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Coordination Complexes

Structure and Reactivity of a Unique Y-Shaped Tricoordinate Bis(silyl)platinum(II)–NHC Complex**

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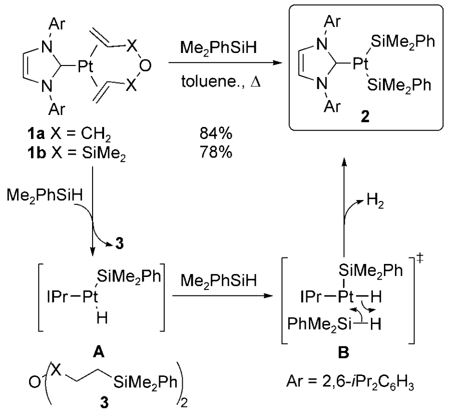
The development of sterically demanding electron-rich ligands for transition metals has led to a number of breakthroughs in homogeneous catalysis.[1] The key to the effectiveness of such ligands is that they prevent high coordination numbers sterically and stabilize highly active coordinatively unsaturated species.[2] Monomeric, neutral, and monoligated tricoordinate 14-electron d^8 ML_3 complexes, such as [Pd(L)(Ar)X], have been postulated as key intermediates in a number of catalytic cycles. However, the isolation of such purely trisubstituted organometallic species has remained elusive. In reported X-ray diffraction (XRD) studies of Group 10 M^{II} tricoordinated complexes, either an agostic interaction or a solvent molecule occupies the fourth coordination site at the metal center.[3] Notable exceptions are the aryl palladium amido complexes reported by Hartwig and Yamashita.[4] Furthermore, all described examples of tricoordinated M^{II} (Ni, Pd, Pt) complexes adopt a T-shaped geometry; a Y-shaped complex is unprecedented. Herein, we disclose the synthesis, structure, and reactivity of the first example of a neutral coordinatively unsaturated 14-electron, purely tricoordinated Pt^{II} complex with a Y-shaped geometry.



Scheme 1. Synthesis of **2** and proposed mechanism for its formation.

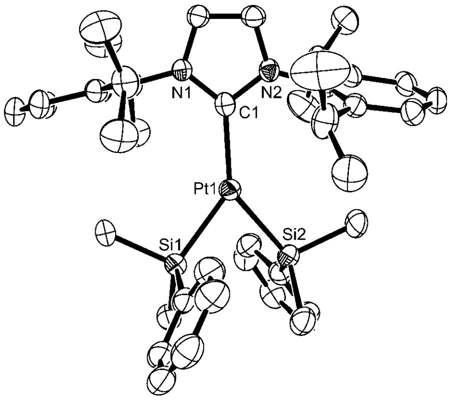


Figure 1. ORTEP diagram of **2** with thermal ellipsoids drawn at the 50% probability level. Two independent molecules of **2** are present in the asymmetric unit, only one of which is depicted. Hydrogen atoms have been omitted for clarity. Average values for the two independent molecules for selected bond lengths [Å] and angles [°]: Pt1–C1 2.124(6), Pt1–Si1 2.294(2), Pt1–Si2 2.300(2), Si1–Si2 2.980(5), C1-Pt1-Si1 137.3(2), C1-Pt1-Si2 141.7(2), Si1-Pt1-Si2 80.9(1), Si1-Pt1-C1-N1 −20.9(7), Si2-Pt1-C1-N2 −15.4(7), Si1-Si2-Pt1-C1 3.7(4).

During the course of our mechanistic investigation of [$Pt^0(IPr)(\eta^2,\eta^2$-diene)] (IPr = bis(2,6-diisopropylphenyl)imidazo-2-ylidene) complexes **1** as catalysts for the hydrosilylation of alkenes and alkynes,[5] the Pt^0 complexes **1a** and **1b** were treated with a large excess of Me_2PhSiH (20 equiv) at 100 °C for 15 h (Scheme 1). The reactions yielded a light-yellow air-sensitive microcrystalline powder. ^1H, ^{13}C, ^{29}Si, and ^{195}Pt NMR spectroscopic studies revealed the formation of [$Pt(IPr)(SiMe_2Ph)_2$] (**2**; Scheme 1). The structure was established unambiguously by X-ray diffraction.[6] Two independent molecules of **2** are found in the asymmetric unit, only one of which is plotted in Figure 1. Although **2** is formally a 14-electron complex, it is stable for extended periods of time under an inert atmosphere and as a solution in a degassed solvent (benzene or toluene). Decomposition is observed in the presence of traces of acid (e.g. residual HCl in $CDCl_3$). Remarkably, solutions of [$Pt(IPr)(SiMe_2Ph)_2$] in Me_2PhSiH are stable under ambient conditions for several weeks.

