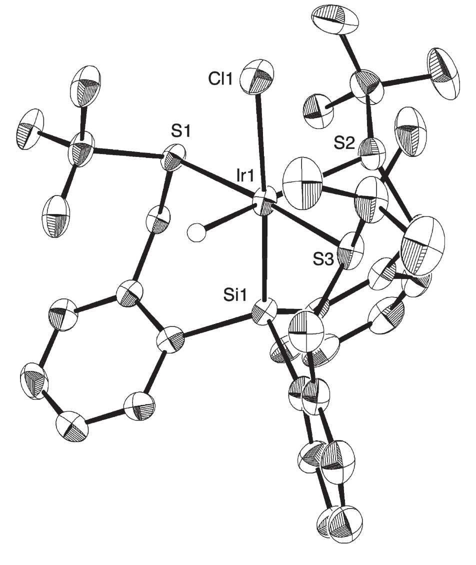


Figure 2. ORTEP drawing of the iridium(III) complex **4** with thermal ellipsoids (50% probability). All H atoms, except for the hydrogen connected to Ir, have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−Si1, 2.3240(15); Ir1−S1, 2.3439(13); Ir1−S2, 2.4693(15); Ir1−S3, 2.3383(14); Ir1−Cl1, 2.5278(15); Si1−Ir1−S1, 90.92(5); Si1−Ir1−S2, 95.00(5); Si1−Ir1−S3, 86.61(5); Si1−Ir1−Cl1, 175.24(5); S1−Ir1−S2, 99.83(5); S2−Ir1−S3, 83.48(5); S1−Ir1−S3, 176.05(6); S1−Ir1−Cl1, 84.32(5); S2−Ir1−Cl1, 85.71(6); S3−Ir1−Cl1, 98.15(6).

The ^1H NMR spectrum of **4** showed the H−Ir signal at a characteristic higher field (−19.66 ppm). In addition, the ^1H NMR spectrum at 60 °C showed the *tert*-butyl protons as two singlet peaks at 1.44 and 1.45 ppm with an integral ratio of 9:18 and the CH_2 protons as one sharp singlet at 4.07 ppm and two doublets at 4.17 and 4.46 ppm with an integral ratio of 2:2:2. These doublets have geminal coupling constants of $^2J_{HH} = 12.6$ Hz. These results strongly suggest the six-coordinate octahedral structure of **4** in solution as well as in the crystalline state and the rapid inversion on the sulfur atoms at 60 °C. The ^{13}C NMR spectrum showed two sets of peaks for the *tert*-butyl groups, which also supports the six-coordinate octahedral structure of **4** in solution.

Reaction of **3** with $[PtCl_2(cod)]$ in the presence of Et_3N resulted in the formation of the four-coordinate platinum complex **5** via dissociation of HCl (Scheme 2). Tilley and a co-worker have reported that treatment of bis(8-quinolyl)-methylsilane with $[PtCl_2(cod)]$ in the presence of Et_3N leads to a similar reaction to give $[PtCl\{SiMe(8\text{-quinolyl})_2\}]$.[8] The structure of **5** was determined by ^1H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray structural analysis.

Figure 3 shows the square-planar structure of platinum(II) complex **5**, in which the tripodal silyl ligand acts as a tridentate ligand. The Pt1−Cl1 bond length (2.455(2) Å) is slightly longer than those (trans to phenyl) (2.403−2.420 Å) of *trans*-$[PtCl(Ph)(SMe_2)_2]$,[9] which suggests a slightly larger or similar trans influence of the silyl group compared with that of the phenyl group. The long Pt1−S3 distance (5.047(2) Å) indicates no interaction between Pt1 and S3 atoms.

The ^1H and ^{13}C NMR spectra of **5** showed that the three *tert*-butyl groups are equivalent at 25 °C, which suggests that

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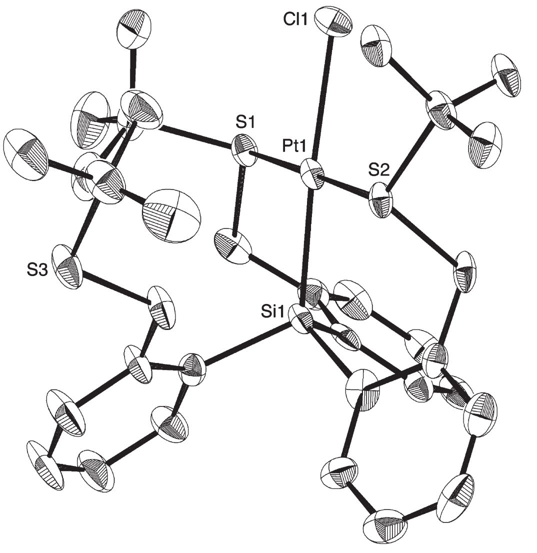


