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Alkyl and Hydrido Complexes of Platinum(IV) Supported by the Bis(8-quinolyl)methylsilyl Ligand

Preeyanuch Sangtrirutnugul and T. Don Tilley*

Department of Chemistry, University of California, Berkeley, Berkeley, California 94720

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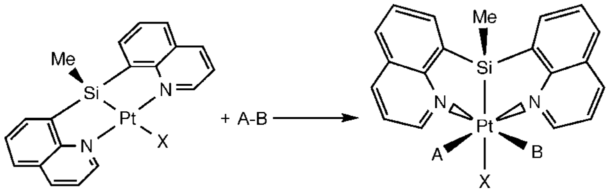
The Pt(II) complex (NSiN)PtCl (**2**; NSiN = bis(8-quinolyl)methylsilyl) was prepared from reaction of (COD)$PtCl_2$, Qn_2SiHMe (**1**) and excess NEt_3 in dichloromethane. The X-ray structure of **2** confirms a square-planar geometry about platinum and a highly distorted tetrahedral geometry at Si. A series of thermally stable (NSiN)Pt(IV) compounds including (NSiN)PtH_2(X) [X = Cl (**5**), OTf (**10**)] and (NSiN)$PtMe_2$(X) [X = I (**6**), OTf (**7**)] were also synthesized. Five-coordinate Pt(IV) complexes of the type [(NSiN)PtR_2][$B(C_6F_5)_4$] (X = Me (**9**), H (**11**)] were generated by treatment of the corresponding triflato derivatives with 1 equiv of $Li(Et_2O)_3[B(C_6F_5)_4]$ in dichloromethane. A crystal structure of **9** reveals a square-pyramidal structure with an empty coordination site *trans* to silicon. Initial reactivity studies have shown that complex **9** is thermally and chemically robust.

Introduction

Organoplatinum compounds are known to mediate a number of important and interesting chemical transformations, including homogeneous C−H bond activation,[1,2] alkene hydrosilylation,[3] and hydroformylation.[4] Many of these complexes feature chelating ligands, which provide higher thermal stability to the resulting platinum complexes as a result of the chelate effect.[1,5–7] Despite extensive research in this field, there are few reports of platinum complexes containing a multidentate ligand framework based on silicon donor atoms.[8–10] Because of their strong electron donor and *trans*-labilizing properties, silyl groups may facilitate bond activation processes, while enforcing coordinative unsaturation at the platinum center. Within this context, exploration of the chemistry of platinum complexes of the bis(8-quinolyl)methylsilyl (NSiN) ligand was of interest. With the sp^3-hybridized Si, the NSiN ligand prefers binding to the metal in a facial manner.[11–13] As a result, square-planar Pt(II) complexes of the type (NSiN)PtX (X = halide, H, and alkyl) are expected to possess ring strain that may be relieved by bond activation reactions to produce octahedral Pt(IV) products (eq 1).



(1)

Platinum(IV) complexes containing alkyl and/or hydride ligands have often been prepared via protonation of the corresponding Pt(II) complexes.[14,15] Other synthetic methods are based on oxidative additions of R_3E−H (R_3E = Me_3Sn,[16] Et_3Si[17]) or C−H[18] bonds to platinum(II) complexes. Elegant mechanistic studies by Puddephatt[19] and Goldberg[20,21] have

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* Address correspondence to this author. E-mail: tdtilley@berkeley.edu.

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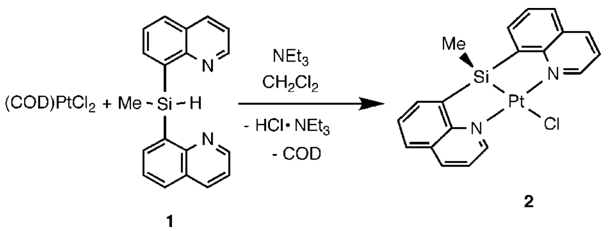
shown that reductive elimination from octahedral Pt(IV) complexes involves dissociation of a ligand to afford an intermediate, five-coordinate species. Complexes of the latter type have also been isolated, and a few of these have been crystallographically characterized.[22–24] Given the known properties of the NSiN ligand, as outlined above, it should be possible to access a range of (NSiN)Pt(IV) complexes. Additionally, the strong *trans*-labilizing ability of silicon should make coordinatively unsaturated, five-coordinate complexes of the type $[(NSiN)PtR_2]^+$ (R = H, alkyl) reasonable synthetic targets. Initial investigations of such systems are described in this paper.

Results and Discussion

Synthesis of (NSiN)Pt(II) Complexes. Treatment of **1** with 1 equiv of $(COD)PtCl_2$[25] (COD = 1,5-cyclooctadiene) and an excess of NEt_3 (ca. 3 equiv) in dichloromethane afforded the chelate-assisted, Si−H bond activation product (NSiN)PtCl (**2**), along with $NEt_3 \cdot HCl$ and COD (eq 2). Complex **2** was crystallized as a fine yellow powder from CH_2Cl_2 solution. Despite successive washings and crystallizations, **2** inevitably contained a small amount of COD, according to ^{1}H NMR spectroscopy. An analytically pure sample of **2**, free of COD, was obtained in relatively low yield (32%) by evaporating a toluene suspension of **2** to dryness at 100 °C.



(2)

The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **2** contain one set of quinolyl resonances, indicating mirror symmetry for the molecule. In the ^{1}H NMR spectrum of **2**, the silyl methyl group ($^3J_{PtH}$ = 45 Hz) and the *ortho* protons of both quinolyl rings ($^3J_{PtH}$ = 22 Hz) display platinum satellites. Despite the preference for facial binding of the NSiN ligand, the NMR data indicate the presence of a square-planar structure, with the NSiN ligand coordinated to the Pt(II) center in a tridentate fashion and a chloride ligand occupying a position *trans* to Si.

X-ray quality crystals were obtained from a dichloromethane solution of **2** at −30 °C. Crystallographic data reveal a distorted square-planar geometry about the Pt(II) center, and the sum of the angles around platinum is essentially 360° (359.7(3)°; Figure 1). The N(1)−Pt−N(2) angle (166.7(2)°) is reduced from 180° as a result of ligand rigidity and the constraint imposed by the sp^3-hybridized silicon. As expected, the Pt−Cl bond distance (2.528(2) Å) is long compared to distances involving Pt−Cl bonds that are *trans* to ligands with a *trans* influence weaker than silicon (e.g., nitrogen and carbon, 2.28–2.39 Å).[26] However, this distance is comparable to that reported for Stobart's Pt(II) complex (PSiP)PtCl (2.44 Å)[8] [PSiP = $-SiMe(CH_2CH_2PPh_2)_2$]. A further apparent consequence of the chelate ring strain in **2** is a significant deviation of the C(8)−Si−C(17) angle (126.1(3)°) from the ideal tetrahedral value. In comparison, the crystal structure of the related octahedral Pt(IV) complex (NSiN)-$PtMe_2OTf$ (**7**) reveals a smaller C(8)−Si−C(17) angle of 109.4(3)° (*vide infra*).

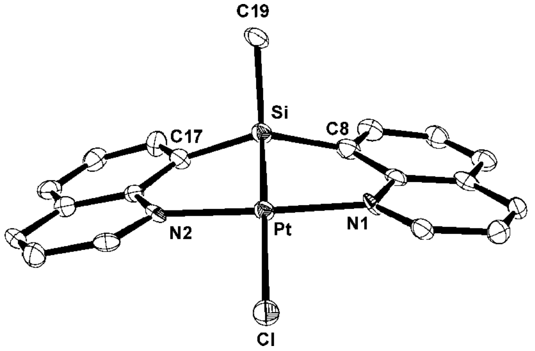


Figure 1. ORTEP diagram of the square-planar complex **2** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pt−Cl = 2.528(2), Pt−Si = 2.225(2). Selected bond angles (deg): C8−Pt−C17 = 126.1(3), N1−Pt−N2 = 166.7(2), Pt−Si−C19 = 120.8(2).

