Silyl Derivatives of [Bis(8-quinolyl)methylsilyl]iridium(III) Complexes: Catalytic Redistribution of Arylsilanes and Dehydrogenative Arene Silylation

Preeyanuch Sangtrirutnugul and T. Don Tilley*

Department of Chemistry and Center for New Directions in Organic Synthesis (CNDOS), University of California, Berkeley, Berkeley, California 94720

Received May 17, 2007

The reactive complex (NSiN)Ir(H)(OTf)(coe) (**1**; NSiN = bis(8-quinolyl)methylsilyl, coe = cyclooctene) was generated by reaction of the previously reported (NSiN)Ir(H)Cl(coe) with 1 equiv of AgOTf. Addition of Ph_3SiH to **1** in benzene led to Si−H bond activation and octane elimination with formation of the α-Ph-migrated, 16-electron product (NSiN)IrPh($SiPh_2OTf$) (**2**). The $^{29}Si\{^1H\}$ NMR resonance of **2** at δ 54.0 indicates iridium silyl character, and X-ray crystallography reveals the presence of a highly distorted triflatosilyl group. In acetonitrile, **1** reacts with various silanes to give stable, cationic Ir(III) complexes of the type [(NSiN)IrSiR_3($NCMe)_2$][OTf] (R = $OSiMe_3$, Et, Ph) or [(NSiN)Ir{SiH(R)Ph}($NCMe)_2$][OTf] (R = H, Ph) in good yields. Complex **1** is an active catalyst for arylsilane redistribution and for the dehydrogenative silylation of arenes. The cationic, THF complex [(NSiN)Ir(H)(coe)(THF)][B($C_6F_5)_4$] (**10**), a product of the reaction of **1** with 1 equiv of Li($Et_2O)_3$[B($C_6F_5)_4$] in THF, is a slower catalyst for silane redistribution and dehydrogenative arene silylation. A series of new iridium phosphine complexes were prepared, including (NSiN)Ir(H)Cl(PMe_3) (**13**), [(κ^2-NSiN)Ir(H)($PMe_3)_3$][Cl] (**14**), and (κ^1-NSiN)-Ir(H)(Me)($PMe_3)_3$ (**15**). Treatment of the previously prepared (NSiN)Ir(H)Cl(PPh_3) with 1 equiv of $LiBEt_3H$ afforded the dihydride complex (NSiN)IrH_2(PPh_3) (**11**), which features a hydride ligand in a coordination site *trans* to the NSiN silyl group. The triflate complex (NSiN)Ir(H)(OTf)(PPh_3) (**16**) was obtained by reaction of (NSiN)Ir(H)Cl(PPh_3) with 1 equiv of AgOTf in dichloromethane or by reaction of **1** with 1 equiv of PPh_3 in dichloromethane.

Introduction

Complexes containing multidentate ligands have attracted considerable interest for their ability to mediate new transformations. These ligands lend stability to their complexes and provide a rigid coordination geometry with "enforced" chemical properties. Notable examples of such complexes include (PCP)IrH_2 (PCP = 2,6-($^tBu_2PCH_2)_2C_6H_3$),[1] which catalytically dehydrogenates alkanes, and the pincer-based complex (NCN)NiBr (NCN = 2,6-($Me_2NCH_2)_2C_6H_3$),[2] which is a catalyst for addition of CCl_4 across alkenes.

Despite considerable recent activity in the development and exploration of multidentate ligands, examples of such ligand frameworks containing silicon donors are rare.[3] Since silicon possesses strong electron-donating and *trans*-labilizing properties,[4] a supporting ligand containing silicon should be effective at stabilizing coordinatively unsaturated complexes. In addition, hard, nitrogen-based ligands combined with soft late transition metals are known to promote a number of bond activation processes.[5] On the basis of these considerations, we became interested in the coordination chemistry of the tridentate bis(8-quinolyl)methylsilyl ligand (NSiN) and the reactivity of its complexes. Given the geometry and rigidity of the ligand structure, *facial* coordination modes are expected to be favored.

The syntheses of bis(8-quinolyl)methylsilane, and rhodium complexes derived therefrom, were recently reported.[6] One theme that emerged from this work is that coordinatively unsaturated (NSiN)Rh(III) derivatives are readily accessible, and along these lines the 16-electron complexes [(NSiN)Rh(H)-(PPh_3)][B(C_6F_5)]$_4$ and (NSiN)Rh($CH_2Ph)_2$ were isolated. In these complexes, the silyl group appears to significantly stabilize coordinatively unsaturated, square-pyramidal structures, and the reactivity of such species seems to be somewhat limited. Further investigations of chemistry associated with (NSiN)M fragments has included examinations of iridium derivatives, especially since iridium can more readily access higher oxidation states and is known to facilitate unusual bond activations in several catalytic systems.[1,7] Previous work involved synthesis and study of the chemically robust, 18-electron complex (NSiN)Ir-(H)Cl(coe).[8] This paper describes investigations of the more

---

* Corresponding author. E-mail: tdtilley@berkeley.edu.

(1) Jensen, C. M. *Chem. Commun.* **1999**, *24*, 2443.

(2) van de Kuil, L. A.; Grove, D. M.; Gossage, R. A.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1997**, *16*, 4985.

(3) (a) Stobart, S. R.; Brost, R. D.; Bruce, G. C.; Joslin, F. L. *Organometallics* **1997**, *16*, 5669. (b) Lee, Y.-J.; Bae, J.-Y.; Kim, S.-J.; Ko, J.; Choi, M.-G.; Kang, S. O. *Organometallics* **2000**, *19*, 5546. (c) Tobita, H.; Hasegawa, K.; Minglana, J. J. G.; Luh, L.-S.; Okazaki, M.; Ogino, H. *Organometallics* **1999**, *18*, 2058. (d) Minato, M.; Nishiuchi, J.; Kakeya, M.; Matsumoto, T.; Yamaguchi, Y.; Ito, T. *Dalton Trans.* **2003**, 483.

(4) (a) Chatt, J.; Eaborn, C.; Ibekwe, S. *J. Chem. Soc., Chem. Commun.* **1966**, 700. (b) Haszeldine, R. N.; Parish, R. V.; Setchfield, J. H. *J. Organomet. Chem.* **1973**, *57*, 279.

(5) (a) Slugovc, C.; Padilla-Martinez, I.; Sirol, S.; Carmona, E. *Coord. Chem. Rev.* **2001**, *213*, 129. (b) Peters, J. C.; Harkins, S. B. *Organometallics* **2002**, *21*, 1753. (c) Rodriguez, P.; Diaz-Requejo, M. M.; Belderrain, T. R.; Trofimenko, S.; Nicasion, M. C.; Perez, P. J. *Organometallics* **2004**, *9*, 2162. (d) Graham, W. A. G.; Ghosh, C. K. *J. Am. Chem. Soc.* **1987**, *109*, 4726. (e) Holtcamp, M. W.; Henling, L. M.; Day, M. W.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chim. Acta* **1998**, *270*, 467.

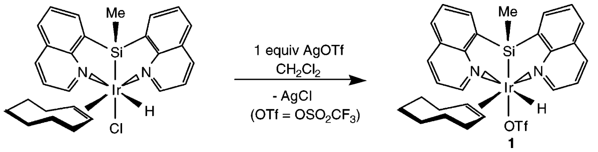
(6) Sangtrirutnugul, P.; Stradiotto, M.; Tilley, T. D. *Organometallics* **2006**, *25*, 1607.

10.1021/om700494q CCC: $37.00
Publication on Web 10/06/2007

reactive triflate analogue, including its use in the catalytic, dehydrogenative silylation of arenes.

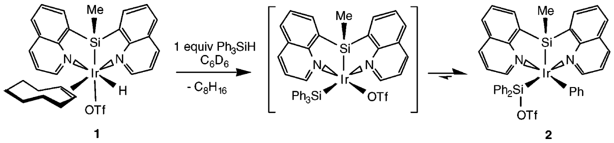
Results and Discussion

Synthesis and Characterization of (NSiN)Ir(H)(OTf)(coe) (1). To access a more reactive, monomeric (NSiN)Ir complex, (NSiN)Ir(H)Cl(coe) was treated with 1.0 equiv of AgOTf in dichloromethane, to produce the corresponding triflate complex (NSiN)Ir(H)(OTf)(coe) (**1**) as an analytically pure, off-white solid in 93% yield (eq 1). The ^{1}H NMR spectrum of **1** contains two sets of quinolyl protons, suggesting C_s symmetry. Additionally, the ^{1}H NMR signals assigned to the hydride (δ −14.7) and cyclooctene (δ 2.07−1.10 and 0.82) ligands are broadened in dichloromethane-d_2 but appear as sharp resonances in benzene-d_6, suggesting an exchange process involving dissociation/association of the triflate anion. The IR spectrum of **1** displays a distinctive band at 2161 cm^{-1}, corresponding to a hydride ligand. On the basis of the NMR and IR data, **1** is believed to possess an octahedral geometry with an inner-sphere triflate weakly bonded to iridium and *trans* to the strongly *trans*-labilizing silyl group.



(1)

Reactions of 1 with Silanes. Treatment of **1** with Ph$_3$SiH in benzene at room temperature resulted in Si−H bond activation, release of cyclooctane, and α-phenyl migration to produce the 16-electron complex (NSiN)IrPh(SiPh$_2$OTf) (**2**, eq 2). This process is related to that found for Cp*(PMe$_3$)IrMe(OTf), which reacts with Ph$_3$SiH to give Cp*(PMe$_3$)IrPh(SiPh$_2$OTf).[9] For both reactions, it is likely that a 16-electron Ir−SiPh$_3$ intermediate rearranges to a phenyl silylene complex of the type (Ph)Ir═SiPh$_2$. This latter, second intermediate then adds triflate to produce the final product.



(2)

An X-ray crystal structure determination of **2** reveals a square-pyramidal geometry about the iridium center with the silyl group in an apical position (Figure 1). The Si2−O1 bond distance of 1.844(5) Å is comparable to the median Si−O bond length for complexes containing a SiR$_2$(OTf) group (1.842 Å).[10] In addition, the sum of the angles around this silicon atom, excluding the triflate substituent, approaches 360° (ca. 350.5°), which is suggestive of a trigonal-planar coordination environment about Si and silylene character. The Ir−Si2 bond distance for the diphenyltriflatosilyl group of **2** (2.289(2) Å) is shorter than those of similar complexes including Cp*(PMe$_3$)IrPh(SiPh$_2$OTf) (2.317(2) Å)[11] and (TFB)(P^{i}Pr$_3$)IrH$_2$(SiPh$_2$OTf) (2.337(2) Å, TFB = tetrafluorobenzobarrelene),[12] but longer than the iridium−silicon bond length in the silylene complex [PhB(CH$_2$PPh$_2$)$_3$]IrH$_2$(SiMes$_2$) (2.260(3) Å).[13] However, the ^{29}Si{^{1}H} NMR signal for the triflatosilyl group of **2** appears at δ 54.0, which is characteristic for a silyl ligand and an sp^3 silicon center.[14]

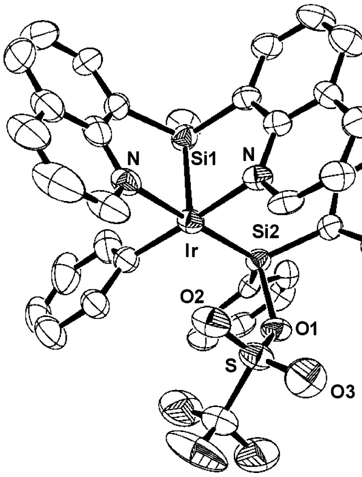


Figure 1. ORTEP diagram of the 16-electron complex **2** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ir−Si2 = 2.289(2), Si2−O1 = 1.844(5). Selected bond angles (deg): C20−Ir−Si2 = 93.1(2), C26−Si2−C32 = 106.4(3).