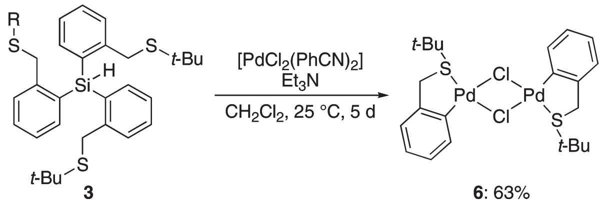
Figure 3. ORTEP drawing for one fragment of two nonidentical platinum complexes **5** in the unit cell with 50% probability thermal ellipsoids. The other fragment has been omitted, due to the small differences between the two fragments. All H atoms and the fragment of solvated hexane have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt1−Si1, 2.326(3); Pt1−S1, 2.308(2); Pt1−S2, 2.304(2); Pt1−Cl1, 2.455(2); Si1−Pt1−S1, 91.59(9); Si1−Pt1−S2, 87.43(9); S1−Pt1−Cl1, 81.04(8); S2−Pt1−Cl1, 99.85(8).

the three *tert*-butylthio moieties rapidly exchange among each other. The rapid exchange of thioether ligands on the platinum(II) atom at 25 °C has been reported in [PtCl$_2${P(2-*i*-PrSC$_6$H$_4$)$_3$}],[10] although it has been reported that the ^{1}H NMR spectrum of [PtCl$_2${PPh[2-MeSC$_6$H$_4$]$_2$}] at 10 °C shows a slower pyramidal inversion of the sulfur atoms and slower exchange between coordinated and uncoordinated sulfur atoms.[11] This difference may be due to the *tert*-butyl and isopropyl groups on the sulfur atoms being bulkier than the methyl groups, which leads to weaker coordination of sulfur to the platinum.

Interestingly, silane **3** underwent Si−C bond cleavage by treatment with [PdCl$_2$(PhCN)$_2$] in the presence of Et$_3$N at 25 °C for 5 days to give the binuclear palladium(II) complex **6** in 63% yield (Scheme 3). The structure of **6** was determined by ^{1}H and ^{13}C NMR spectroscopy and X-ray structural analysis (Figure 4). This Si−C cleavage is very interesting, since the Si−C bonds are relatively stable and the cleavage of an Si−C(aromatic) bond by the use of palladium complexes is very rare.[12]

In this paper, we have synthesized a new silyl ligand tethered with three thioether moieties and its iridium(III) and platinum(II) complexes (**4** and **5**). The X-ray structural analyses of **4** and **5** indicated the octahedral structure of **4** and square-planar structure of **5**. The relatively longer M−Cl (M = Ir in **4**, M = Pt in **5**) bond lengths indicate the strong trans influence of the silyl group, which suggests the ready cleavage of the M−Cl bonds situated trans to the silyl group.

Scheme 3. Reaction of Silane 3 with [PdCl$_2$(PhCN)$_2$]



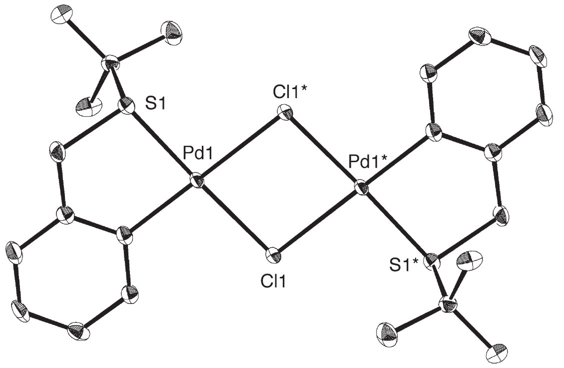


Figure 4. ORTEP drawing of palladium complex **6** with 50% probability thermal ellipsoids. All H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−C1, 2.000(3); Pd1−S1, 2.2646(7); Pd1−Cl1, 2.3691(7); Pd1−Cl1*, 2.4513(7); C1−Pd1−S1, 85.78(8); C1−Pd1−Cl1, 96.10(8); S1−Pd1−Cl1*, 93.57(2); Cl1−Pd1−Cl1*, 84.57(2).

The NMR studies of **5** revealed rapid exchange among coordinated and uncoordinated thioether moieties in solution. Due to these properties, these complexes have potential for application to catalysts, activation of small molecules, and stabilization of reactive species. In addition, we found the Si−C cleavage in the reaction of silane **3** with [PdCl$_2$(PhCN)$_2$]. This Si−C cleavage is applicable to the development of new reactions for the synthesis of organic and organosilicon compounds.

The elucidation of the reactivities of complexes **4** and **5** and the mechanism in the reaction of silane **3** with [PdCl$_2$(PhCN)$_2$] is in progress.

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Note Added after ASAP Publication. In the version of this paper published on the Web on June 8, 2010, ^{29}Si NMR characterization was incorrectly noted for compounds **4** and **5**. References to ^{29}Si NMR for these compounds have been deleted in the version that appears as of July 6, 2010.

Supporting Information Available: Text and tables giving experimental details and characterization data for all new compounds and CIF files giving crystallographic data for compounds **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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