Syntheses of more electron-rich, square-planar complexes of the type (NSiN)PtR (R = H, alkyl, aryl) were also attempted. Efforts to generate these platinum(II) complexes focused on reactions of platinum compounds such as $(COD)PtMe_2$[25] and $(COD)PtPh_2$[27] with **1**, as it was anticipated that Si−H oxidative addition would be followed by rapid elimination of hydrocarbons (e.g., CH_4 or C_6H_6). However, ^{1}H NMR spectroscopy indicated that conversions did not occur even at a reaction temperature of 80 °C (in benzene or dichloromethane solvent). Prolonged heating of the reaction mixtures at this temperature eventually resulted in decomposition of the platinum starting materials. In addition, reactions of **1** with various Pt(0) complexes such as $Pt(PPh_3)_2(C_2H_4)$,[28] $Pt(PPh_3)_4$,[29] and $Pt(dba)_2$ (dba = dibenzylideneacetone)[30] in benzene-d_6 resulted in intractable mixtures of products.

Similar observations regarding the lower reactivity of $(COD)PtR_2$ dialkyl compounds, compared to that of $(COD)PtCl_2$, toward Si−H bond oxidative addition were previously noted for the syntheses of dimeric Pt(II) complexes $(\mu\text{-}Cl)_2[(\eta^2\text{-}COD)Pt(SiR_3)]_2$ (SiR_3 = $SiEt_3$, $SiMe_2Cl$, $SiMeCl_2$, $Si(OEt)_3$, $SiPhMe_2$, $SiMe_2OSiMe_3$).[31] A possible explanation for this difference is that COD binds more strongly to the platinum center in $(COD)PtR_2$ (when R = alkyl or phenyl).[25] On the basis of this reasoning, platinum complexes containing a more labile ligand such as tetramethylethylenediamine (tmeda) were expected to be more reactive toward Si−H bond activation.

Indeed, treatment of **1** with $(tmeda)PtMe_2$ in benzene at 80 °C afforded a new platinum complex (**3**) via CH_4 elimination. Although the ^{1}H NMR spectrum of **3** in dichloromethane-d_2 contains one set of quinolyl protons, no ^{1}H NMR resonance assignable to a Pt−CH_3 group is observed. Multinuclear NMR spectroscopy combined with elemental analysis identify **3** as

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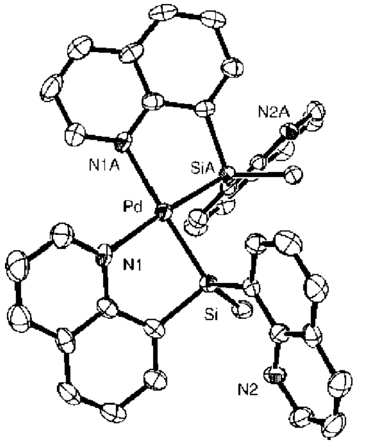
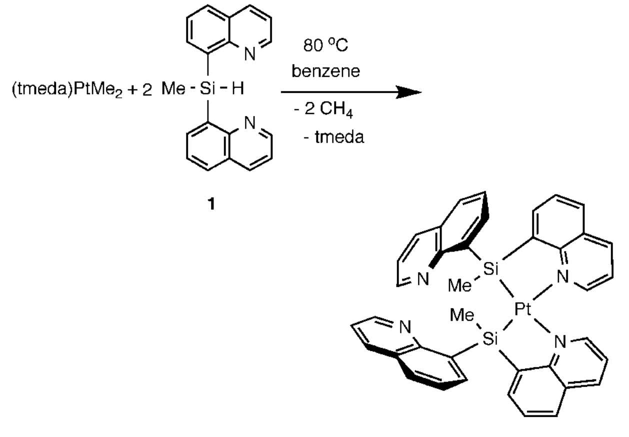


Figure 2. ORTEP diagram of the square-planar complex *cis*-(κ^2-NSiN)$_2$Pd with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å): Pd−N1 = 2.231(5), Pd−Si = 2.276(2). Selected bond angles (deg): Si−Pd−N1 = 83.9(1), Si−Pd−SiA = 90.66(10), N1−Pd−N1A = 101.8(3).

the bidentate complex *cis*-(κ^2-NSiN)$_2$Pt (eq 3). An analogous palladium complex, *cis*-(κ^2-NSiN)$_2$Pd,[32] was synthesized from reaction of **1** with (tmeda)PdMe$_2$.[33] The X-ray crystal structure of *cis*-(κ^2-NSiN)$_2$Pd reveals a distorted square-planar structure with each NSiN ligand binding through only one quinolyl nitrogen and the silyl group, in a bidentate manner (Figure 2). Observation of only one set of quinolyl protons in the spectrum of the related Pt complex **3** at room temperature suggests a fluxional process that rapidly interconverts the quinolyl groups. At −80 °C, the ^{1}H NMR resonances of **3** (dichloromethane-d_2) are broader, but no decoalescence was apparent.



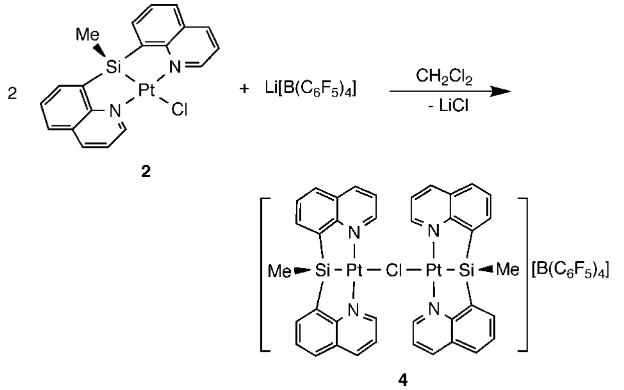
(3)

Complex **3** results from Si−H bond activations of 2 equiv of **1** by (tmeda)PtMe$_2$. A plausible mechanism involves the formation of a transient intermediate, (NSiN)PtMe, which adds another equivalent of **1** via methane loss. Given the reactive nature of (tmeda)PtMe$_2$, it is reasonable to assume that (NSiN)PtMe would also react rapidly with **1**, especially given the more electron-rich Pt center and the expected chelate ring strain of the NSiN ligand. Thus, this alkyl platinum(II) intermediate is not observed, presumably because it rapidly adds another equivalent of **1** to yield the final product **3**.

Reactions of Complex 2. Attempts were also made to prepare alkyl and aryl complexes of the type (NSiN)PtR via reaction of **2** with various reagents including MeLi, EtMgCl, PhMgBr, and Mg(CH$_2$Ph)$_2$(THF)$_2$. However, the ^{1}H NMR spectra of the resulting reaction mixtures reveal a complex mixture of products, and no pure products were isolated.

It was also of interest to generate 14-electron complexes of the type [(NSiN)Pt][X], since such three-coordinate Pt(II) species are believed to be key intermediates in C−H bond activations.[34] Given the strong *trans*-labilizing ability of Si, it seemed that chloride displacement of **2** by more weakly coordinating anions should readily take place. In related Rh complexes, it has been found that the NSiN ligand promotes lability in ligands *trans* to Si and stabilizes five-coordinate Rh(III) complexes.[12]

Reaction of **2** with either 0.5 or 1 equiv of Li(Et$_2$O)$_3$[B(C$_6$F$_5$)$_4$] in dichloromethane afforded a yellow solid (**4**), which was crystallized from diethyl ether at room temperature. The ^{1}H NMR spectrum of **4** (dichloromethane-d_2) contains one set of quinolyl protons and a singlet resonance at δ 0.24 ($^3J_{\mathrm{PtH}}$ = 35 Hz), corresponding to the SiCH_3 group. In addition, no diethyl ether ligand was observed by ^{1}H NMR spectroscopy. Elemental analysis of **4** is consistent with a dinuclear, chloro-bridged platinum structure (eq 4). A related chloride-bridged structure has previously been observed for the cationic Ir(III) complex (μ-Cl)[(NSiN)Ir(H)(coe)]$_2$[B(C$_6$F$_5$)$_4$][11] (coe = cyclooctene).