Given the isoelectronic relationship between NSiN and the well-known Cp* ligand, it is of interest to compare reactivities of the (NSiN)Ir and Cp*Ir fragments. Reaction of the 18-electron complex Cp*(PMe$_3$)IrPh(SiPh$_2$OTf) with 1 equiv of Li(Et$_2$O)$_3$[B(C$_6$F$_5$)$_4$] in dichloromethane-d_2 leads to intramolecular C−H activation of the *o*-hydrogen of the diphenyltriflatosilyl group to afford the four-membered Ir(V) metallacycle [Cp*(PMe$_3$)Ir(η^2-SiPh$_2$C$_6$H$_4$)(H)][B(C$_6$F$_5$)$_4$].[15] In contrast, treatment of **2** with Li(Et$_2$O)$_3$[B(C$_6$F$_5$)$_4$] in dichloromethane-d_2 resulted in a mixture of products based on ^{1}H NMR spectroscopy, and no iridium hydride species were observed.

Addition of (Me$_3$SiO)$_3$SiH to **1** in benzene resulted in the formation of **3**, obtained as an orange microcrystalline solid in 48% yield from slow evaporation of benzene at room temperature (Scheme 1). The ^{1}H NMR spectrum of **3** in benzene-d_6 exhibits one set of quinolyl protons, indicating mirror symmetry for the molecule, and a single resonance is observed for the −OSi*Me*$_3$ groups at δ 0.023. Consistently, there is a distinct ^{29}Si{^{1}H} NMR signal at δ 4.1 assignable to the −O*Si*Me$_3$ group (by a 2D ^{1}H,^{29}Si HMBC NMR experiment). However, the ^{29}Si{^{1}H} NMR shift corresponding to −*Si*(OSiMe$_3$)$_3$ could not be detected, by 2D ^{1}H,^{29}Si HMBC or by direct detection experiments. Variable-temperature ^{1}H NMR experiments revealed that the −OSiMe$_3$ peak becomes broader at lower temperature, but no decoalescence was observed at temperatures as low as −90 °C. The elemental analysis of **3** is consistent with a compound having the empirical formula (NSiN)Ir[Si(OSiMe$_3$)$_3$](OTf). Possible structures of **3** include a five-

---

(7) (a) Göttker-Schnetmann, I.; White, P.; Brookhart, M. *J. Am. Chem. Soc.* **2004**, *126*, 1804. (b) Goldman, A. S.; Roy, A. H.; Huang, Z.; Ahuja, R.; Schinski, W.; Brookhart, M. *Science* **2006**, *312*, 257. (c) Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *Chem. Commun.* **1996**, 2083.

(8) Stradiotto, M.; Fujdala, K.; Tilley, T. D. *Chem. Commun.* **2001**, *13*, 1200.

(9) Burger, P.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 10462.

(10) The Si−OTf median bond length was obtained from the Cambridge Structure Database.

(11) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *Organometallics* **2002**, *21*, 3376.

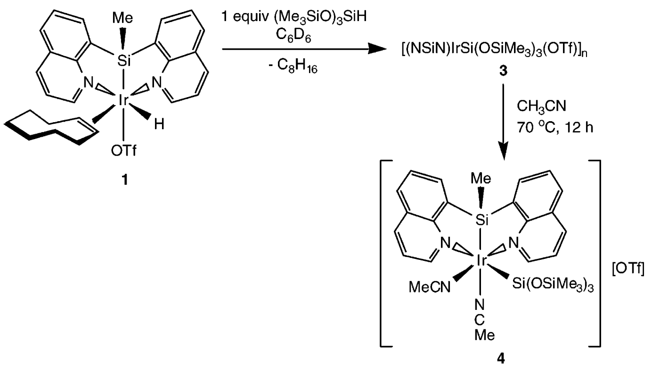
(12) Chen, W.; Edwards, A. J.; Esteruelas, M. A.; Lahoz, F. J.; Oliván, M.; Oro, L. A. *Organometallics* **1996**, *15*, 2185.

(13) Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871.

(14) Corey, J. Y.; Braddock-Wilking, J. *Chem. Rev.* **1999**, *99*, 175.

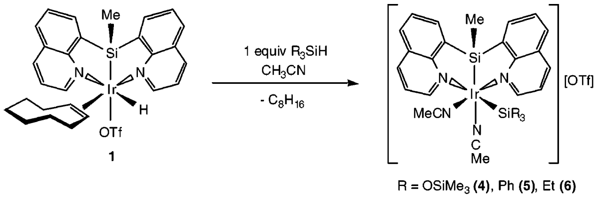
(15) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 1816.

Scheme 1



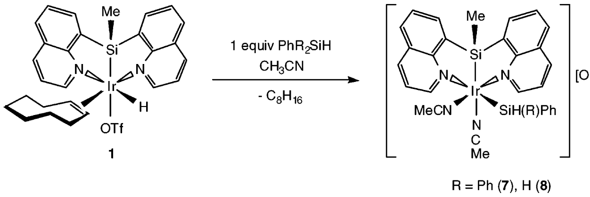
coordinate monomeric complex and a related six-coordinate geometry with an $-OSiMe_3$ group bonded to iridium via the oxygen atom. Additionally, **3** may possess oligomeric structures involving bridging $-Si(OSiMe_3)_3$ groups. A dynamic process involving rapid dissociation and association of the triflate group would explain the apparent equivalency of the quinolyl protons (by ^1H NMR spectroscopy).

Synthesis of 18-Electron Complexes [(NSiN)IrSiR$_3$(NCMe)$_2$][OTf]. Heating an acetonitrile solution of **3** at 70 °C for 12 h quantitatively generated the nitrile complex [(NSiN)IrSi(OSiMe$_3$)$_3$(NCMe)$_2$][OTf] (**4**), which was characterized by multinuclear NMR spectroscopy and combustion analysis. Formation of the acetonitrile complex **4** prompted attempts to trap the proposed triflate intermediate (NSiN)Ir(SiPh$_3$)(OTf) (*vide supra*) with acetonitrile. Thus, reaction of **1** with Ph_3SiH in acetonitrile resulted in release of cyclooctane and formation of a new compound, **5**. Combustion analysis and NMR data identify **5** as the 18-electron complex [(NSiN)IrSiPh$_3$(NCMe)$_2$][OTf] (eq 3). In addition, ^1H NMR spectroscopy reveals that **5** was generated from heating a benzene-d_6 solution of **2** with excess acetonitrile (ca. 10 equiv) at 60 °C for 1 day, indicating that **2** is in equilibrium with the 16-electron intermediate (NSiN)Ir(SiPh$_3$)(OTf) (eq 2). X-ray quality crystals of **5** were obtained by layering diethyl ether onto a dichloromethane solution of the complex at room temperature. Complex **5** possesses a distorted octahedral geometry and an outer-sphere triflate anion. The Ir−NCMe bond *trans* to Si is approximately 0.20 Å longer than that *trans* to the quinolyl N atom. Additional Si−H bond activations were found to give complexes analogous to **5**, as shown in eq 3. Complex **1** oxidatively adds the Si−H bonds of $(Me_3SiO)_3SiH$ and Et_3SiH in acetonitrile at ambient temperature to produce the corresponding products **4** and **6**, respectively. Note that the related nitrile adduct [Cp*(PMe$_3$)RhSiPh$_3$(NCMe)][BAr′$_4$] was reported to undergo intramolecular C−C bond activation to afford the isocyanide complex [Cp*(PMe$_3$)RhMe(CNSiPh$_3$)][BAr′$_4$] at room temperature.[16] In contrast, no reaction was observed for a dichloromethane-d_2 solution of **5** either at ambient temperature or at 60 °C over 2 days.



(3)

It was also of interest to investigate the possible role of α-H migration in the chemistry of (NSiN)Ir silyl complexes. This type of bond activation appears to occur in the reaction of Cp*(PMe$_3$)Ir(Me)(OTf) with Ph_2SiH_2 to afford the hydride-migration product Cp*(PMe$_3$)Ir(H)(SiPh$_2$OTf) via CH_4 elimination.[9] A similar α-H migration results from reaction of [PhB(CH$_2$PPh$_2$)$_3$]Ir(H)(η^3-C$_8$H$_{13}$) with Mes_2SiH_2, to give the iridium silylene complex [PhB(CH$_2$PPh$_2$)$_3$]IrH$_2$(SiMes$_2$).[13] Unfortunately, related reactions of **1** with Ph_2SiH_2 and $PhSiH_3$ in various solvents (e.g., benzene and THF) at room temperature or at 70 °C resulted in intractable mixtures of products. Analysis of the reaction mixtures by ^1H NMR spectroscopy revealed the presence of iridium hydride complexes. Much cleaner reactions were observed with acetonitrile as the solvent, and this allowed synthesis of the Ir(III) complexes **7** and **8** (eq 4).



(4)

The ^1H NMR spectrum of **7** (acetonitrile-d_3) contains a ^1H NMR signal at δ 4.33 assigned to the silicon-bound hydrogen, and the $^{29}Si\{^1H\}$ chemical shift for **7** appears at δ −25 ($^1J_{SiH}$ = 173 Hz). The ^1H NMR spectrum of **8** (acetonitrile-d_3) displays two diastereotopic protons for the phenylsilyl group, observed as doublets at δ 3.39 ($^2J_{HH'}$ = 6.0 Hz, $^1J_{SiH}$ = 171 Hz) and 3.84 ($^2J_{HH'}$ = 6.0 Hz, $^1J_{SiH}$ = 169 Hz). The large Si−H coupling constants for **7** and **8** are within the $^1J_{SiH}$ values reported for free silanes (150−200 Hz) and, hence, suggest no α-H agostic interaction between an Si*H* group and the iridium center.[14] Heating dichloromethane-d_2 solutions of **7** and **8** at 50 °C over 1 day resulted in unidentified products (by ^1H NMR spectroscopy).

Addition of 1 equiv of cyclooctene to a reaction mixture of **1** and Ph_2SiH_2 (1 equiv) in benzene-d_6 at ambient temperature allowed observation of **2** and the new complex (NSiN)IrPh[SiPh(H)OTf] (**9**; 30% formation using a ferrocene standard) after 1 h at room temperature, as identified by ^1H, ^{19}F, and ^{29}-

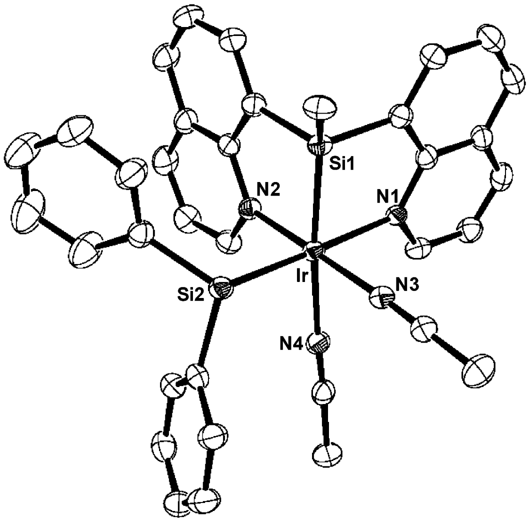


Figure 2. ORTEP diagram of complex **5** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms, one of the phenyl rings on Si2, and a OTf counterion are omitted for clarity. Selected bond lengths (Å): Ir−Si2 = 2.369(1), Ir−N3 = 1.990(3), Ir−N4 = 2.190(3). Selected bond angles (deg): Si2−Ir−N3 = 92.24(8), Si1−Ir−N4 = 171.89(7).

---

[16] Taw, F. L.; White, P. S.; Bergman, R. G.; Brookhart, M. *J. Am. Chem. Soc.* **2002**, *124*, 4192.