The most striking feature of the solid-state structure of **2** is its unique trigonal-planar Y-shaped geometry, which is highly unusual for Pt^{II}. The mean deviation of the carbene center (C1) from the Si1-Pt1-Si2 plane is only 0.02(3) Å. The arrangement of the ligands around the platinum center deviates markedly from an ideal trigonal geometry (120°),

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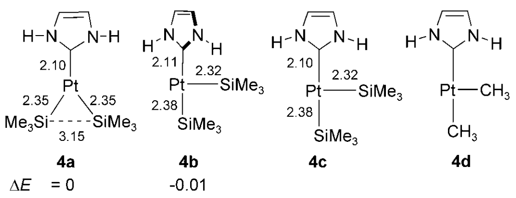
with C1-Pt1-Si2 and Si1-Pt1-Si2 angles of 141.7(2)° and 80.9(1)°, respectively.

A trigonal planar geometry is common for Pt^0, but not for Pt^{II}, which most commonly adopts a square-planar geometry; the dissociation of one ligand generally yields a T-shaped geometry.[3] The DFT-optimized geometry of **2** reveals the same Y-shaped trigonal-planar arrangement as in the X-ray crystal structure (Si-Pt-Si 83°, $C_{carbene}$-Pt-Si 138°).

Comparison of the structure of **2** with the related Pt^{II} complex described by Ozawa and Kamite proved informative.[7a] In marked contrast to **2**, the platinum center in $[Pt(SiMe_2Ph)_2(PPhMe_2)_2]$ is in a twisted square-planar arrangement, which is significantly distorted from planarity. The second unusual feature of **2** is the relatively short Si···Si distance (Si1-Si2 2.980(5) Å) compared to that in $[Pt(SiMe_2Ph)_2(PPhMe_2)_2]$ (3.233(1) Å). We initially considered that the Y shape and the resulting short Si···Si distance might be caused purely by the steric pressure imposed by the hindered IPr carbene on the two silyl ligands. However, comparison of the structure of **2** with that of $[Pt(SiMe_2Ph)_2(PPhMe_2)_2]$ revealed that the closest distance between IPr and the silyl ligands in **2** (C21-C37 3.540(10) Å) is actually longer than the shortest contact in $[Pt(SiMe_2Ph)_2(PPhMe_2)_2]$ (3.384(8) Å). The metal–ligand bonding of NHC ligands is generally believed to be dominated by $L\rightarrow M$ σ donation, with minor $M\rightarrow L$ π back donation. On this basis, one would expect shorter M−C bonds for higher oxidation states of the metal. Contrary to our expectations, the platinum–carbene bond length of 2.123(6) Å is longer in the Pt^{II} complex **2** than in the parent Pt^0 complex [Pt(IPr)(dvtms)] (**1b**, dvtms = divinyltetramethyldisiloxane; Pt-$C_{carbene}$ 2.068(4) Å)[5c] and is among the longest Pt−NHC bonds reported.[8] Furthermore, the ^{13}C chemical shift of the carbene center in **2** ($\delta = 219.7$ ppm, C_6D_6) is substantially further downfield than that of the parent complex **1b** ($\delta = 186.4$ ppm, $CDCl_3$) and is upfield of that of free IPr ($\delta = 220.6$ ppm, C_6D_6) by only 1 ppm.[9] These observations point to substantial $M\rightarrow L$ π backbonding with the NHC and a relatively weak Pt−NHC bond. The Pt−Si bonds (2.291(2) and 2.299(2) Å) are appreciably shorter than in $[Pt(SiMe_2Ph)_2(PPhMe_2)_2]$ (2.37(1) Å) and related structures,[8] which suggests the existence of additional bonding interactions between Pt and Si. Finally, the plane of the NHC carbene (C1-N1-N2-C3-C4) is tilted by an average of 16° from the plane formed by the Si1-Pt1-Si2-C1 arrangement.