(4)

Synthesis of (NSiN)Pt(IV) Complexes. The square -planar complex **2** was expected to readily undergo oxidative addition reactions to afford Pt(IV) complexes in which the NSiN ligand is facially bonded to platinum. Heating a dichloromethane-d_2 solution of **2** under 1–2 atm of H$_2$ at 60 °C resulted in formation of a new product (**5**) in approximately 15% yield after 2 days (by ^{1}H NMR, with Si(SiMe$_3$)$_4$ as an internal standard). The ^{1}H NMR spectrum of the reaction mixture reveals unreacted **2** as a major species, and a hydride resonance for **5** at δ −18.3 ($^1J_{\mathrm{PtH}}$ = 1274 Hz). Prolonged heating of the reaction mixture did not result in an increase in the amount of **5**. Notably, although platinum is involved in both heterogeneous[35] and homoge-

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(32) Crystal data: C$_{49}$H$_{46}$N$_4$Si$_2$O$_3$Pd, *Pbcn* (#60), *a* = 8.8297(2) Å, *b* = 27.9592(6) Å, *c* = 18.1044(4) Å, *V* = 4469.5(2) Å^3, *Z* = 4, R1 = 0.047, wR2 = 0.061. See Supporting Information for more detailed crystallographic parameters.

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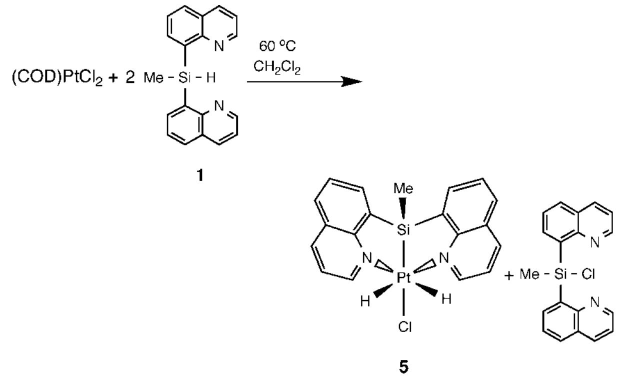
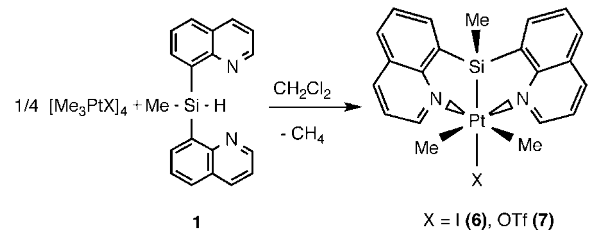
neous[36] hydrogenation catalysis, few examples of H−H oxidative additions to Pt(II) complexes have previously been reported.[37]

Complex **5** was independently synthesized by heating a dichloromethane solution of (COD)$PtCl_2$ and 2 equiv of **1** at 60 °C for 36 h (eq 5). A second equivalent of **1** serves as a reducing agent, to produce the byproduct $Qn_2Si(Cl)Me$. Crystallization of **5** from a 1:1 mixture of dichloromethane and diethyl ether at −30 °C afforded the pure product in 56% yield.



(5)

The related dimethyl Pt(IV) complexes (NSiN)$PtMe_2$(X) [X = I (**6**), OTf (**7**)] were obtained in high yields from addition of **1** to 0.25 equiv of $[Me_3PtX]_4$ (X = I, OTf) in dichloromethane solution (eq 6). Alternatively, **7** was generated from reaction of **6** with 1 equiv of AgOTf in dichloromethane. Formation of **6** and **7** involves an interesting Si−H activation at a Pt(IV) center, for which the mechanism (e.g., oxidative addition vs σ-bond metathesis) is currently unknown.



(6)

The ^1H NMR spectra of **6** and **7** (dichloromethane-d_2) contain single resonances at δ 1.17 ($^2J_{PtH} = 63$ Hz) and 0.844 ($^2J_{PtH} =$ 60 Hz), respectively, which can be assigned to the Pt−CH_3 groups. Consistently, the $^{13}C\{^1H\}$ resonances for the methyl groups in **6** and **7** appear at δ −13.3 ($^1J_{PtC} = 640$ Hz) and −9.80 ($^1J_{PtC} = 645$ Hz), respectively. X-ray quality crystals of **7** were obtained by slow vapor diffusion of diethyl ether into a dichloromethane solution of **7** at room temperature. The crystal structure reveals a distorted octahedral complex with an inner-sphere triflate anion bonded to the platinum center *trans* to the quinolylsilyl group (Figure 3). The Pt−C bond distances of 2.043(7) and 2.052(7) Å are within the expected range for a methyl ligand *trans* to nitrogen in a Pt(IV) complex.[38,39] The Pt−O bond distance (2.425(4) Å) is longer than corresponding distances in Pt−OTf complexes with the triflate group *trans* to amido or methyl ligands (2.099–2.320 Å).[38,40]

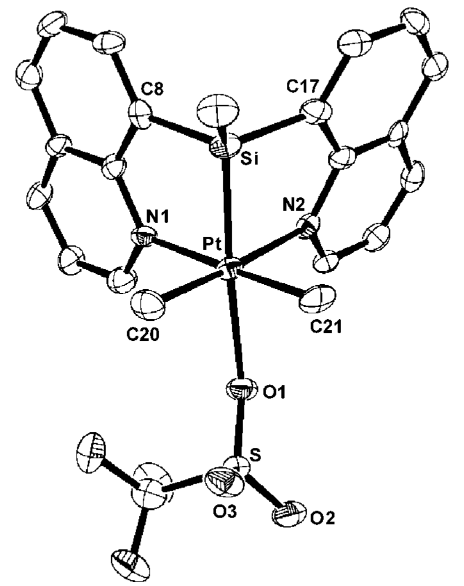


Figure 3. ORTEP diagram of the triflato complex **7** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Pt−O1 = 2.425(4), Pt−Si = 2.244(2), Pt−C20 = 2.043(7). Selected bond angles (deg): C8−Pt−C17 = 109.4(3), N1−Pt−N2 = 87.0(2), Si−Pt−O1 = 172.1(1).

Five-Coordinate (NSiN)Pt(IV) Complexes. Given the unusual stability of five-coordinate (NSiN)Rh(III) complexes,[12] and the ability of silyl ligands to stabilize high oxidation states,[9,15,22,23,41] it seemed that coordinatively unsaturated dialkyl complexes of the type (NSiN)PtR_2^+ might be unusually stable toward the reductive elimination of alkane. Treatment of **6** with either 0.5 or 1.0 equiv of $Li(Et_2O)_3[B(C_6F_5)]_4$ in dichloromethane resulted in the same product (**8**), which was isolated in 85% yield from a mixture of dichloromethane and diethyl ether. The ^1H NMR spectrum of **8** contains resonances at δ 1.28 ($^2J_{PtH} = 62$ Hz) and 1.13 ($^3J_{PtH} = 25$ Hz), corresponding to Pt−CH_3 and Si−CH_3 groups, respectively. The combustion analysis of **8** is consistent with the iodo-bridged diplatinum complex shown in eq 7.

The displacement of triflate from **7** is a more efficient process for synthesis of a five-coordinate Pt(IV) complex. Reaction of **7** with 1 equiv of $Li(Et_2O)_3[B(C_6F_5)]_4$ in dichloromethane afforded the cationic complex [(NSiN)$PtMe_2$][$B(C_6F_5)_4$] (**9**), isolated in 91% yield by vapor diffusion of pentane into a dichloromethane solution of **9** at room temperature (eq 8).

Although **9** was generated in the presence of diethyl ether, no ether coordination to platinum was observed for the isolated,

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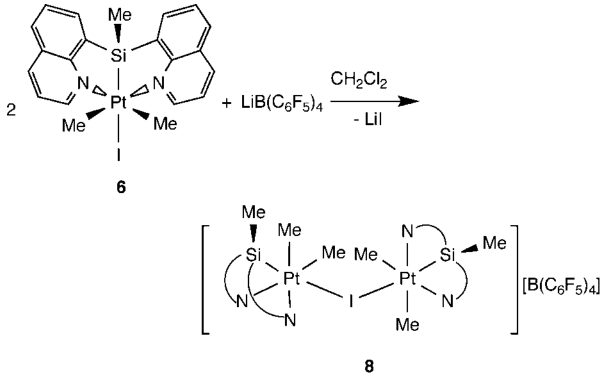

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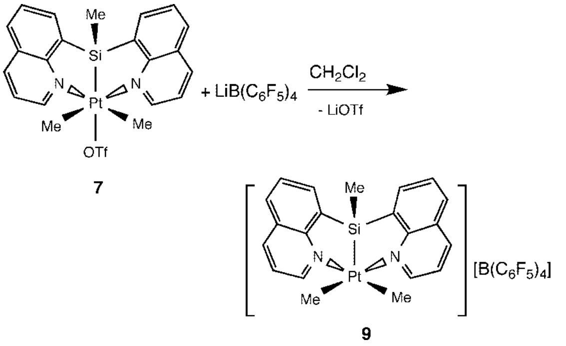

(8)

crystalline product, according to NMR spectroscopy and elemental analysis. A single crystal of **9** suitable for X-ray crystallographic analysis was obtained from vapor diffusion of pentane into a dichloromethane solution of **9** at room temperature. The X-ray data reveal a square-pyramidal structure for the platinum molecule, with the silyl group in an apical position *trans* to an empty coordination site (Figure 4). The $B(C_6F_5)_4$ counterion is not in the vicinity of the platinum center (the shortest Pt···F distance is 5.16 Å).