Table 1. Results of Catalytic Redistributions Using Catalyst 1 (10 mol %) in the Presence of 1 equiv of Cyclooctene at 85 °C in Benzene-d_6 (reaction time of 24 h)

entry	silane	products (% yield)[a]
1	Ph_2SiH_2	Ph_3SiH (24%), Ph_2SiH_2 (40%), $PhSiH_3$ (trace), SiH_4[b]
2	$PhSiH_3$	Ph_2SiH_2 (11%), $PhSiH_3$ (50%), Ph_3SiH (<3%), SiH_4[b]
3	$MesSiH_3$[c]	Mes_2SiH_2 (25%), $MesSiH_3$ (21%), Mes_3SiH (5%), SiH_4[b]
4	(*p*-tol)SiH_3	(*p*-tol)$_2SiH_2$ (12%), (*p*-tol)SiH_3 (44%), (*p*-tol)$_3SiH$ (<3%), SiH_4[b]
5	$(C_6F_5)SiH_3$	$(C_6F_5)_2SiH_2$ (15%), $(C_6F_5)SiH_3$ (32%), $(C_6F_5)_3SiH$ (14%), SiH_4[b]
6	Et_2SiH_2	N/A

[a] Based on ^1H NMR spectroscopy with a ferrocene standard and GC/MS. [b] Amount of SiH_4 was not determined. [c] Mes = 2,4,6-trimethylphenyl.

Si{^1H} NMR spectroscopy. The ^1H NMR signal at δ 5.49 ($^1J_{SiH}$ = 176 Hz) is assigned to the silyl proton of **9**, for which a 2D $^1H,^{29}Si$ HMBC experiment revealed a correlation between this ^1H NMR resonance and a $^{29}Si\{^1H\}$ resonance at δ −24.5. However, attempts to isolate **9** were unsuccessful, as the product mixtures converted to Ph_3SiH (ca. 60% by ^1H NMR spectroscopy), SiH_4 (trace, δ 3.09), and **2** after 1 day at room temperature (Scheme 2). A GC/MS analysis of the Ph_3SiH did not reveal the presence of deuterated phenyl groups, confirming that silane redistribution of Ph_2SiH_2, rather than benzene activation, had occurred. Interestingly, while complex mixtures in benzene-d_6 were obtained in the absence of cyclooctene (*vide supra*), in the presence of cyclooctene, the silane redistribution products Ph_3SiH and SiH_4 formed cleanly.

Complex 1 as a Catalyst for Arylsilane Redistribution. The activity of **1** as a silane redistribution catalyst was examined further with reactions of 10 mol % of **1** and cyclooctene with a variety of primary and secondary silanes in benzene-d_6 at 85 °C for 24 h. The results obtained are summarized in Table 1. The product yields relative to silane consumption are consistent with an arylsilane redistribution process. For example, consumption of 1 equiv of Ph_2SiH_2 resulted in production of 2/3 equiv of Ph_3SiH. Similarly, 1 equiv of a primary aryl silane $ArSiH_3$ is expected to yield 0.5 equiv of Ar_2SiH_2 and SiH_4 products. However, since Ar_2SiH_2 undergoes further silane redistribution to the tertiary silane Ar_3SiH, lower yields of the secondary silane products were observed. This redistribution chemistry appears to be limited to aryl and hydrogen substituents at silicon, since the non-aryl silane Et_2SiH_2 did not give redistribution products under the same reaction conditions.

A plausible mechanism for silane redistribution, based on α-migration chemistry, is proposed in Scheme 3. The Si−H bond oxidative addition of Ph_2SiH_2 to **1** generates the 16-electron intermediate (NSiN)Ir($SiPh_2H$)(OTf) (**A**), which may undergo α-Ph migration to produce the observed Ir(III) species **9**. An Si−H oxidative addition to **9**, followed by Si−C bond reductive elimination, affords Ph_3SiH and the 16-electron iridium hydride species (NSiN)IrH[SiPh(H)OTf]. An α-H migration from iridium to silicon and Si−H bond activation of Ph_2SiH_2 may result in an Ir(V) disilylhydride, which could reductively eliminate $PhSiH_3$ and reproduce **A**. Phenylsilane may re-enter the catalytic cycle as a starting material to be converted to redistribution products (Ph_3SiH, Ph_2SiH_2, and SiH_4). This repeated silane redistribution may account for the fact that $PhSiH_3$ is undetected (by ^1H NMR spectroscopy and GC/MS).

Since complex **2** is observed by ^1H NMR spectroscopy at the end of the catalytic reaction with Ph_2SiH_2 as a substrate, formation of **2** is believed to arise from addition of the redistribution product, Ph_3SiH, to the intermediate **A**, as shown in Scheme 3. At elevated temperature, **2** may rearrange to (NSiN)Ir($SiPh_3$)(OTf), which is expected to react with Ph_2SiH_2 to produce **A** and Ph_3SiH. Consistent with this, it was found that **2** is a catalyst for the arylsilane redistribution of Ph_2SiH_2 to Ph_3SiH (benzene-d_6, 85 °C, 24 h, 10 mol % **2**).

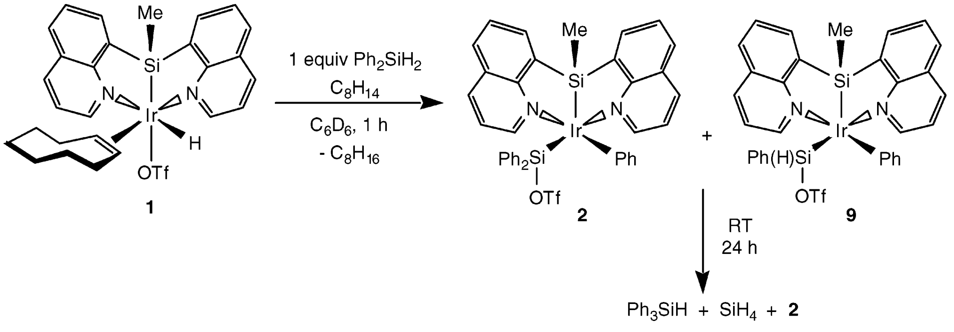
To investigate the role of cyclooctene as a promoter in the catalytic redistribution, it was removed from the reaction system. By ^1H NMR spectroscopy, only about 30% of the Ph_2SiH_2 was consumed, compared to 60% consumption of Ph_2SiH_2 in the presence of cyclooctene after 24 h (Table 1). While the exact role of cyclooctene in the catalysis is still unclear, its presence apparently speeds up the reaction rate, possibly through stabilization of the reactive, 16-electron species **A** and **B**.

Complex 1 as a Catalyst for Dehydrogenative Arene Silylation. The chemistry described above established the utility of (NSiN)Ir fragments in Si−H bond activation and Si−C bond formation. Thus, it seemed possible to observe dehydrogenative couplings of silanes with hydrocarbons, given the ability of (NSiN)Ir species to activate C−H bonds.

A benzene-d_6 solution of Ph_3SiH, the hydrogen-acceptor *tert*-butylethylene (TBE), and 10 mol % of **1** was heated to 120 °C for 24 h. These conditions resulted in consumption of 67% of the Ph_3SiH and formation of $Ph_3SiC_6D_5$ along with $Ph_3SiCH{=}CH^tBu$ as a minor product, based on ^1H NMR spectroscopy and GC/MS analysis (Table 2). The scope of this dehydrogenative arene silylation catalysis was then examined with other arene substrates including trifluoromethylbenzene and chlorobenzene. Under the same catalytic conditions, higher conversions were obtained for the latter substrates, but the selectivity was lower. The hydrogen acceptor is essential for the catalytic conversions, as only trace amounts of $Ph_3SiC_6D_5$ were detected in the absence of TBE after 24 h at 120 °C in benzene-d_6.

By replacing TBE with norbornene as the hydrogen acceptor, fewer coproducts and none of the reductive alkene hydrosilylation products were observed under the same reaction conditions (entries **4**−**7**; Table 2). The best result was obtained from

Scheme 2



Scheme 3

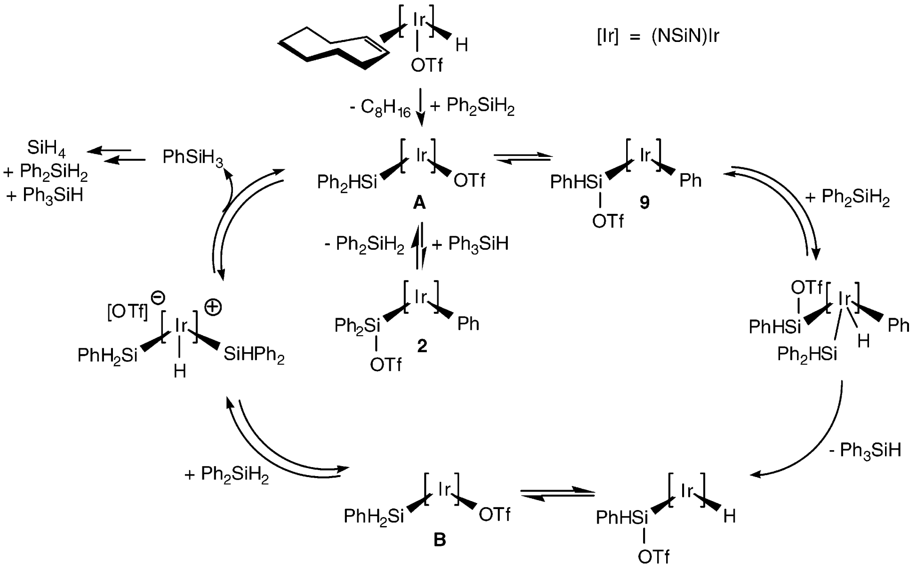


Table 2. Results for Catalytic Dehydrogenative Silylation of Arenes, Using 1 (10 mol %) and Ph_3SiH at 120 °C (reaction time of 24 h)

entry	solvent	alkene	products (yield)[a]
1	C_6D_6	TBE	$Ph_3SiC_6D_5$ (51%), $Ph_3SiCH{=}CH^tBu$ (11%)
2	$C_6H_5CF_3$	TBE	$Ph_3SiC_6H_4CF_3$ (43%),[b] $Ph_3SiCH{=}CH^tBu$ (32%), Ph_3SiF (10%)
3	C_6H_5Cl	TBE	$Ph_3SiC_6H_4Cl$ (53%),[b] $Ph_3SiCH{=}CH^tBu$ (42%)
4[c]	C_6D_6	norbornene	$Ph_3SiC_6D_5$ (100%)
5	$C_6H_5CF_3$	norbornene	$Ph_3SiC_6H_4CF_3$ (81%),[b] Ph_3SiF (15%)
6	C_6H_5Cl	norbornene	$Ph_3SiC_6H_4Cl$ (45%)[b]
7	$C_6H_5CH_3$	norbornene	$Ph_3SiC_6H_4CH_3$ (71%)[b]

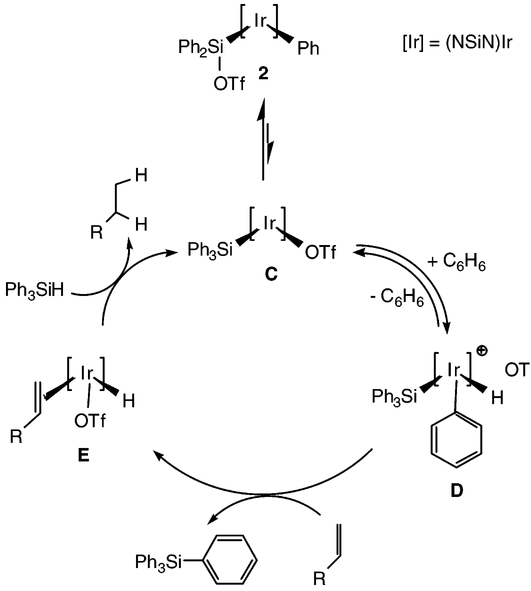
[a] Based on GC/MS with a ferrocene standard. [b] *m*- and *p*-substitutions based only on GC/MS results. [c] Reaction time is 48 h.

a catalytic system containing 10 mol % of **1**, Ph_3SiH, and norbornene in benzene-d_6, which resulted in complete conversion to $Ph_3SiC_6D_5$ after 2 days at 120 °C.