The ^1H and ^{29}Si NMR spectra of **2** reveal only one set of signals for the two $SiMe_2Ph$ ligands: an indication of a symmetrical structure, which is consistent with a Y-shaped geometry in solution. In the ^{195}Pt NMR spectrum of the bissilyl complex **2**, the chemical shift of $\delta = -5493$ ppm is further upfield than is usual for a Pt^{II} complex.[10,11] This chemical shift reflects the electron-rich nature of the Pt^{II} center as a result of the combination of three electron-releasing ligands.

To gain fundamental insight into the underlying electronic factors behind the unusual Y-shaped geometry and the stability of **2**, we performed DFT calculations on the model complex $[Pt(SiMe_3)_2(Im)]$ (**4**; Im = imidazo-2-ylidene), which is devoid of steric hindrance.[12] Surprisingly, even in this unhindered system, the Y-shaped geometry (see structure **4a**) is one of the preferred geometries (Scheme 2). The other stable geometry is T-shaped (see **4b**), but in this case the plane of the NHC ligand is orthogonal to the coordination plane. These two calculated complexes are equal in energy. If in the T-shaped geometry the NHC plane is coplanar with the coordination plane, the calculated complex, **4c**, is 4.2 kcal mol^{-1} higher in energy than **4a**. Remarkably, if we replace the NHC ligand in **4** by PPh_3, the Y shape is no longer a stable geometry; all structures converge to a T-shaped geometry for $[Pt(SiMe_3)_2(PPh_3)]$.

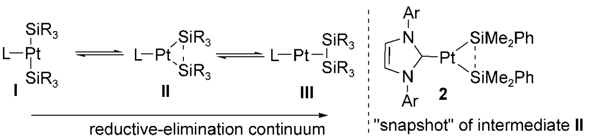


Scheme 2. DFT-optimized geometries of **4**. Relative energies are given in kcal mol^{-1} and bond lengths in Å.

The preference for the Y-shaped geometry of **2** over the expected T-shaped geometry thus seems to be the result of a fine balance of different steric and electronic factors: a) The powerful *trans* influence of the σ-donating silyl and NHC ligands strongly disfavors mutual *trans* arrangements (especially for the two Si ligands) and thus disfavors a T-shaped geometry. b) A *trans* positioning of the NHC ligand relative to a silyl substituent in a T-shaped geometry is less unfavorable if the NHC plane is oriented perpendicular to the plane of the T, because this arrangement enables the metal to use different filled d_π orbitals for π backbonding to all three ligands. c) If the perpendicular geometry **4b** is not accessible for steric reasons, the preferred geometry is a Y-shaped geometry, as observed for **2**. As in T-shaped **4b**, in Y-shaped **4a** the metal can use different d orbitals for π backbonding to all three ligands.[12]

It thus transpires that the overall bonding interactions within **2** are dominated by π-backbonding from Pt^{II} to the ligands, which compensates for the unfavorable σ-bonding interactions imposed by the Y shape (in which one of the ligands necessarily interacts with a filled d_σ orbital). In fact, silyl ligands are good π acceptors, and there is ample evidence that π back donation of late transition metals to NHCs is a significant contribution to overall bonding[13] and even the key to the stabilization of low-valent complexes.[13e] This hypothesis was confirmed by calculating the geometry of complex **4d**, which bears two methyl groups. Methyl groups are σ-donating ligands with no π-acceptor properties. Complex **4d** only adopts a T-shaped geometry.[14] The analysis of three-coordinate Cr^{II} complexes led to similar observations and conclusions. These complexes can adopt either a Y-shaped or a T-shaped geometry, depending on the electronic nature of the ligands.[15]