Although five-coordinate platinum(IV) species are proposed as intermediates in bond activation chemistry,[19,21,42] only a few X-ray structures of complexes of this type have been reported.[22–24] The crystallographically characterized complex [κ^2-((Hpz*)-BHpz*$_2$)PtH_2($SiEt_3$)][BAr′$_4$] (BHpz*$_3$ = hydridotris(3,5-dimethylpyrazolyl)borate) decomposes slowly in dichloromethane to form (BHpz*$_3$)PtH_3 via a heterolytic Pt−Si cleavage.[22] Similarly, in the presence of light, the five-coordinate Pt(IV) complex (nacnac′)$PtMe_3$ [nacnac′ = {(o-^{i}$Pr_2C_6H_3$)NC(CH_3)}$_2$-CH^-] converts to the corresponding Pt(II) dimethyl complex, as a result of a CH_3^+ transfer from platinum to the central anionic carbon of the diimine ligand.[23] Thermal decomposition of (nacnac′)$PtMe_3$ occurs in benzene at 150 °C in the absence of light, with elimination of ethane and methane.[7]

Notably, **9** is thermodynamically stable, as no reaction was observed upon heating a dichloromethane-d_2 solution of **9** to 90 °C for 3 days (by ^{1}H NMR spectroscopy). In the presence of an atmosphere of C_2H_4, **9** does not react to form an ethylene adduct or insertion product, as no conversion was observed at 90 °C after 3 days. Given the exceptional C−H bond activation chemistry of the electronically related complex [Cp*(PMe_3)Ir-(Me)(CH_2Cl_2)][BAr_{f4}],[43] reactions of **9** with small molecules such as isotopically labeled $^{13}CH_4$ and C_6H_6 were investigated. Treatment of the dichloromethane-d_2 solution of **9** with 1–2 atm of $^{13}CH_4$ did not result in the incorporation of ^{13}C into the platinum methyl groups at 90 °C over 2 days. Similarly, heating a dichloromethane-d_2 solution of **9** with an excess of C_6H_6 (ca. 20 equiv) at 115 °C resulted in no reaction after 2 days, according to ^{1}H NMR spectroscopy. This unusual stability of **9** is believed to be due to the preference of the NSiN ligand for binding facially to the platinum center and its ability to stabilize a coordinatively unsaturated, high oxidation state Pt(IV) complex.

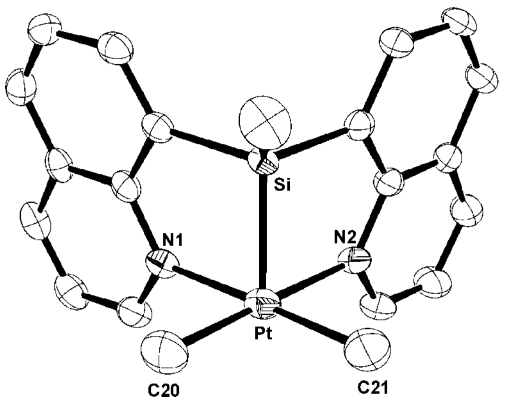

Figure 4. ORTEP diagram of the cationic complex **9** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms and the $B(C_6F_5)_4$ anion are omitted for clarity. Selected bond lengths (Å): Pt−Si = 2.256(1), Pt−N1 = 2.142(3), Pt−C20 = 2.036(5). Selected bond angles (deg): C20−Pt−C21 = 90.9(2), N1−Pt−N2 = 91.4(1), Si−Pt−C20 = 95.5(2).

Given the observed stability of (NSiN)Pt(IV) complexes, it was of interest to examine the ability of this fragment to support alkyl hydride complexes, especially given the generally high tendency for such species to undergo reductive elimination. In addition, alkyl hydrides such as (NSiN)$PtMe_2$(H) might offer an intriguing route to Pt(II) square-planar complexes of the type (NSiN)PtMe, if methane elimination was to cleanly occur. However, treatment of **6** and **7** with various hydride sources such as $LiBH_4$, $LiBEt_3H$, and NaH under various reaction conditions resulted in no conversion of the starting materials. Heating a PhF/benzene-d_6 (1:1) solution of **7** and 1 equiv of NEt_3 under 1–2 atm of H_2 at 60 °C yielded the Si−C reductive coupling product Qn_2SiMe_2[44] and CH_4, based on ^{1}H NMR spectroscopy.

The successful synthesis of **9**, and its remarkable stability, prompted us to investigate the synthesis of a cationic Pt(IV) dihydride complex. The reactivity of [(NSiN)PtH_2][$B(C_6F_5)_4$] was of interest, given the known bond activation chemistry of the electronically analogous complex (PCP)IrH_2.[5] Reaction of **5** with 1 equiv of AgOTf in dichloromethane readily afforded the corresponding triflato complex (NSiN)PtH_2(OTf) (**10**) as an off-white solid in 88% yield (eq 9). The ^{1}H NMR spectrum of **10** in dichloromethane-d_2 is similar to that of **5**, with a hydride resonance at δ −17.3 ($^1J_{PtH}$ = 1312 Hz; for **5**: δ −18.3, $^1J_{PtH}$

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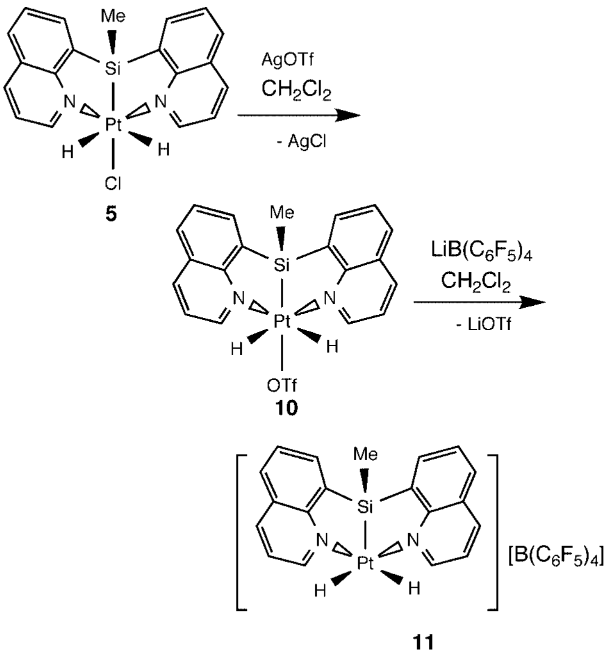
(44) Qn_2SiMe_2 was independently synthesized from lithiation of 8-bromoquinoline using BuLi, followed by addition of 0.5 equiv of Cl_2SiMe_2 in THF at−78 °C. ^{1}H NMR (C_6D_6, 500 MHz): δ 8.63 (d, J_{HH} = 4.1 Hz, of d, J_{HH} = 1.8 Hz, 2 H, ArH), 7.94 (d, J_{HH} = 6.7 Hz, of d J_{HH} = 1.4 Hz, 2 H, ArH), 7.52 (d, J_{HH} = 8.2 Hz, of d, J_{HH} = 1.8 Hz, 2 H, ArH), 7.44 (d, J_{HH} = 8.2 Hz, of d J_{HH} = 1.5 Hz, 2 H, ArH), 7.19 (d, J_{HH} = 8.2 Hz, of d, J_{HH} = 6.7 Hz, 2 H, ArH), 6.70 (d, J_{HH} = 8.2 Hz, of d, J_{HH} = 4.1 Hz, 2 H, ArH), 1.32 (s, 6 H, SiCH3). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 153.3, 149.2, 141.4, 137.9, 136.0, 129.2, 126.3, 120.6 (aryl carbons), 0.47 (SiCH3). ^{29}Si{^{1}H} NMR (C_6D_6, 99 MHz): δ−5.9. Anal. Calcd (%) for $C_{20}H_{18}N_2Si$: C, 76.39, H, 5.77, N, 8.91. Found: C, 76.11, H, 5.73, N, 8.62.