Related arene dehydrogenative silylations have been reported by Berry and co-workers.[17] Using $[Cp^*RhCl_2]_2$ as a catalyst, various arenes were silylated with Et_3SiH at 150 °C, with TBE as a hydrogen acceptor. The relative reactivities of monosubstituted arene compounds C_6H_5X, as measured by GC/MS, revealed enhanced dehydrogenative coupling rates with more electron-withdrawing arene substituents (e.g., CF_3 (2.8) > F (1.4) > H (1.0) > CH_3 (0.32)). This trend reflects the results often observed for nucleophilic C−H activation by low-valent late transition metals,[18,19] since more electron-deficient π-systems should react more rapidly with metal-based nucleophiles. Thus, activation of electron-deficient arenes is kinetically preferred over the activation of electron-rich arenes.[19] In comparison, the reactivity trend observed for our system is similar although less pronounced:

$$CF_3\,(2.3) > Cl\,(2.0) > CH_3\,(1.2) > H\,(1.0)$$

Scheme 4



A proposed mechanism for catalytic dehydrogenative arene silylation is given in Scheme 4. As with the silane redistribution mechanism, reversible α-Ph migration in **2** results in the 16-electron intermediate (NSiN)Ir($SiPh_3$)(OTf) (**C**), which may be capable of arene C−H bond activation at 120 °C to give the cationic Ir(V) arylsilylhydride species **D**. A Si−C bond reductive elimination step then produces the coupling product and an iridium hydride species. Addition of a hydrogen acceptor, TBE, and another Ph_3SiH molecule to this iridium hydride intermediate would regenerate **A**, with elimination of *tert*-butylethane. Presumably, the vinylsilane byproducts are formed by a competing, dehydrogenative hydrosilylation process.

Synthesis and Reactivity of [(NSiN)Ir(H)(coe)(THF)]-[$B(C_6F_5)_4$]. Given the interesting bond activation and catalytic chemistry associated with **1**, potentially more reactive complexes were targeted. Specifically, an attempt was made to replace the triflate anion in **1** with the less coordinating anion $B(C_6F_5)_4^-$. The triflate moiety in **1** was exchanged using 1 equiv of Li-$(Et_2O)_3[B(C_6F_5)_4]$ in dichloromethane to afford the five-coordinate, cationic complex [(NSiN)Ir(H)(coe)][$B(C_6F_5)_4$], based on ^1H NMR spectroscopy (dichloromethane-d_2). Attempts to isolate this cationic compound were unsuccessful, but the analytically pure THF adduct [(NSiN)Ir(H)(coe)(THF)][$B(C_6F_5)_4$]

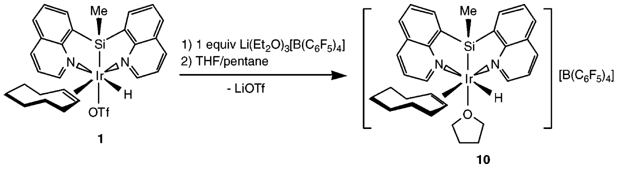
---

(17) Ezbiansky, K.; Djurovich, P. I.; La Forest, M.; Sinning, D. J.; Zayes, R.; Berry, D. H. *Organometallics* **1998**, *17*, 1455.

(18) (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (b) Tolman, C. A.; Ittel, S. D.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* **1979**, *101*, 1742.

(19) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.

(**10**) was obtained from a 1:1 mixture of THF/pentane as a flaky, yellow solid in 76% yield (eq 5). The ^{1}H NMR resonance (THF-d_8) at δ −14.5 is assigned to Ir−*H*, and the IR band corresponding to the hydride ligand appears at 2035 cm^{-1}.

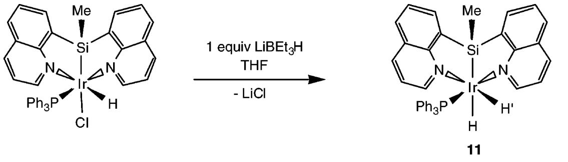


(5)

Treatment of **10** with Ph$_3$SiH in a variety of solvents including dichloromethane-d_2, PhF/benzene-d_6, *o*-dichlorobenzene-d_4, and THF-d_8 resulted in an intractable mixture of complexes similar to those observed with reaction of **2** with Li(Et$_2$O)$_3$[B(C$_6$F$_5$)$_4$]. Employing **10** as a catalyst for both silane redistribution and dehydrogenative arene silylation did not reveal any improvements over **1**. For the dehydrogenative coupling reaction, 10 mol % of **10** in a benzene-d_6 solution of Ph$_3$SiH and norbornene gave only 50% conversion to Ph$_3$SiC$_6$D$_5$ compared to complete conversion with **1** as a catalyst under the same reaction conditions (2 days, 120 °C). The low yield is partly a result of formation of a significant amount of side products including Ph$_3$SiF (12%), a product obtained from C−F bond activation of the perfluoroaryl rings of B(C$_6$F$_5$)$_4$$^-$. In addition, the inferior catalytic reactivity of **10** probably results from the lower solubility of **10** in arene solvents and its decreased stability at high temperature.

Synthesis of (NSiN)Ir(H)(R)(L) [R = H, alkyl]. For explorations of bond activations by the (NSiN)Ir fragment, hydrides of the type (NSiN)Ir(H)(R)(L) (R = H, alkyl) were targeted. Such species were envisioned as precursors to Ir(I) “(NSiN)Ir(L)” species via reductive elimination of R−H. Furthermore, the coordinatively unsaturated (NSiN)Ir(L) is expected to be a highly reactive fragment, given the chelate ring strain that should be imposed by the sp^3-hybridized silicon center of the NSiN ligand in a square-planar complex.

A simple synthetic pathway to (NSiN)Ir(H)(R)(L) complexes would involve halide displacement reactions at the iridium center. Synthesis of the previously reported, 18-electron phosphine complex (NSiN)Ir(H)Cl(PPh$_3$) involved addition of 1 equiv of PPh$_3$ to (NSiN)Ir(H)Cl(coe) in dichloromethane.[8] Reaction of (NSiN)Ir(H)Cl(PPh$_3$) with 1 equiv of LiBEt$_3$H in THF at room temperature afforded a red microcrystalline solid, characterized as the iridium dihydride complex (NSiN)IrH$_2$(PPh$_3$) (**11**) (eq 6).

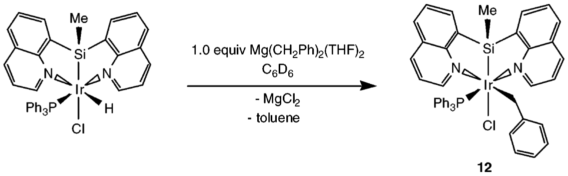


(6)

The ^{1}H NMR spectrum of **11** in THF-d_8 contains two sets of quinolyl hydrogens, indicating the absence of mirror symmetry for the molecule, and two hydride resonances as doublets of doublets at δ −2.07 ($^2J_{\mathrm{HP}}$ = 15 Hz, $^2J_{\mathrm{HH'}}$ = 3.2 Hz) and −19.0 ($^2J_{\mathrm{H'P}}$ = 23 Hz, $^2J_{\mathrm{H'H}}$ = 3.2 Hz). One of the hydride resonances of **11** (δ −19.0) exhibits a chemical shift similar to that of its chloride analogue (NSiN)Ir(H)Cl(PPh$_3$) (δ −19.1), suggesting a hydride ligand located *cis* to the silyl group. Consequently, the more downfield-shifted peak at δ −2.07 is assigned to the hydride *trans* to Si. The IR spectrum of **11** consists of two strong hydride bands at 2122 and 1778 cm^{-1}, corresponding to *cis*-hydride (H′) and *trans*-hydride (H), respectively.

Complex **11** is sparingly soluble in benzene but completely soluble in THF and dichloromethane. Although **11** is stable in THF solution and as a solid, it was found to slowly react with dichloromethane solvent at room temperature ($t_{1/2} \approx$ 3 days) to cleanly produce (NSiN)Ir(H)Cl(PPh$_3$) and chloromethane. Reaction of **11** with C$_2$H$_4$ in benzene-d_6 at ambient temperature resulted in decomposition of the starting materials, although the ^{1}H NMR spectrum indicated the formation of C$_2$H$_6$.

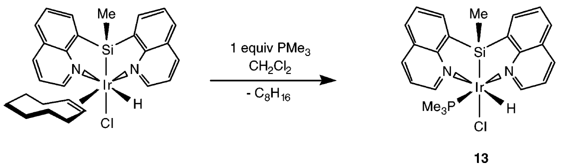
Previous attempts to synthesize Rh(III) complexes of the type (NSiN)Rh(H)(R)(PPh$_3$) included the alkylation of (NSiN)Rh(H)Cl(PPh$_3$) with 1 equiv of Mg(CH$_2$Ph)$_2$(THF)$_2$ in benzene to afford the 18-electron, Rh(III) complex (NSiN)Rh(CH$_2$Ph)Cl(PPh$_3$) and toluene.[6] Although the mechanism of this reaction is still unclear, the alkyl hydride species (NSiN)Rh(H)(CH$_2$Ph)(PPh$_3$) is believed to be generated as a transient intermediate. Given the greater strength of Ir−R (vs Rh−R) bonds, it was of interest to investigate related alkylations with iridium in search of intermediates and further mechanistic information.



(7)

Slow addition of a benzene solution of (NSiN)Ir(H)Cl(PPh$_3$) to a benzene solution of either 0.5 or 1.0 equiv of Mg(CH$_2$Ph)$_2$(THF)$_2$ resulted in clean formation of the 18-electron complex (NSiN)Ir(CH$_2$Ph)Cl(PPh$_3$) (**12**) and toluene (eq 7). Analytically pure **12** was obtained from slow evaporation of a benzene solution of the reaction mixture. The hydrocarbyl intermediate (NSiN)Ir(H)(CH$_2$Ph)(PPh$_3$) was not detected in the benzene-d_6 reaction solution (by ^{1}H NMR spectroscopy at room temperature).

To explore related reactivity for a more electron-rich PMe$_3$ derivative, attempts were made to synthesize (NSiN)Ir(H)Cl(PMe$_3$). Slow addition of 1 equiv of PMe$_3$ to (NSiN)Ir(H)Cl(coe) in dichloromethane afforded **13**, obtained as a crystalline yellow solid from THF (eq 8). According to ^{1}H NMR spectroscopy, the product was characterized as the desired complex (NSiN)Ir(H)Cl(PMe$_3$) (**13**) with ^{1}H resonances at δ −19.6 (d, $^2J_{\mathrm{HP}}$ = 22 Hz) and 1.30 (d, $^2J_{\mathrm{HP}}$ = 22 Hz), corresponding to the hydride and PMe$_3$ groups, respectively. The ^{31}P{^{1}H} NMR spectrum contains a singlet at δ −40.3 assigned to the PMe$_3$ ligand.



(8)

Interestingly, addition of an excess amount (ca. 10 equiv) of PMe$_3$ to a dichloromethane solution of (NSiN)Ir(H)Cl(coe) resulted in a different product. This product was identified, by NMR spectroscopy, as the cationic κ^2-NSiN complex [(κ^2-NSiN)Ir(H)(PMe$_3$)$_3$][Cl] (**14**) (eq 9). The ^{31}P{^{1}H} NMR spectrum of **14** consists of three distinct ^{31}P{^{1}H} multiplets at δ −50.9 (dd, $^2J_{\mathrm{PP'}}$ = 20 Hz, $^2J_{\mathrm{PP'}}$ = 10 Hz), −51.2 (br m), and −51.6 (br m). Two of these multiplets are broadened, presumably as a result of their *trans* coordination to the strongly *trans*-influencing hydride and silyl ligands. The ^{1}H NMR spectrum

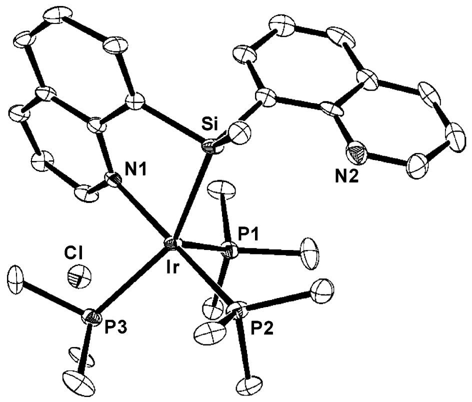
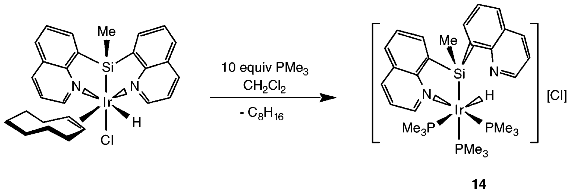


Figure 3. ORTEP diagram of the cationic complex **14** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms and a dichloromethane molecule are omitted for clarity. Selected bond lengths (Å): Ir−P1 = 2.363(3), Ir−P2 = 2.262(3), Ir−P3 = 2.411(3). Selected bond angles (deg): N1−Ir−Si = 80.0(2), Si−Ir−P3 = 150.27(10), N1−Ir−P2 = 175.1(2), P1−Ir−P2 = 94.34(10).