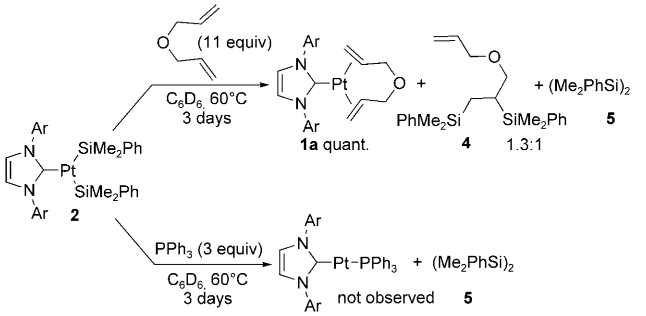
Importantly, the Y-shaped geometry also imposes a degree of σ bonding between the two Si ligands. This interaction might further contribute to the relative stability of the Y-shaped geometry. The Y-shaped complex **2** could thus be regarded as an intermediate in the continuum of the reductive elimination of $R_3Si{-}SiR_3$ from $[Pt^{II}(SiR_3)_2]$ (Scheme 3).



Scheme 3. The complex **2** as a snapshot of $Pt^{II}(SiR_3)_2$ during the reductive elimination of the disilane.

The mechanism for the formation of **2** has not been thoroughly established, but we surmise that an initial hydrosilylation of the diene ligand leads to a putative [Pt(IPr)] intermediate. Oxidative addition of the silane to this intermediate would then give a Pt^{II} complex **A** (Scheme 1). This complex could react further with the silane either by σ-bond metathesis involving a Pt–H bond and an Si–H bond (Scheme 1, **B**) or via a Pt^{IV} species obtained through a second oxidative addition of the silane with subsequent reductive elimination of hydrogen. During the course of the reaction, compound **3** was observed: this product originates from the hydrosilylation of allyl ether or tetramethyldivinyl siloxane by $PhMe_2SiH$. It is known that hydrido silyl complexes of platinum react rapidly with $HSiR_3$ to give the corresponding bis(silyl)platinum complexes.[16]

We examined the reactivity of **2** by treating it with a tenfold excess of diallyl ether (AE). After the addition of diallyl ether to complex **2**, a slow but clean conversion of **2** into [Pt(IPr)(AE)] (**1a**) was observed by ^1H NMR spectroscopy (Scheme 4). Complete conversion occurred within 3 days at 60 °C. Importantly, the concomitant formation of the disilylated allyl ether, **4**, and $(SiMe_2Ph)_2$ (**5**) in a 1.3:1 ratio was observed (Scheme 4). This experiment indicates that under these reaction conditions direct reductive elimination and insertion of the alkene into the Pt–Si bond with subsequent reductive elimination occur at similar rates. Ozawa and Kamite described the reaction of $[Pt(SiR'_3)_2(PR_3)_2]$ complexes in the presence of alkynes; only insertion of the alkynes into the Pt–Si bond was observed, with no concomitant disilane formation.[7a] Taken together, these observations provide further evidence that **2** is an intermediate in the reductive elimination of a disilane.



Scheme 4. Reactivity of **2**.

To probe whether the disilane **5** could be obtained exclusively, **2** was treated with three equivalents of triphenylphosphane at 60 °C in C_6D_6. Under these conditions, no new species were observed by ^1H or ^{31}P NMR spectroscopy. This result suggests that the π-acidic nature of an alkene is necessary to favor the direct reductive-elimination process.[17]

Whereas there are numerous reports in the literature of the use of four-coordinate complexes of the type $[Pt(SiR_3)_2(PR'_3)_2]$ to study bissilylation reactions,[7b,c18] monoligated bis(silyl)platinum complexes of type **2** have until now only been postulated as the active species in platinum-catalyzed bissilylation reactions.[19]

In summary, we have isolated the first purely tricoordinated Pt^{II} complex. This complex displays an unprecedented Y-shaped geometry, which can be regarded as a "snapshot" in the reaction pathway for the reductive elimination of $R_3Si{-}SiR_3$ from $[Pt^{II}(SiR_3)_2]$. We are currently investigating the possible intermediacy of **2** and related complexes in hydrosilylation and bissilylation reactions.

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