= 1274 Hz). In addition, the IR spectrum of **10** contains a strong Pt−*H* band at 2231 cm^{-1}. The structure of **10** is believed to be similar to that of **7**, with the triflate bound to platinum. Both NMR spectroscopy and elemental analysis reveal no solvent in the isolated product, and this is also consistent with an inner-sphere triflate structure.



(9)

Treatment of **10** with 1 equiv of $Li(Et_2O)_3[B(C_6F_5)_4]$ in dichloromethane yielded a new complex (**11**), which was crystallized from dichloromethane as a white microcrystalline solid in 58% yield. Elemental analysis and the ^1H NMR spectrum of **11** are consistent with its formulation as the cationic Pt(IV) complex $[(NSiN)PtH_2][B(C_6F_5)_4]$. The ^1H NMR spectrum of **11** in dichloromethane-d_2 contains a broad resonance at δ −16.1 ($^1J_{PtH} = 1314$ Hz) corresponding to two hydride ligands. The Pt−*H* vibrational stretch appears as a broad band at 2228 cm^{-1} in the IR spectrum. Once isolated, **11** is only sparingly soluble in dichloromethane. In addition, **11** slowly decomposes in dichloromethane to give intractable products over several days at room temperature.

Concluding Remarks. Despite its strong tendency to bind to metal centers in a *facial* manner, the NSiN ligand has been found to form a square-planar complex of platinum (NSiN)PtCl (**2**). However, initial investigations indicate that related Pt(II) derivatives with more electron-donating ligands (e.g., X = H, alkyl, aryl) are highly reactive and difficult to isolate. Several reactions described in this paper have shown that the NSiN ligand is readily installed via reactions of the Si−H bond of Qn_2SiHMe (**1**) at a Pt(II) center. A related reaction of note involves addition of **1** to $[PtMe_3X]_4$ (X = I, OTf), which involves a particularly unusual activation of an Si−H bond at a Pt(IV) center, to form $(NSiN)PtMe_2(X)$ complexes. In addition, reaction of **1** with $(COD)PtCl_2$ in dichloromethane to afford $(NSiN)PtH_2Cl$ (**5**) represents a convenient, new synthetic route to a Pt(IV) hydride complex.

The structural and electronic properties of the NSiN ligand promote the formation of five-coordinate complexes, as seen in the isolation of $[(NSiN)PtR_2][B(C_6F_5)_4]$ [R = Me (**9**), H (**11**)]. This observation is consistent with earlier investigations of (NSiN)Ir[11,13] and (NSiN)Rh[12] complexes and suggests that (NSiN)Pt(IV) complexes should generally be substitutionally labile. This lability appears to play a role in the clean, facile formation of **9** and **11**.

Further investigations of (NSiN)Pt complexes will attempt to establish reaction pathways for the activation of substrate molecules and incorporation of observed reactivity into catalytic cycles involving Pt(II)/Pt(IV) interconversions.

Experimental Sections

General Procedures. Manipulations involving air-sensitive compounds were conducted using standard Schlenk techniques under a purified N_2 atmosphere or in a Vacuum Atmospheres drybox. In general, solvents were distilled under N_2 from appropriate drying agents and stored in PTFE-valved flasks. Deuterated solvents were purchased from Cambridge Isotopes, dried with appropriate drying agents, and vacuum-transferred before use. NEt_3, tetramethylethylene diamine (tmeda), and COD (Aldrich) were dried with CaH_2 and distilled prior to use. Dihydrogen (Praxair), ethylene (Airgas), and $^{13}CH_4$ (Aldrich) were used as received.

The reagents bis(8-quinolyl)methylsilane (**1**),[12] $(COD)PtCl_2$,[25] $(tmeda)PtMe_2$,[25] $(tmeda)PdMe_2$,[33] $[PtMe_3X]_4$ (X = I,[45] OTf[46]), 8-bromoquinoline,[47] and $Li(Et_2O)_3[B(C_6F_5)_4]$[48] were prepared according to literature procedures. AgOTf and BuLi (1.6 M in hexanes) were purchased from Aldrich and used without further purification.

^1H (500.1 MHz), $^{13}C\{^1H\}$ (124.7 MHz), and $^{29}Si\{^1H\}$ (99.3 MHz) NMR spectra were acquired on Bruker DRX-500, AV-500, or AVB-400 spectrometers. The DRX-500 and AVB-400 spectrometers are each equipped with a 5 mm Z-gradient proton/broadband probe, while the AV-500 instrument features a 5 mm TBI (triple inverse broadband) probe with Z-gradient. ^{19}F (376.5 MHz) NMR spectra were obtained from an AVQ-400 spectrometer containing a 5 mm QNP probe. Unless otherwise noted, NMR spectra were recorded at room temperature and were referenced to protic impurities in the deuterated solvent for ^1H, solvent peaks for $^{13}C\{^1H\}$, $CFCl_3$ for ^{19}F, or $SiMe_4$ for $^{29}Si\{^1H\}$. The $^1H,^{29}Si\{^1H\}$ HMBC experiments were carried out to determine the $^{29}Si-^{195}Pt$ coupling constants. The $^{13}C\{^1H\}$ resonances corresponding to the $B(C_6F_5)_4$ anion or the CF_3 group of the triflate are not reported. Elemental analyses were performed by the University of California, Berkeley College of Chemistry Microanalysis Facility. Infrared spectra were recorded as Nujol mulls on a Nicolet Nexus 6700 FT-IR spectrometer with a liquid nitrogen cooled MCT-B detector.

(NSiN)PtCl (2). A 100 mL Schlenk flask equipped with a magnetic stir bar was charged with $(COD)PtCl_2$ (0.200 g, 0.532 mmol) and **1** (0.160 g, 0.533 mmol). To this solid mixture, approximately 60 mL of CH_2Cl_2 was added, followed by neat NEt_3 (0.21 μL, 1.73 mmol). After 8 h of stirring at room temperature, the reaction solution was evaporated to dryness. The remaining orange residue was dissolved in approximately 8 mL of CH_2Cl_2. At −30 °C, a yellow precipitate was obtained. Drying a 5 mL toluene suspension of this solid at 100 °C under vacuum afforded the COD-free product **2** in 32% yield (0.090 g, 0.170 mmol). ^1H NMR (CD_2Cl_2, 500 MHz): δ 10.2 (d $J_{HH} = 4.0$ Hz, of d $J_{HH} = 2.0$ Hz, 2 H, Ar*H*, $^3J_{PtH} = 45$ Hz), 8.44 (d $J_{HH} = 8$ Hz, of d $J_{HH} = 1.5$ Hz, 2 H, Ar*H*), 8.31 (d $J_{HH} = 7.0$ Hz, of d $J_{HH} = 1.5$ Hz, 2 H, Ar*H*), 7.92 (d $J_{HH} = 8$ Hz, of d $J_{HH} = 1.5$ Hz, 2 H, Ar*H*), 7.66 (d $J_{HH} = 8$ Hz, of d $J_{HH} = 6.5$ Hz, 2 H, Ar*H*), 7.44 (d $J_{HH} = 5.8$ Hz, of d $J_{HH} = 5$ Hz, 2 H, Ar*H*), 0.405 (s, 3 H, SiC*H*$_3$, $^3J_{PtH} = 22$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 158.5, 155.4, 141.6, 138.2, 135.0, 129.8, 128.8, 127.8, 122.2 (aryl carbons), 2.75 (Si*C*H$_3$).

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^{29}Si{^{1}H} NMR (CD_2Cl_2, 99 MHz): δ 14.9 (s, $^1J_{PtSi} = 1414$ Hz). Anal. Calcd (%) for $C_{19}H_{15}N_2SiClPt$: C, 43.06, H, 2.85, N, 5.29. Found: 42.77, H, 2.81, N, 5.01.