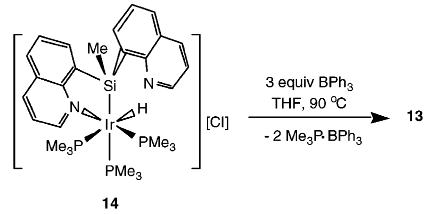
of **14** displays a hydride signal that is downfield-shifted (δ −10.9) relative to that for **13** (δ −19.6). Consistent with the NMR results, the IR spectrum reveals a strong band corresponding to the hydride ligand at 2022 cm^{-1}. For comparison, the analogous stretch for **13** is at higher wave number (2105 cm^{-1}).



(9)

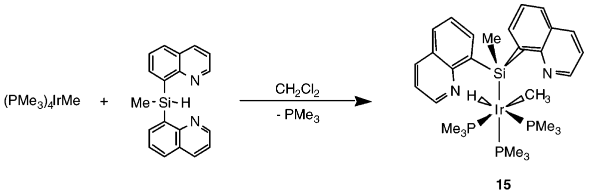
X-ray quality single crystals of **14** were obtained from a 3:1 mixture of pentane and dichloromethane at room temperature. Cationic complex **14** may be described as having an octahedral geometry with the NSiN ligand bonded to the iridium center in a bidentate fashion at the N and Si atoms (Figure 3). This bidentate coordination presumably relieves angle strain at silicon and allows a stronger Ir−P (vs Ir−N) bond to form. The N−Ir−Si bite angle is small (80.0(2)°) due to the NSiN ligand rigidity. The three PMe_3 ligands occupy facial coordination sites about the iridium center and there is an outer-sphere chloride atom. Although the hydride ligand could not be located in the difference Fourier map, it is presumed to occupy the coordination site *trans* to one of the PMe_3 groups. As expected, the longest Ir−P bond distance (2.411(3) Å) belongs to that *trans* to silicon.

An attempt to remove a PMe_3 ligand was made by the addition of BPh_3 to **14**.[20] Treatment of **14** with 3 equiv of BPh_3 in THF at 90 °C resulted in the previously prepared complex **13** and $Me_3P{\cdot}BPh_3$ after 2 days, as evidenced by NMR spectroscopy. However, prolonged heating of **13** in the presence of BPh_3 at 90 °C in THF did not yield the PMe_3-free species (NSiN)Ir(H)Cl (by ^1H NMR spectroscopy). With complex **13** in hand, an attempt was made to obtain the PMe_3 analogue of **12**, $(NSiN)IrH_2(PMe_3)$. Unfortunately, no reaction was observed from addition of 1 equiv of $LiBEt_3H$ to a THF solution of **13** even upon heating the reaction mixture to 90 °C for 2 days.



(10)

Possible synthetic pathways to alkyl hydride complexes of the type (NSiN)Ir(H)(R)(L) include methods that introduce the NSiN ligand into a complex already containing an Ir−alkyl bond. One such attempt involved addition of bis(8-quinolyl)methylsilane to 1 equiv of $(PMe_3)_4IrMe$ in benzene to produce the alkyl hydride Ir(III) product $(\kappa^1\text{-NSiN})Ir(H)(Me)(PMe_3)_3$ (**15**) as an orange solid in 71% yield (eq 11). The $^{31}P\{^1H\}$ NMR spectrum in benzene-d_6 exhibits three different PMe_3 groups at δ −59.6 (br m), −60.6 (t, $^2J_{PP}$ = 17 Hz), and −62.7 (t, $^2J_{PP}$ = 17 Hz). A broad $^{31}P\{^1H\}$ shift at δ −59.6 is assigned to the PMe_3 ligand *trans* to the strongly *trans*-labilizing silicon. According to ^1H NMR spectroscopy, a hydride resonance appears as a doublet of virtual triplets at δ −11.3 (dt, $^2J_{HP}$ = 131 Hz, $^2J_{HP'} \approx 17$ Hz), suggesting a hydride with one *trans* and two *cis* PMe_3 groups.



(11)

The X-ray structure of **15** reveals a highly distorted octahedral geometry about the iridium center with the NSiN ligand bound in a monodentate fashion and the three PMe_3 groups bonded in a *fac* arrangement to iridium (Figure 4). The Si−Ir−P(2) angle of 155.33(7)° is smaller than the ideal value of 180°, as a result of a compact size of the hydride ligand and/or to avoid having the PMe_3 group directly *trans* to silicon. The iridium hydride ligand was located *trans* to a PMe_3 ligand and was positionally refined.

Complex **15** is similar to complexes of the type $(PMe_3)_3Ir(H)(Me)(SiR_3)$, reported by Milstein and co-workers.[21] The latter complex, which also possesses a *fac* geometry, eliminates alkane upon heating to give a reactive Ir(I) silyl derivative. This species then undergoes quantitative and regioselective intramolecular C−H activations. For comparison, thermal decomposition of **15** was conducted under similar reaction conditions (C_6D_6, 100 °C, 12 h). However, ^1H and $^{31}P\{^1H\}$ NMR spectroscopy reveals that the decomposition of **15** produces a complex mixture including free PMe_3.

Synthesis and Reactivity of (NSiN)Ir(H)(OTf)(L) Complexes. In the related (NSiN)Rh system, the 16-electron, cationic complex $[(NSiN)Rh(H)(PPh_3)][B(C_6F_5)_4]$ exhibits no bond activation reactivity toward Et_3SiH and H_2 even at elevated temperature.[6] Given the higher stability of Ir(V) species, bond activations involving (NSiN)Ir(III) complexes are expected to be more facile. Thus, syntheses and reactivity studies of triflate complexes of the type (NSiN)Ir(H)(OTf)(L) [L = PPh_3, PMe_3] were explored.

The triflate complex $(NSiN)Ir(H)(OTf)(PPh_3)$ (**16**) was isolated as a yellow solid (68% yield) from reaction of the corresponding chloride complex with 1 equiv of AgOTf in

---

(20) Dioumaev, V. K.; Plossl, K.; Carroll, P. J.; Berry, D. H. *Organometallics* **2000**, *19*, 3374.

(21) Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 6456.

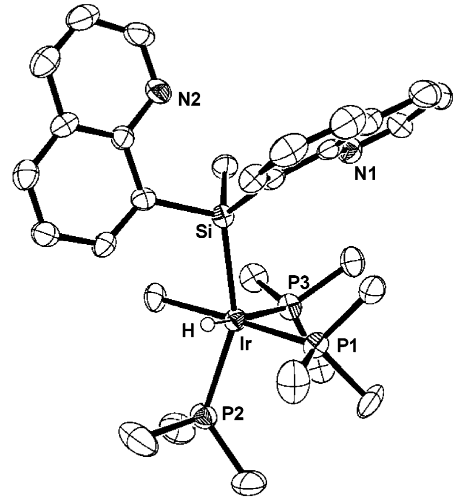
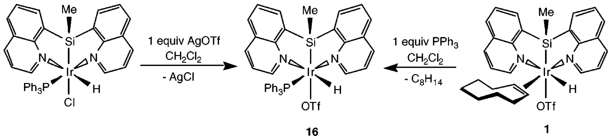


Figure 4. ORTEP diagram of complex **15** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms, except Ir−*H*, and half a diethyl ether molecule are omitted for clarity. Selected bond lengths (Å): Ir−P1 = 2.294(2), Ir−P2 = 2.353(2), Ir−P3 = 2.325(2). Selected bond angles (deg): Si−Ir−P2 = 155.33(7), C20−Ir−P1 = 172.9(2).

dichloromethane (eq 12). The ^{1}H NMR spectrum of **16** (d_8-THF) contains an Ir−*H* resonance as a doublet at δ −16.5 ($^1J_{HP}$ = 19 Hz) with a broad ^{31}P{^{1}H} NMR shift at δ 9.3 in the ^{31}P{H} NMR spectrum. The infrared stretching band for the hydride group was observed at 2120 cm^{-1}.



(12)

Alternatively, **16** may be synthesized in good yield (84%) by addition of 1 equiv of PPh$_3$ to **1** in dichloromethane at room temperature. Monitoring the reaction by ^{1}H NMR spectroscopy showed that the reaction was complete within 1 h. Preliminary reactivity studies with **16** indicate that it is rather inert, as it does not react with Et$_3$SiH or H$_2$ in dichloromethane-d_2, even at temperatures up to 80 °C for 2 days.

Conclusions

The iridium triflate complex (NSiN)Ir(H)(OTf)(coe) (**1**) may be viewed as a convenient synthon for the "(NSiN)Ir" fragment, since the triflate anion is readily displaced, and the (H)(coe) ligand set behaves as a cyclooctyl leaving group in reactions with silanes. Thus, the activation of phenylsilanes by **1** produces putative intermediates of the type (NSiN)Ir(SiRPh$_2$)OTf (R = H, Ph), which undergo rapid α-Ph migrations to produce **2** and **9**, respectively. Iridium silyl complexes have previously been associated with α-migration chemistry,[9,11,22] but it is worth noting that phenyl groups appear to migrate more readily than hydride in this system, and α-H migration products have yet to be observed for (NSiN)Ir compounds. The migration of phenyl groups in this system appears to be reversible, as indicated by the addition of acetonitrile to **2** to form the silyl derivatives [(NSiN)IrSiPh$_3$(NCMe)$_2$][OTf]$_2$ (**5**) at 60 °C. Generally, acetonitrile allows isolation of silyl complexes of the latter type (e.g., **4**−**8**).

Given the ability of **1** to activate silanes, it is not too surprising that this compound is a catalyst for the redistribution of aryl and hydrogen groups at silicon. At this time, the mechanism of this process is uncertain. Several mechanisms for such redistribution reactions have been proposed, including pathways involving 1,3-migration of groups between silicon centers and a silyl(silylene) complex,[23] bimolecular reactions between silyl and silylene complexes,[24] and 1,2- or α-migrations involving the metal and silicon centers.[25] The mechanism of redistribution as catalyzed by **1** likely involves α-migration chemistry, since this has been observed in stoichiometric reactions of this system.

Interestingly, **1** represents one of the few complexes known to catalyze the dehydrogenative coupling of silanes and arenes.[17,26] Thus, (NSiN)Ir complexes may also participate in C−H activation processes, and this suggests the possibility of further catalytic reactions involving such iridium species. Given the observed reactivity with PMe$_3$, involving different binding modes for the NSiN ligand, it appears that bond activations and catalytic mechanisms may involve unsaturated intermediates produced by dissociation of quinolyl groups. Further explorations of this system are expected to provide more complete descriptions of possible reactivity modes.

Experimental Procedures

General Procedures. All manipulations were conducted under an N$_2$ atmosphere using standard Schlenk techniques or a Vacuum Atmospheres Unilab drybox. In general, solvents were distilled under N$_2$ from appropriate drying agents and stored in PTFE-valved flasks. Deuterated solvents (Cambridge Isotopes) were dried with appropriate drying agents and vacuum-transferred prior to use.