***cis*-(κ^2-NSiN)$_2$Pt (3).** A PTFE-valved heavy-walled sealable reaction flask equipped with a micromagnetic stir bar was charged with (tmeda)PtMe$_2$ (0.055 g, 0.161 mmol), **1** (0.100 g, 0.333 mmol), and 10 mL of benzene. The flask was sealed, and the reaction solution was stirred in a temperature-controlled oil bath at 80 °C for 12 h, resulting in a color change from yellow to dark red. Then, the solution was concentrated to a volume of approximately 3 mL and filtered through Celite. Slow evaporation of this benzene solution at room temperature afforded a yellow microcrystalline solid in 64% yield (0.081 g, 0.103 mmol). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 8.79 (d $J_{HH} = 4.4$ Hz, of d $J_{HH} = 1.7$ Hz, 4 H, Ar*H*), 8.16 (m, 8 H, Ar*H*), 7.63 (d $J_{HH} = 8.0$ Hz, of d $J_{HH} = 1.4$ Hz, 4 H, Ar*H*), 7.33 (d $J_{HH} = 8.2$ Hz, of d $J_{HH} = 4.6$ Hz, 4 H, Ar*H*), 7.27 (d $J_{HH} = 8.0$ Hz, of d $J_{HH} = 6.9$ Hz, 4 H, Ar*H*), 0.915 (s, 6 H, SiC*H*$_3$, $^3J_{PtH} = 45$ Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 153.3, 148.7, 148.4, 138.2, 137.3, 128.7, 127.5, 126.7, 120.7 (aryl carbons), 2.24 (Si*C*H$_3$). ^{29}Si{^{1}H} NMR (CD_2Cl_2, 99 MHz): δ −6.0 ($^1J_{PtSi} = 1670$ Hz). Anal. Calcd (%) for $C_{38}H_{30}N_4Si_2Pt$: C, 57.48, H, 3.81, N, 7.06. Found: C, 57.69, H, 3.92, N, 7.09.

(μ-Cl)[(NSiN)Pt]$_2$[B(C$_6$F$_5$)$_4$] (4). To a 10 mL CH_2Cl_2 solution of **2** (0.090 g, 0.170 mmol) was slowly added a 5 mL CH_2Cl_2 solution of Li(Et$_2$O)$_3$[B(C$_6$F$_5$)$_4$] (0.085 g, 0.0935 mmol). The reaction mixture was stirred at room temperature for 4 h, after which it was filtered through Celite and evaporated to dryness, resulting in a yellow foamy residue. The resulting solid was stirred in approximately 10 mL of diethyl ether for 15 min, and then a yellow precipitate started to form. The yellow supernatant was decanted, leaving a yellow solid (**4**) in 68% yield (0.098 g, 0.0575 mmol). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.51 (d $J_{HH} = 6$ Hz, 2 H, Ar*H*, $^3J_{PtH} = 59$ Hz), 8.18 (d $J_{HH} = 8.4$ Hz, 2 H, Ar*H*), 8.04 (d $J_{HH} = 11$ Hz, 2 H, Ar*H*), 7.73 (d $J_{HH} = 10$ Hz, 2 H, Ar*H*), 7.64 (m, 2 H, Ar*H*), 6.71 (d $J_{HH} = 11$ Hz, of d $J_{HH} = 6.8$ Hz, 2 H, Ar*H*), 0.239 (s, 3 H, SiC*H*$_3$, $^3J_{PtH} = 35$ Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 157.6, 155.3, 140.1, 138.8, 135.8, 130.0, 129.9, 128.8, 122.6 (aryl carbons), 2.80 (Si*C*H$_3$). ^{19}F NMR (CD_2Cl_2, 376.5 MHz): −132.3 (br s), −162.8 (t $^3J_{FF} = 21$ Hz), −166.7 (br t $^3J_{FF} = 17$ Hz). ^{29}Si{^{1}H} NMR (CD_2Cl_2, 99 MHz): δ 14.8 ($^1J_{SiPt} = 1378$ Hz). Anal. Calcd (%) for $C_{62}H_{30}N_4Si_2ClBF_{20}Pt_2$: C, 43.71, H, 1.77, N, 3.29. Found: 43.99, H, 1.85, N, 3.21.

(NSiN)PtH$_2$(Cl) (5). A PTFE-valved heavy-walled sealable reaction flask equipped with a small magnetic stir bar was charged with (COD)PtCl$_2$ (0.150 g, 0.401 mmol), **1** (0.253 g, 0.842 mmol), and approximately 15 mL of CH_2Cl_2. The reaction mixture was stirred at 60 °C for 36 h, after which all volatiles were removed under vacuum. The remaining pale yellow solid was washed with benzene (2 × 3 mL) and dissolved in 10 mL of CH_2Cl_2, and the resulting solution was filtered through Celite. The resulting filtrate was concentrated to a volume of approximately 3 mL and layered with 3 mL of diethyl ether. A yellow microcrystalline solid was obtained at room temperature in 54% yield (0.115 g, 0.216 mmol). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 10.3 (m, 1 H, Ar*H*, $^3J_{PtH} = 17$ Hz), 8.28 (d $J_{HH} = 8.0$ Hz, of d $J_{HH} = 1.5$ Hz, 2 H, Ar*H*), 8.18 (d $J_{HH} = 6.5$ Hz, of d $J_{HH} = 1.0$ Hz, 2 H, Ar*H*), 7.81 (d $J_{HH} = 8.5$ Hz, of d $J_{HH} = 1.0$ Hz, 2 H, Ar*H*), 7.62 (d $J_{HH} = 8.0$ Hz, of d $J_{HH} = 7.0$ Hz, 2 H, Ar*H*), 7.55 (d $J_{HH} = 8.0$ Hz, of d $J_{HH} = 5.0$ Hz, 2 H, Ar*H*), 1.31 (s, 3 H, SiC*H*$_3$, $^3J_{PtH} = 36$ Hz), −18.3 (s, 2 H, Pt*H*, $^1J_{PtH} = 1274$ Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 152.4, 152.1, 143.7, 139.3, 136.2 ($J_{PtC} = 18$ Hz), 129.6, 129.4, 127.9, 122.7 ($J_{PtC} = 10$ Hz) (aryl carbons), −3.85 (s, Si*C*H$_3$). ^{29}Si{^{1}H} NMR (CD_2Cl_2, 99 MHz): δ 6.7 (s, *Si*CH$_3$, $^1J_{PtSi} = 982$ Hz). Anal. Calcd (%) for $C_{19}H_{17}N_2SiClPt$: C, 42.89, H, 3.22, N, 5.27. Found: C, 42.58, H, 3.23, N, 5.01. IR (cm^{-1}): 2243 (Pt*H*).

(NSiN)PtMe$_2$(I) (6). To a 100 mL Schlenk flask charged with a 40 mL CH_2Cl_2 solution of [PtMe$_3$I]$_4$ (0.300 g, 0.204 mmol) was added a 20 mL CH_2Cl_2 solution of **1** (0.246 g, 0.819 mmol). The yellow reaction mixture was stirred at room temperature for 24 h, after which the CH_2Cl_2 solution was reduced to a volume of approximately 8 mL. Vapor diffusion of diethyl ether into this CH_2Cl_2 solution at room temperature afforded a yellow crystalline solid in 82% yield (0.436 g, 0.669 mmol). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 11.0 (m, 2 H, Ar*H*), 8.28 (d $J_{HH} = 8$ Hz, of d $J_{HH} = 1.5$ Hz, 2 H, Ar*H*), 8.16 (d $J_{HH} = 6.5$ Hz, of d $J_{HH} = 1.5$ Hz, 2 H, Ar*H*), 7.84 (d $J_{HH} = 8$ Hz, of d $J_{HH} = 1$ Hz, 2 H, Ar*H*), 7.59 (d $J_{HH} = 8$ Hz, of d $J_{HH} = 7$ Hz, 2 H, Ar*H*), 7.46 (d $J_{HH} = 8$ Hz, of d $J_{HH} = 5$ Hz, 2 H, Ar*H*), 1.17 (s, 6 H, PtC*H*$_3$, $^2J_{PtH} = 63$ Hz), 1.00 (s, 3 H, SiC*H*$_3$, $^3J_{PtH} = 22$ Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 158.7, 151.0, 142.6, 139.4, 137.2, 130.3, 130.2, 128.0, 123.9 (aryl carbons), −9.3 (Si*C*H$_3$, $^2J_{PtC} = 57.5$ Hz), −13.3 (Pt*C*H$_3$, $^1J_{PtC} = 640$ Hz). ^{29}Si{^{1}H} NMR (CD_2Cl_2, 99 MHz): δ 9.3 ($^1J_{PtSi} = 1143$ Hz). Anal. Calcd (%) for $C_{21}H_{21}N_2SiIPt$: C, 38.71, H, 3.25, N, 4.30. Found: C, 39.04, H, 3.33, N, 4.11.

(NSiN)PtMe$_2$(OSO$_2$CF$_3$) (7). (1) To a 10 mL CH_2Cl_2 solution of [PtMe$_3$OTf]$_4$ (0.100 g, 0.062 mmol) was added a 5 mL CH_2Cl_2 solution of **1** (0.078 g, 0.260 mmol). After 10 h of stirring at room temperature, the reaction mixture was filtered through Celite. The yellow filtrate was concentrated to a volume of approximately 3 mL. Vapor diffusion of diethyl ether into this CH_2Cl_2 solution at room temperature afforded a yellow crystalline solid in 83% yield (0.138 g, 0.205 mmol).

(2) Complex **7** can be alternatively synthesized from addition of approximately 50 mL of CH_2Cl_2 to a solid mixture of **6** (0.217 g, 0.333 mmol) and AgOTf (0.090 g, 0.350 mmol). The reaction flask was covered with aluminum foil, and the reaction mixture was stirred for 4 h at room temperature. Cannula filtration afforded a clear yellow filtrate, which was concentrated to ca. 5 mL. Vapor diffusion of diethyl ether into this CH_2Cl_2 solution produced **7** in 89% yield (0.199 g, 0.296 mmol). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 9.72 (m, 2 H, Ar*H*), 8.34 (d $J_{HH} = 8.4$ Hz, 2 H, Ar*H*), 8.20 (d $J_{HH} = 6.8$ Hz, 2 H, Ar*H*), 7.92 (d $J_{HH} = 8$ Hz, 2 H, Ar*H*), 7.64 (m, 4H, Ar*H*), 1.12 (s, 3 H, SiC*H*$_3$, $^3J_{PtH} = 28$ Hz), 0.844 (s, 6 H, PtC*H*$_3$, $^2J_{PtH} = 60$ Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 151.7, 150.3, 139.8, 139.6, 136.7, 130.5, 130.3, 128.3, 123.7 (aryl carbons), −7.7 (Si*C*H$_3$, $^2J_{PtC} = 71.2$ Hz), −9.8 (Pt*C*H$_3$, $^1J_{PtC} = 645$ Hz). ^{19}F{^{1}H} NMR (CD_2Cl_2, 376.5 MHz): δ −79.2. ^{29}Si{^{1}H} NMR (CD_2Cl_2, 99 MHz): δ 7.4 ($^1J_{PtSi} = 1223$ Hz). Anal. Calcd (%) for $C_{22}H_{21}N_2O_3F_3SiSPt$: C, 39.22, H, 3.14, N, 4.16. Found: C, 39.25, H, 3.03, N, 4.00.

(μ-I)[(NSiN)PtMe$_2$]$_2$[B(C$_6$F$_5$)$_4$] (8). To a 3 mL CH_2Cl_2 solution of Li(Et$_2$O)$_3$[B(C$_6$F$_5$)$_4$] (0.074 g, 0.0849 mmol) was added a 5 mL CH_2Cl_2 solution of **6** (0.100 g, 0.153 mmol). After 4 h of stirring at room temperature, the reaction mixture was concentrated to ca. 3 mL and filtered through Celite. The resulting filtrate was then layered with 3 mL of diethyl ether at room temperature to afford a pale yellow solid in 85% yield (0.121 g, 0.0650 mmol). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 10.6 (br m, 2 H, Ar*H*), 8.37 (d $J_{HH} = 8.5$ Hz, of d $J_{HH} = 1.5$ Hz, 2 H, Ar*H*), 8.23 (d $J_{HH} = 7.0$ Hz, of d $J_{HH} = 1.5$ Hz, 2 H, Ar*H*), 7.93 (d $J_{HH} = 8.0$ Hz, d $J_{HH} = 1.0$ Hz, 2 H, Ar*H*), 7.67 (d $J_{HH} = 8.0$ Hz, of d $J_{HH} = 7.0$ Hz, 2 H, Ar*H*), 7.49 (d $J_{HH} = 8.0$ Hz, of d $J_{HH} = 5.0$ Hz, 2 H, Ar*H*), 1.28 (s, 6 H, PtC*H*$_3$, $^2J_{PtH} = 62$ Hz), 1.13 (s, 3 H, SiC*H*$_3$, $^3J_{PtH} = 25$ Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 156.4, 150.2, 140.2, 140.0, 137.4, 130.7, 130.3, 128.3, 123.6 (aryl carbons), −8.2 (Si*C*H$_3$), −10.8 (Pt*C*H$_3$). ^{19}F NMR (CD_2Cl_2, 376.4 MHz): δ −132.3 (br m), −162.9 (t $^3J_{FF} = 18.8$ Hz), −166.8 (br t $^3J_{FF} = 18.8$ Hz). ^{29}Si{^{1}H} NMR (CD_2Cl_2, 99 MHz): δ 12.6 (s, $^1J_{PtSi} = 1168$ Hz). Anal. Calcd (%) for $C_{66}H_{42}N_4BF_{20}Si_2IPt_2$: C, 42.73, H, 2.28, N, 3.02. Found: C, 42.66, H, 2.43, N, 2.75.

[(NSiN)PtMe$_2$][B(C$_6$F$_5$)$_4$] (9). To a 5 mL CH_2Cl_2 solution of Li(Et$_2$O)$_3$[B(C$_6$F$_5$)$_4$] (0.126 g, 0.145 mmol) was added a 5 mL CH_2Cl_2 solution of **7** (0.090 g, 0.134 mmol). After 2 h of stirring at room temperature, the reaction mixture was concentrated to 4 mL and filtered through Celite. The resulting yellow filtrate was layered with approximately 4 mL of pentane. At room temperature, a colorless microcrystalline solid was obtained in 91% yield (0.146 g, 0.121 mmol). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 9.17 (br m, 2 H, Ar*H*), 8.47 (d J_{HH} = 8.5 Hz, of d J_{HH} = 1.5 Hz, 2 H, Ar*H*), 8.27 (d J_{HH} = 7.0 Hz, of d J_{HH} = 1.0 Hz, 2 H, Ar*H*), 8.05 (d J_{HH} = 8.0 Hz, d J_{HH} = 1.0 Hz, 2 H, Ar*H*), 7.73 (d J_{HH} = 8.0 Hz, of d J_{HH} = 7.0 Hz, 2 H, Ar*H*), 7.70 (d J_{HH} = 8.0 Hz, of d J_{HH} = 5.0 Hz, 2 H, Ar*H*), 1.31 (s, 3 H, $SiCH_3$, $^3J_{PtH}$ = 32 Hz), 1.03 (s, 6 H, $PtCH_3$, $^2J_{PtH}$ = 60 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 150.4, 149.0, 141.0, 137.1, 136.1, 131.4, 130.5, 128.8, 123.7 (aryl carbons), −5.0 ($PtCH_3$, $^1J_{PtC}$ = 645 Hz), −5.1 ($SiCH_3$, $^2J_{PtC}$ = 71.2 Hz). ^{19}F NMR (CD_2Cl_2, 376.4 MHz): δ −132.3 (br m), −162.9 (t $^3J_{FF}$ = 18.8 Hz), −166.8 (br t $^3J_{FF}$ = 18.8 Hz). $^{29}Si\{^1H\}$ NMR (CD_2Cl_2, 99 MHz): δ 22.8 (s, $^1J_{PtSi}$ = 1126 Hz). Anal. Calcd (%) for $C_{45}H_{21}N_2BF_{20}SiPt$: C, 44.90, H, 1.76, N, 2.33. Found: C, 45.20, H, 1.88, N, 2.33.