The reagents bis(8-quinolylmethyl)silane,[6] (NSiN)Ir(H)Cl(coe),[8] (Me$_3$P)$_4$IrMe,[27] (NSiN)Ir(H)Cl(PPh$_3$),[8] Mg(CH$_2$Ph)$_2$(THF)$_2$,[28] and Li(Et$_2$O)$_3$[B(C$_6$F$_5$)$_4$][29] were prepared according to literature procedures. Norbornene was purchased from Aldrich and purified by vacuum sublimation. Cyclooctene and *tert*-butylethylene (Aldrich) were distilled under N$_2$ and stored in a silylated PTFE-valve storage flask. All other chemicals were purchased from Aldrich or Gelest and used without further purification. Ethylene (Air Gas) was used as received.

^{1}H (500.1 MHz), ^{13}C{^{1}H} (124.7 MHz), and ^{29}Si{^{1}H} (99.3 MHz) NMR spectra were acquired on Bruker DRX-500 or AV-500 spectrometers. The DRX-500 spectrometer is equipped with a 5 mm Z-gradient proton/broad band probe, while the AV-500 instrument features a 5 mm TBI (triple inverse broad-band) probe with Z-gradient. ^{19}F (376.5 MHz) and ^{31}P{^{1}H} (162 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

---

(22) (a) Esteruelas, M. A.; Lahoz, F. J.; Oliván, M.; Offate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 4246. (b) Klei, S. R.; Bergman, R. G.; Tilley, T. D. *Organometallics* **2001**, *20*, 3220.

(23) (a) Jones, K. L.; Pannell, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 11336. (b) Pannell, K. H.; Cervantes, J.; Hernandez, C.; Cassias, J.; Vincenti, S. *Organometallics* **1986**, *5*, 1056. (c) Pannell, K. H.; Rozell, J. M.; Hernandez, C. *J. Am. Chem. Soc.* **1989**, *111*, 4482. (d) Pannell, K. H.; Wang, L.-J.; Rozell, J. M. *Organometallics* **1989**, *8*, 550, and references therein.

(24) Grumbine, S. K.; Tilley, T. D. *J. Am. Chem. Soc.* **1994**, *116*, 6951.

(25) (a) Kobayashi, T.; Hayashi, T.; Yamashita, H.; Tanaka, M. *Chem. Lett.* **1988**, 1411. (b) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

(26) (a) Dioumaev, V. K.; Yoo, B. R.; Procopio, L. J.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **2003**, *125*, 8936. (b) Dioumaev, V. K.; Procopio, L. J.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **2003**, *125*, 8043. (c) Kakiuchi, F.; Matsumoto, M.; Sonoda, M.; Fukuyama, T.; Chatani, M.; Murai, S.; Furukawa, N.; Seki, Y. *Chem. Lett.* **2000**, *7*, 750.

(27) Thorn, D. L. *Organometallics* **1982**, *1*, 197.

(28) Shrock, R. R. *J. Organomet. Chem.* **1976**, *122*, 209.

(29) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.

impurities in the deuterated solvent (for ^{1}H), solvent peaks (for ^{13}C{^{1}H}), $CFCl_3$ (for ^{19}F), $SiMe_4$ (for ^{29}Si{^{1}H}), or 85% H_3PO_4 (for ^{31}P{^{1}H}). 2D NMR ^{1}H,^{29}Si{^{1}H} HMBC experiments were carried out to help assign ^{29}Si{^{1}H} NMR resonances to the corresponding silyl groups. Elemental analyses were performed by the Micro-Mass Facility in the College of Chemistry at the University of California, Berkeley. GC-MS was conducted using an Agilent Technology 6890N 6C system with an HP-5MS column. Infrared spectra were recorded either as KBr pellets on a Mattson FTIR 3000 instrument or as Nujol mulls on a Nicolet Nexus 6700 FT-IR spectrometer with a liquid nitrogen cooled MCT-B detector.

(NSiN)Ir(H)(OTf)(coe) (1). A 200 mL Schlenk flask equipped with a stir bar was covered with an aluminum foil and charged with AgOTf (0.28 g, 1.1 mmol) and (NSiN)Ir(H)(Cl)(coe) (0.62 g, 0.97 mmol). To this solid mixture was added 100 mL of CH_2Cl_2, and the reaction mixture was stirred at ambient temperature for 4 h, after which the resulting mixture was allowed to settle, giving a beige-colored precipitate. The off-white supernatant was filtered via cannula filtration. The remaining residue was washed with CH_2Cl_2 (2 × 10 mL). The filtrates were combined and evaporated to dryness to give the crude product. Vapor diffusion of diethyl ether into a concentrated CH_2Cl_2 solution of the product afforded an analytically pure compound as an off-white precipitate in 93% yield (0.68 g, 0.90 mmol). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 9.66 (d J_{HH} = 5.0 Hz, 1 H, Ar*H*), 9.59 (br s, 1 H, Ar*H*), 8.33 (d J_{HH} = 7.0 Hz, 1 H, Ar*H*), 8.28 (d J_{HH} = 8.5 Hz, 1 H, Ar*H*), 8.06 (d J_{HH} = 6.5 Hz, 1 H, Ar*H*), 7.98 (d J_{HH} = 6.0 Hz, 1 H, Ar*H*), 7.79 (m, 2 H, Ar*H*), 7.63 (m, 2 H, Ar*H*), 7.54 (m, 1 H, Ar*H*), 7.35 (br m, 2 H, Ar*H*), 4.51 (m, 1 H, C*H*═CH of coe), 3.72 (m, 1 H, CH═C*H* of coe), 2.07 (br m, 1 H, C*H* of coe), 1.91 (br m, 1 H, C*H* of coe), 1.65 (br m, 1 H, C*H* of coe), 1.31 (br m, 5 H, C*H* of coe), 1.10 (br m, 1 H, C*H* of coe), 0.980 (s, 3 H, SiCH_3), 0.820 (br m, 1 H, C*H* of coe), −14.7 (br s, 1 H, Ir*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 154.2, 153.9, 152.4, 152.3, 145.6, 144.8, 139.7, 139.2, 135.4, 134.9, 129.9, 129.2, 129.1, 128.7, 128.2, 127.8, 123.1, 122.6 (aryl carbons), 67.2 (Ir*C*H), 66.3 (Ir*C*H), 32.6, 31.8, 30.9, 30.0, 26.5, 26.4 (alkyl carbons), −7.40 (Si*C*H_3). ^{19}F NMR (CD_2Cl_2, 376.5 MHz): δ −75.9 (s). ^{29}Si{^{1}H} NMR (CD_2Cl_2, 99 MHz): δ −8.2 (s). Anal. Calcd (%) for $C_{28}H_{30}N_2SiO_3SF_3Ir$: C, 44.72, H, 4.02, N, 3.73. Found: C, 44.33, H, 3.99, N, 3.61. IR (cm^{-1}): ν_{IrH} 2161.

(NSiN)IrPh(SiPh$_2$OTf) (2). To a 10 mL C_6H_6 solution of **1** (0.085 g, 0.11 mmol) was added 5 mL of a C_6H_6 solution of Ph_3SiH (0.030 g, 0.12 mmol). After 4 h of stirring at room temperature, the homogeneous, bright yellow reaction mixture was evacuated to dryness. The remaining yellow residue was then dissolved in 10 mL of diethyl ether, and the resulting solution was filtered through Celite. The solution was then concentrated to approximately 3 mL. At room temperature, orange crystals were obtained in 88% yield (0.089 g, 0.099 mmol). ^{1}H NMR (C_6D_6, 500 MHz): δ 9.62 (m, 1 H, Ar*H*), 9.18 (d J_{HH} = 6.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 7.76 (m, 2 H, Ar*H*), 7.71 (m, 2 H, Ar*H*), 7.48 (m, 2 H, Ar*H*), 7.05−6.80 (m, 14 H, Ar*H*), 6.63 (m, 1 H, Ar*H*), 6.50 (m, 3 H, Ar*H*), 6.44 (m, 1 H, Ar*H*), 1.37 (s, 3 H, SiCH_3). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 153.8, 151.2, 150.2, 146.7, 146.1, 140.4, 140.0, 138.4, 137.5, 137.3, 136.5, 135.9, 134.4, 133.7, 131.8, 129.3, 129.2, 129.0, 127.3, 127.2, 127.1, 126.9, 126.5, 122.1, 122.0, 121.7 (aryl carbons), −5.70 (Si*C*H_3). ^{19}F NMR (C_6D_6, 376.5 MHz): δ −74.3 (s). ^{29}Si{^{1}H} NMR (C_6D_6, 99 MHz): δ 54.0 (s, *Si*Ph$_2$OTf), −8.4 (s, *Si*CH$_3$). Anal. Calcd (%) for $C_{38}H_{30}N_2Si_2O_3SF_3Ir$: C, 50.70, H, 3.36, N, 3.11. Found: C, 50.73, H, 3.44, N, 3.12.

[(NSiN)IrSi(OSiMe$_3$)$_3$(OTf)]$_n$ (3). To a 5 mL C_6H_6 solution of **1** (0.11 g, 0.15 mmol) was added $(Me_3SiO)_3SiH$ (0.046 g, 0.16 mmol) in 5 mL of C_6H_6. The reaction mixture was stirred for 1 h, after which the clear yellow solution was filtered through Celite. The filtrate was concentrated to approximately 2 mL, and 1 mL of diethyl ether was added. At room temperature, a yellow flaky solid was obtained in 48% yield (0.065 g, 0.069 mmol). ^{1}H NMR (C_6D_6, 500 MHz): δ 9.42 (d J_{HH} = 5.0 Hz, of d J_{HH} = 1.5 Hz, 2 H, Ar*H*), 7.90 (d J_{HH} = 6.8 Hz, of d J_{HH} = 1.2 Hz, 2 H, Ar*H*), 7.35 (d J_{HH} = 8.2 Hz, of d J_{HH} = 1.2 Hz, 2 H, Ar*H*), 7.14 (m, 2 H, Ar*H*), 7.09 (m, 2 H, Ar*H*), 6.66 (d J_{HH} = 8.2 Hz, of d J_{HH} = 5.0 Hz, 2 H, Ar*H*), 0.71 (s, 3 H, SiCH_3), 0.023 (s, 27 H, Si[OSi(CH_3)$_3$]$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 158.8, 155.1, 141.7, 137.8, 135.6, 129.3, 128.8, 127.6, 121.8 (aryl carbons), 2.85 (Si*C*H$_3$), 2.12 (Si[OSi(*C*H$_3$)$_3$]$_3$). ^{19}F NMR (C_6D_6, 376.5 MHz): δ −76.8 (s). ^{29}Si{^{1}H} NMR (C_6D_6, 99 MHz): δ 8.8 (s, *Si*CH$_3$), 4.1 (s, Si[O*Si*(CH$_3$)$_3$]$_3$). Anal. Calcd (%) for $C_{29}H_{42}N_2Si_5O_6SF_3Ir$: C, 37.20, H, 4.52, N, 2.99. Found: C, 36.84, H, 4.28, N, 3.14.

[(NSiN)IrSi(OSiMe$_3$)$_3$(NCMe)$_2$][OSO$_2$CF$_3$] (4). (1) To a stirred 10 mL CH_3CN solution of **1** (0.055 g, 0.073 mmol) was added a 5 mL CH_3CN solution of $(Me_3SiO)_3SiH$ (0.023 g, 0.078 mmol). After 4 h at room temperature, the reaction mixture was filtered through Celite, resulting in a clear yellow filtrate. The CH_3CN filtrate was concentrated to approximately 2 mL and washed with 2 × 2 mL of pentane. The resulting solution was evaporated to dryness, providing a crystalline yellow residue in 79% yield (0.056 g, 0.058 mmol).