(NSiN)PtH$_2$(OTf) (10). To an aluminum foil-covered reaction flask was added a 3 mL CH_2Cl_2 solution of AgOTf (0.036 g, 0.140 mmol) and a 8 mL CH_2Cl_2 solution of **5** (0.070 g, 0.132 mmol). The reaction mixture was stirred at room temperature for 12 h, after which it was filtered through Celite. The pale green filtrate was evaporated to dryness, leaving an analytically pure pale green solid in 88% yield (0.075 g, 0.116 mmol). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 9.56 (m, 2 H, Ar*H*), 8.34 (d J_{HH} = 8.2 Hz, of d J_{HH} = 1.4 Hz, 2 H, Ar*H*), 8.18 (d J_{HH} = 7.0 Hz, of d J_{HH} = 1.4 Hz, 2 H, Ar*H*), 7.88 (d J_{HH} = 8.2 Hz, of d J_{HH} = 1.0 Hz, 2 H, Ar*H*), 7.66–7.61 (m, 4 H, Ar*H*), 1.30 (s, 3 H, $SiCH_3$, $^3J_{PtH}$ = 42 Hz), −17.3 (s, 2 H, Pt*H*, $^1J_{PtH}$ = 1312 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 151.3, 151.2, 141.0, 139.9, 136.5, 129.9, 129.8, 128.2, 123.1 (aryl carbons), −4.03 (s, $SiCH_3$). ^{19}F NMR (CD_2Cl_2, 376.4 MHz): δ −77.0. $^{29}Si\{^1H\}$ NMR (CD_2Cl_2, 99 MHz): δ 2.3 (s, *Si*CH$_3$, $^1J_{PtSi}$ = 1029 Hz). Anal. Calcd (%) for $C_{20}H_{17}N_2SiO_3SF_3Pt$: C, 37.20, H, 2.65, N, 4.34. Found: C, 36.83, H, 2.65, N, 4.68. IR (cm^{-1}): 2231 (Pt*H*).

[(NSiN)PtH$_2$][B(C$_6$F$_5$)$_4$] (11). To a 3 mL CH_2Cl_2 solution of $Li(Et_2O)_3[B(C_6F_5)_4]$ (0.071 g, 0.082 mmol) was added a 5 mL CH_2Cl_2 solution of **10** (0.050 g, 0.077 mmol). After 1 h of stirring, the reaction mixture was concentrated under vacuum to a volume of approximately 2 mL and filtered through Celite and a glass fiber filter. The resulting filtrate was then layered with ca. 2 mL of diethyl ether. After 3 h at room temperature, a white microcrystalline solid was collected in 58% yield (0.052 g, 0.045 mmol). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 9.19 (br m, 2 H, Ar*H*), 8.44 (d J_{HH} = 8.0 Hz, 2 H, Ar*H*), 8.21 (d J_{HH} = 7.0 Hz, of d J_{HH} = 1.0 Hz, 2 H, Ar*H*), 7.95 (d J_{HH} = 8.0 Hz, 2 H, Ar*H*), 7.70 (t J_{HH} = 7.0, 2 H, Ar*H*), 7.66 (d J_{HH} = 8.5 Hz, of d J_{HH} = 5.0 Hz, 2 H, Ar*H*), 1.33 (s, 3 H, $SiCH_3$, $^3J_{PtH}$ = 43 Hz), −16.1 (s, 2 H, Pt*H*, $^1J_{PtH}$ = 1314 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 150.6, 147.5, 141.0, 137.6, 137.3, 130.5, 130.1, 128.2, 123.2 (aryl carbons), −3.8 ($SiCH_3$). ^{19}F NMR (CD_2Cl_2, 376.4 MHz): δ −132.3 (br m), −162.9 (t $^3J_{FF}$ = 18.8 Hz), −166.8 (br t $^3J_{FF}$ = 18.8 Hz). $^{29}Si\{^1H\}$ NMR (CD_2Cl_2, 99 MHz): δ 14.9 (s). Anal. Calcd (%) for $C_{43}H_{17}N_2BF_{20}SiPt$: C, 43.93, H, 1.46, N, 2.38. Found: C, 44.23, H, 1.30, N, 2.22. IR (cm^{-1}): 2228 (Pt*H*).

***cis*-(κ^2-NSiN)$_2$Pd.** To a stirred 5 mL C_6H_6 solution of (tmeda)PdMe$_2$ (0.060 g, 0.237 mmol) was added a 5 mL C_6H_6 solution of **1** (0.143 g, 0.477 mmol). After 8 h at room temperature, the reddish reaction solution was filtered through Celite and dried under vacuum. The resulting solid was redissolved in approximately 3 mL of THF. Crystallization from a 1:1 mixture of THF/diethyl ether at −30 °C afforded *cis*-(κ^2-NSiN)$_2$Pd in 44% yield (0.074 g, 0.104 mmol). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.48 (d J_{HH} = 4.0 Hz, of d J_{HH} = 1.5 Hz, 2 H, Ar*H*), 8.04 (d J_{HH} = 6.5 Hz, of d J_{HH} = 1.5 Hz, 2 H, Ar*H*), 7.49 (d J_{HH} = 8.0 Hz, of d J_{HH} = 2.0 Hz, 2 H, Ar*H*), 7.29 (d J_{HH} = 6.5 Hz, of d J_{HH} = 1.5 Hz, 2 H, Ar*H*), 7.11 (d J_{HH} = 8.0 Hz, of d J_{HH} = 2.0 Hz, 2 H, Ar*H*), 6.62 (d J_{HH} = 8.0 Hz, of d J_{HH} = 4.0 Hz, 2 H, Ar*H*), 1.04 (s, 3 H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 153.0, 150.4, 148.2, 137.0, 136.2, 128.1, 126.7, 126.2, 119.5 (aryl carbons), 2.67 ($SiCH_3$). $^{29}Si\{^1H\}$ NMR (C_6D_6, 99 MHz): δ 13.2 (s). Anal. Calcd (%) for $C_{36}H_{30}N_4Si_2Pd$: C, 57.07, H, 4.31, N, 6.66. Found: C, 56.68, H, 4.17, N, 6.35.

X-ray Crystallography. General Considerations. The single-crystal X-ray analyses of compounds **2**, **7**, **9**, and *cis*-(κ^2-NSiN)$_2$Pd were carried out at the UC Berkeley CHEXRAY crystallographic facility. All measurements were made on a Bruker SMART or APEX CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Crystals were mounted on capillaries or a Kapton loop with Paratone N hydrocarbon oil and held in a low-temperature N_2 stream during data collection. Frames were collected using ω scans at 0.3° increments, using exposures of 10 s (**7** and *cis*-(κ^2-NSiN)$_2$Pd) or 20 s (**2** and **9**). Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the measured positions of reflections in the range $3.5° < 2\theta < 49.4°$. The frame data were integrated by the program SAINT (SAX Area-Detector Integration Program; V4.024; Siemens Industrial Automation, Inc.: Madison, WI, 1995) and corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP. Empirical absorption corrections based on comparison of redundant and equivalent reflections were applied using SADABS. The structures were solved using the teXsan crystallographic software package of Molecular Structure Corporation, using direct methods or Patterson methods, and expanded with Fourier techniques. Unless stated otherwise, all non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions but not refined. The function minimized in the full-matrix least-squares refinement was $\sum w(F_o - F_c)^2$. The weighting scheme was based on counting statistics and included a p-factor to downweight the intense reflections. Crystallographic data are summarized in the Supporting Information.

For **2**: Crystals were grown from a concentrated dichloromethane solution of **2** at −30 °C.

For **7**: Crystals were grown by a vapor diffusion of diethyl ether into a dichloromethane solution of **7** at room temperature.

For **9**: Crystals were grown by a vapor diffusion of pentane into a dichloromethane solution of **9** at room temperature.

For *cis*-(κ^2-NSiN)$_2$Pd: Crystals were grown by layering diethyl ether onto a THF solution of *cis*-(κ^2-NSiN)$_2$Pd at −30 °C.[30] Each asymmetric unit contains one palladium molecule and three THF molecules. A disordered THF molecule lying on the crystallographic C_2 axis was assigned half-occupancy of O(2), C(24)−C(26), and refined isotropically.

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Supporting Information Available: X-ray experimental details and structural data for **2**, **7**, **9**, and *cis*-(κ^2-NSiN)$_2$Pd. This material is available free of charge via the Internet at http://pubs.acs.org.

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