(2) Alternatively, **4** was generated by heating a 5 mL CH_3CN solution of **3** at 70 °C for 12 h. The reaction was quantitative according to ^{1}H NMR spectroscopy. ^{1}H NMR (CD_3CN, 500 MHz): δ 9.60 (d J_{HH} = 5.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 9.38 (d J_{HH} = 5.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.35 (d J_{HH} = 8.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.28 (d J_{HH} = 8.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.26 (d J_{HH} = 6.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.07 (d J_{HH} = 6.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 7.83 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.2 Hz, 1 H, Ar*H*), 7.71 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.2 Hz, 1 H, Ar*H*), 7.62 (d J_{HH} = 8.0 Hz, of d J_{HH} = 6.5 Hz, 1 H, Ar*H*), 7.53 (d J_{HH} = 8.5 Hz, of d J_{HH} = 5.0 Hz, 1 H, Ar*H*), 7.49 (d J_{HH} = 8.0 Hz, of d J_{HH} = 6.0 Hz, 1 H, Ar*H*), 7.34 (d J_{HH} = 8.5 Hz, of d J_{HH} = 5.5 Hz, 1 H, Ar*H*), 2.12 (s, 3 H, IrNCCH_3), 1.18 (s, 3 H, SiCH_3), −0.136 (s, 27 H, Si[OSi(CH_3)$_3$]$_3$). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 156.47, 156.45, 152.9, 152.6, 148.4, 148.0, 140.2, 139.5, 137.0, 136.7, 130.5, 130.3, 129.6, 129.5, 128.8, 128.5, 123.2, 123.1 (aryl carbons), 118.7 (IrN*C*CH$_3$), 4.70 (IrNC*C*H$_3$), 2.66 (Si[OSi(*C*H$_3$)$_3$]$_3$), −6.79 (Si*C*H$_3$). ^{19}F NMR (CD_3CN, 376.5 MHz): δ −78.6 (s). ^{29}Si{^{1}H} NMR (CD_3CN, 99 MHz): δ 1.4 (s, *Si*CH$_3$), 1.6 (s, Si[O*Si*(CH$_3$)$_3$]$_3$). Anal. Calcd (%) for $C_{33}H_{48}N_4Si_5O_6SF_3Ir$: C, 38.91, H, 4.75, N, 5.50. Found: C, 39.23, H, 4.99, N, 5.47. IR (cm^{-1}): ν_{CN} 2274 (w), 2297 (w).

[(NSiN)IrSiPh$_3$(NCMe)$_2$][OSO$_2$CF$_3$] (5). To a 10 mL CH_3CN solution of **1** (0.065 g, 0.086 mmol) was added a 5 mL CH_3CN solution of Ph_3SiH (0.025 g, 0.096 mmol). After 12 h of stirring at room temperature, the reaction mixture was evaporated to dryness to give a yellow solid. This solid was washed with pentane (2 × 2 mL) and dissolved in approximately 5 mL of diethyl ether. This solution was then concentrated to 3 mL. Approximately 0.5 mL of CH_3CN was added to help solubilize the product. The yellow, crystalline product was obtained at −30 °C in 56% yield (0.045 g, 0.048 mmol). ^{1}H NMR (CD_3CN, 500 MHz): δ 9.47 (d J_{HH} = 5.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 9.37 (d J_{HH} = 5.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.37 (d J_{HH} = 8.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.19 (d J_{HH} = 6.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.16 (d J_{HH} = 8.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 7.84 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.0 Hz, 1 H, Ar*H*), 7.74 (d J_{HH} = 7.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 7.61 (d J_{HH} = 8.0 Hz, of d J_{HH} = 7.0 Hz, 1 H, Ar*H*), 7.57 (d J_{HH} = 8.5 Hz, of d J_{HH} = 1.0 Hz, 1 H, Ar*H*), 7.52 (d J_{HH} = 8.5 Hz, of d J_{HH} = 5.0 Hz, 1 H, Ar*H*), 7.35 (m, 1 H, Ar*H*), 7.18 (d J_{HH} = 8.0 Hz, of d J_{HH} = 5.5 Hz, 1 H, Ar*H*), 7.15 (m, 6 H, Ar*H*), 7.10 (m, 3 H, Ar*H*), 7.01 (m, 6 H, Ar*H*), 2.10 (s, 3 H, IrNCCH_3), 0.801 (s, 3 H, SiCH_3). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz): δ 156.12, 156.1, 148.0, 147.7, 141.7, 140.4, 139.8, 136.8, 136.7, 136.4, 130.33, 130.31, 129.71, 129.66, 129.3, 128.8, 128.7, 128.1, 127.6, 123.5, 123.2 (aryl carbons), 121.6 (br, IrNCCH$_3$), 4.55 (IrNCC*H*$_3$), −6.30 (SiC*H*$_3$). ^{19}F NMR (CD$_3$CN, 376.5 MHz): δ −76.8 (s). ^{29}Si{^{1}H} NMR (CD$_3$CN, 99 MHz): δ −1.2 (s, *Si*CH$_3$), −25.3 (s, *Si*Ph$_3$). Anal. Calcd (%) for C$_{40}$H$_{33}$N$_3$Si$_2$O$_3$SF$_3$Ir: C, 51.04, H, 3.53, N, 4.46. Found: C, 51.38, H, 3.58, N, 4.41. IR (cm^{-1}): ν_{CN} 2187 (w), 2297 (w).

[(NSiN)IrSiEt$_3$(NCMe)$_2$][OSO$_2$CF$_3$] (6). To a 15 mL CH$_3$CN solution of **1** (0.14 g, 0.19 mmol) was added a 5 mL CH$_3$CN solution of Et$_3$SiH (30 μL, 0.19 mmol). The reaction mixture was stirred at ambient temperature for 1 day, after which it was filtered through Celite and a glass fiber filter. The yellow CH$_3$CN filtrate was concentrated to approximately 2 mL and washed with 2 × 2 mL of pentane. The resulting solution was evaporated to dryness, providing a foamy yellow residue in 86% yield (0.13 g, 0.16 mmol). ^{1}H NMR (CD$_3$CN, 500 MHz): δ 9.72 (d J_{HH} = 5.5 Hz, of d J_{HH} = 1.0 Hz, 1 H, Ar*H*), 9.46 (d J_{HH} = 5.0 Hz, of d J_{HH} = 2.0 Hz, 1 H, Ar*H*), 8.36 (d J_{HH} = 8.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.30 (d J_{HH} = 8.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.24 (d J_{HH} = 6.5 Hz, of d J_{HH} = 1.0 Hz, 1 H, Ar*H*), 8.10 (d J_{HH} = 7.0 Hz, of d J_{HH} = 2.0 Hz, 1 H, Ar*H*), 7.83 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.0 Hz, 1 H, Ar*H*), 7.73 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.0 Hz, 1 H, Ar*H*), 7.61 (d J_{HH} = 8.0 Hz, of d J_{HH} = 6.5 Hz, 1 H, Ar*H*), 7.55−7.50 (m, 2 H, Ar*H*), 7.32 (d J_{HH} = 8.5 Hz, of d J_{HH} = 5.5 Hz, 1 H, Ar*H*), 2.15 (s, 3 H, IrNCC*H*$_3$), 1.10 (s, 3 H, SiC*H*$_3$), 0.66 (t J_{HH} = 7.8 Hz, 9 H, SiCH$_2$C*H*$_3$), 0.51 (m, 3 H, SiC*H*H'CH$_3$), 0.39 (m, 3 H, SiCH*H'*CH$_3$). ^{13}C{^{1}H} NMR (CD$_3$CN, 125 MHz): δ 156.8, 156.1, 152.8, 152.4, 148.6, 148.0, 140.0, 139.4, 136.6, 136.5, 130.3, 130.2, 129.64, 129.56, 129.1, 128.5, 123.4, 123.2 (aryl carbons), 119.9 (IrN*C*CH$_3$), 8.96 (SiCH$_2$*C*H$_3$), 6.90 (Si*C*H$_2$CH$_3$), 4.17 (IrNC*C*H$_3$), −6.79 (Si*C*H$_3$). ^{19}F NMR (CD$_3$CN, 376.5 MHz): δ −76.8 (s). ^{29}Si{^{1}H} NMR (CD$_3$CN, 99 MHz): δ 1.8 (s, *Si*CH$_3$), −12.8 (s, *Si*(CH$_2$CH$_3$)$_3$). Anal. Calcd (%) for C$_{28}$H$_{33}$N$_3$Si$_2$O$_3$SF$_3$Ir: C, 42.19, H, 4.17, N, 5.27. Found: C, 42.21, H, 4.14, N, 5.27. IR (cm^{-1}): ν_{CN} 2273 (w), 2291 (w).

[(NSiN)IrSiHPh$_2$(NCMe)$_2$][OSO$_2$CF$_3$] (7). To a stirred 10 mL CH$_3$CN solution of **1** (0.060 g, 0.080 mmol) was slowly added a 5 mL CH$_3$CN solution of Ph$_2$SiH$_2$ (0.016 g, 0.087 mmol). After 2 h, the reaction mixture was filtered through Celite and a glass fiber filter. The yellow CH$_3$CN solution was concentrated to approximately 2 mL and washed with 2 × 2 mL of pentane. The resulting solution was evaporated to dryness to give the yellow product in 82% yield (0.054 g, 0.066 mmol). ^{1}H NMR (CD$_3$CN, 500 MHz): δ 9.53 (d J_{HH} = 5.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 9.19 (d J_{HH} = 5.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.38 (d J_{HH} = 8.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.24 (d J_{HH} = 7.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.13−8.11 (m, 2 H, Ar*H*), 7.84 (d J_{HH} = 8.0 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 7.71−7.66 (m, 3 H, Ar*H*), 7.60 (d J_{HH} = 8.0 Hz, of d J_{HH} = 7.0 Hz, 1 H, Ar*H*), 7.56 (d J_{HH} = 8.0 Hz, of d J_{HH} = 5.0 Hz, 1 H, Ar*H*), 7.52 (d J_{HH} = 8.0 Hz, of d J_{HH} = 7.0 Hz, 1 H, Ar*H*), 7.32−7.25 (m, 3 H, Ar*H*), 7.03−6.98 (m, 2 H, Ar*H*), 6.87 (m, 4 H, Ar*H*), 4.33 (s $^1J_{SiH}$ = 173 Hz, 1 H, Si*H*Ph$_2$), 2.16 (s, 3 H, IrNCC*H*$_3$), 1.07 (s, 3 H, SiC*H*$_3$). ^{13}C{^{1}H} NMR (CD$_3$CN, 125 MHz): δ 156.04, 155.98, 153.6, 152.7, 147.5, 147.0, 140.9, 140.40, 140.36, 139.4, 137.2, 136.9, 135.9, 134.7, 130.5, 130.2, 129.9, 129.8, 128.9, 128.62, 128.58, 128.4, 128.0, 127.9, 123.5, 123.4 (aryl carbons), 4.03 (IrNC*C*H$_3$), −8.8 (Si*C*H$_3$). ^{19}F NMR (CD$_3$CN, 376.5 MHz): δ −76.8 (s). ^{29}Si{^{1}H} NMR (CD$_3$CN, 99 MHz): δ 2.8 (s, *Si*CH$_3$), −25.0 (s, *Si*HPh$_2$). Anal. Calcd (%) for C$_{34}$H$_{29}$N$_4$Si$_2$O$_3$SF$_3$Ir: C, 47.22, H, 3.38, N, 4.86, S, 3.71. Found: C, 46.92, H, 3.30, N, 3.44. IR (cm^{-1}): ν_{CN} 2271 (w), 2294 (w); ν_{SiH} 2040 (m).

[(NSiN)IrSiH$_2$Ph(NCMe)$_2$][OSO$_2$CF$_3$] (8). To a stirred 10 mL CH$_3$CN solution of **1** (0.085 g, 0.11 mmol) was added a 5 mL CH$_3$CN solution of PhSiH$_3$ (0.013 mg, 0.12 mmol). After 1 h at room temperature, the reaction solution was filtered through Celite, and the resulting CH$_3$CN filtrate was concentrated to approximately 2 mL and washed with 2 × 2 mL of pentane. The yellow solution was evaporated to dryness, resulting in a yellow solid in 77% yield (0.065 g, 0.087 mmol). ^{1}H NMR (CD$_3$CN, 500 MHz): δ 9.54 (d J_{HH} = 6.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 9.40 (d J_{HH} = 5.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.40 (d J_{HH} = 11 Hz, of d J_{HH} = 2.0 Hz, 1 H, Ar*H*), 8.24 (d J_{HH} = 8.5 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.23 (d J_{HH} = 10 Hz, of d J_{HH} = 1.5 Hz, 1 H, Ar*H*), 8.16 (m, 1 H, Ar*H*), 7.86 (d J_{HH} = 10 Hz, of d J_{HH} = 2.0 Hz, 1 H, Ar*H*), 7.73 (d J_{HH} = 10 Hz, 1 H, Ar*H*), 7.62 (d J_{HH} = 10 Hz, of d J_{HH} = 8.5 Hz, 1 H, Ar*H*), 7.58−7.53 (m, 2 H, Ar*H*), 7.22 (d J_{HH} = 10 Hz, of d J_{HH} = 7.0 Hz, 1 H, Ar*H*), 7.15 (m, 3 H, Ar*H*), 7.06 (m, 2 H, Ar*H*), 3.84 (d $^2J_{HH'}$ = 6.0 Hz, $^1J_{SiH}$ = 169 Hz, Si*H*H′Ph), 3.39 (**d** $^2J_{HH'}$ = 6.0 Hz, $^1J_{SiH'}$ = 171 Hz, 1 H, SiH*H′*Ph**)**, 2.12 (s, 3 H, C*H*$_3$CN), 1.09 (s, 3 H, SiC*H*$_3$). ^{13}C{^{1}H} NMR (CD$_3$CN, 125 MHz): δ 156.1, 156.0, 153.8, 152.7, 147.3, 147.0, 140.4, 139.6, 138.7, 137.2, 137.0, 135.3, 130.5, 130.3, 130.0, 129.9, 129.1, 128.6, 128.3, 128.1, 123.5, 123.4 (aryl carbons), 4.10 (IrNC*C*H$_3$), −8.8 (Si*C*H$_3$). ^{19}F NMR (CD$_3$CN, 376.5 MHz): δ −76.8 (s). ^{29}Si{^{1}H} NMR (CD$_3$CN, 99 MHz): δ 2.2 (s, *Si*CH$_3$), −51.6 (s, *Si*H$_2$Ph). Anal. Calcd (%) for C$_{30}$H$_{28}$N$_4$Si$_2$O$_3$SF$_3$Ir: C, 43.41, H, 3.40, N, 6.75. Found: C, 43.39, H, 3.22, N, 7.09. IR (cm^{-1}): ν_{CN} 2273 (w), 2295 (w); ν_{SiH} 2051 (br m).

Observation of (NSiN)IrPh[Si(H)PhOTf] (9). Compound **9** was generated *in situ* by adding neat Ph$_2$SiH$_2$ (0.007 g, 0.040 mmol) to an approximately 3 mL benzene-*d*$_6$ solution of **1** (0.03 g, 0.04 mmol), ferrocene (0.004 g, 0.02 mmol), and cyclooctene (0.005 g, 0.04 mmol). The reaction mixture was allowed to stand at ambient temperature for 1 h before being analyzed by multinuclear NMR spectroscopy. ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 5.49 (s $^1J_{SiH}$ = 176 Hz, 1 H, Si*H*Ph), 0.761 (s, 3 H, SiC*H$_3$).* ^{19}F NMR (C$_6$D$_6$, 376.5 MHz): δ −73.4 (s). ^{29}Si{^{1}H} NMR (C$_6$D$_6$, 99 MHz): δ −24.5 (s, *Si*(H)PhOTf).

[(NSiN)Ir(H)(coe)(THF)][B(C$_6$F$_5$)$_4$] (10). To a 10 mL CH$_2$Cl$_2$ solution of Li(Et$_2$O)$_3$[B(C$_6$F$_5$)$_4$] (0.15 g, 0.16 mmol) was added dropwise a 20 mL CH$_2$Cl$_2$ solution of **1** (0.11 g, 0.16 mmol). The reaction mixture was vigorously stirred at room temperature for 1 h, after which it was filtered through Celite. The clear yellow solution was evaporated to dryness and redissolved in 10 mL of THF. The THF solution was concentrated to approximately 2 mL and layered with 4 mL of pentane. At −30 °C, a yellow crystalline solid was obtained in 76% yield (0.17 g, 0.12 mmol). Due to broadened ^{1}H NMR resonances, all multinuclear NMR spectra were obtained at 50 °C. ^{1}H NMR (THF-*d*$_8$, 500 MHz): δ 9.75 (br s, 2 H, Ar*H*), 8.52 (d J_{HH} = 8.0 Hz, 1 H, Ar*H*), 8.43 (d J_{HH} = 8.0 Hz, 1 H, Ar*H*), 8.16 (d J_{HH} = 6.5 Hz, 1 H, Ar*H*), 8.08 (d J_{HH} = 6.5 Hz, 1 H, Ar*H*), 7.91 (d J_{HH} = 8.0 Hz, 1 H, Ar*H*), 7.84 (d J_{HH} = 8.0 Hz, 1 H, Ar*H*), 7.71 (d J_{HH} = 8.0 Hz, of d J_{HH} = 5.0 Hz, 1 H, Ar*H*), 7.59 (m, 2 H, Ar*H*), 7.43 (br m, 1 H, Ar*H*), 4.20 (br m, 1 H, C*H*═CH of coe), 3.79 (br m, 1 H, CH═C*H* of coe), 2.20 (br m, 1 H, C*H* of coe), 2.04 (br m, 1 H, C*H* of coe), 1.60−1.12 (br m, 9 H, C*H* of coe), 1.07 (s, 3 H, SiC*H$_3$*), 0.90 (br m, 1 H, C*H* of coe), −14.5 (br s, 1 H, Ir*H*). ^{13}C{^{1}H} NMR (THF-*d*$_8$, 125 MHz): δ 155.0, 154.4 (br s), 153.4, 153.1, 145.8, 145.0, 141.3, 140.9, 136.8, 136.2, 130.9, 130.2, 129.7, 129.2, 128.8, 123.5, 122.9, (aryl carbons), 68.2 (THF), 66.8 (*C*H═CH of coe), 65.8 (CH═*C*H of coe), 33.0, 32.4, 31.8, 30.1, 27.04, 26.95 (alkyl carbons), 26.4 (THF), −7.23 (Si*C*H$_3$). ^{19}F NMR (THF-*d*$_8$, 376.5 MHz): δ −133.8 (br s), −166.3 (t), −169.7 (br t). ^{29}Si{^{1}H} NMR (THF-*d*$_8$, 99 MHz): δ −4.2 (s). ^{11}B{^{1}H} NMR (THF-*d*$_8$, 128.4 MHz): δ −16.7 (s). Anal. Calcd (%) for C$_{55}$H$_{38}$N$_2$SiOBF$_{20}$Ir: C, 48.78, H, 2.81, N, 2.07. Found: C, 49.16, H, 2.91, N, 2.35. IR (cm^{-1}): ν_{IrH} 2035.

(NSiN)IrH$_2$(PPh$_3$) (11). To a 15 mL THF solution of (NSiN)Ir(H)Cl(PPh$_3$) (0.095 g, 0.12 mmol) was slowly added a 1.0 M THF solution of LiBEt$_3$H (0.13 mL, 0.13 mmol) at ambient temperature. A color change to orange was immediately observed. The reaction mixture was stirred for 4 h before all volatiles were removed under vacuum. The remaining orange solid was dissolved in 20 mL of THF. The resulting solution was filtered through Celite and concentrated to a volume of 3 mL. Cooling this THF solution to −30 °C afforded orange blocks in 78% yield (0.071 g, 0.094 mmol). ^{1}H NMR (THF-d_8, 400 MHz): δ 10.85 (m, 1 H, ArH), 9.99 (d $J_{\rm HH}$ = 4.8 Hz, 1 H, ArH), 8.17 (d $J_{\rm HH}$ = 8.0 Hz, 1 H, ArH), 7.97 (d $J_{\rm HH}$ = 6.8 Hz, 1 H, ArH), 7.83 (d $J_{\rm HH}$ = 7.2 Hz, of d $J_{\rm HH}$ = 0.8 Hz, 2 H, ArH), 7.58 (m, 6 H, ArH), 7.51 (d $J_{\rm HH}$ = 8.0 Hz, 1 H, ArH), 7.32 (m, 2 H, ArH), 7.25 (m, 1 H, ArH), 7.10 (d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 5.2 Hz, 1 H, ArH), 6.98 (m, 9 H, ArH), 6.68 (d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 4.8 Hz, 1 H, ArH), 0.40 (s, 3 H, SiCH_3), −2.07 (d $^{2}J_{\rm HP}$ = 15 Hz, of d $^{2}J_{\rm HH'}$ = 3.2 Hz, 1 H, IrH), −19.0 (d $^{2}J_{\rm H'P}$ = 23 Hz, of d $^{2}J_{\rm H'H}$ = 3.2 Hz, 1 H, IrH'). ^{13}C{^{1}H} NMR (THF-d_8, 125 MHz): δ 163.7, 161.0, 156.4, 155.81, 155.79, 155.0, 153.6, 135.2, 134.8 ($J_{\rm CP}$ = 2.5 Hz), 134.7, 132.6 ($J_{\rm CP}$ = 7.5 Hz), 131.7, 131.6, 126.8, 126.0 ($J_{\rm CP}$ = 2.5 Hz), 124.8 ($J_{\rm CP}$ = 53.8 Hz), 124.5, 124.4, 119.9, 119.8, 119.5 (aryl carbons), −8.2 (SiCH$_3$). ^{29}Si{^{1}H} NMR (THF-d_8, 99 MHz): δ 19.1 ($^{2}J_{\rm SiP}$ = 12 Hz). ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz): δ 26.0 (s). Anal. Calcd (%) for $C_{37}H_{32}N_2SiPIr$: C, 58.80, H, 4.27, N, 3.71. Found: C, 58.91, H, 4.51, N, 3.58. IR (cm^{-1}): $\nu_{\rm IrH}$ 2122; $\nu_{\rm IrH'}$ 1779.

(NSiN)Ir(CH$_2$Ph)Cl(PPh$_3$) (12). To a 5 mL C_6H_6 solution of (NSiN)Ir(H)Cl(PPh$_3$) (0.090 g, 0.11 mmol) was slowly added a 5 mL C_6H_6 solution of Mg(CH$_2$Ph)$_2$(THF)$_2$ (0.025 g, 0.071 mmol). The reaction mixture immediately became reddish-orange, and it was allowed to stir at ambient temperature for 30 min. Then, the reaction mixture was concentrated to a volume of approximately 6 mL and filtered through Celite and a glass fiber filter. Slow evaporation of this filtrate at room temperature afforded a yellow powder in 68% yield (0.068 g, 0.077 mmol). ^{1}H NMR (C_6D_6, 500 MHz): δ 9.73 (t $J_{\rm HH}$ = 5.0 Hz, of d $J_{\rm HH}$ = 2.0 Hz, 2 H, ArH), 8.16 (d $J_{\rm HH}$ = 7.0 Hz, of d $J_{\rm HH}$ = 1.5 Hz, 1 H, ArH), 7.84 (d $J_{\rm HH}$ = 5.0 Hz, of d $J_{\rm HH}$ = 3.6 Hz, 1 H, ArH), 7.40 (m, 6 H, ArH), 7.26 (d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 2.0 Hz, 1 H, ArH), 7.19 (m, 1 H, ArH), 7.06 (d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 1.5 Hz, 1 H, ArH), 6.85 (m, 2 H, ArH), 6.79 (t $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 1.5 Hz, 6 H, ArH), 6.72 (m, 4 H, ArH), 6.52 (d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 5.0 Hz, 1 H, ArH), 6.49 (d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 5.0 Hz, 1 H, ArH), 6.32 (v br s, 2 H, ArH), 6.14 (t $J_{\rm HH}$ = 8.0 Hz, 1 H, ArH), 1.98 (vt $J_{\rm HH'} \approx J_{\rm HP} \approx$ 7.0 Hz, 1 H, CHH′Ph), 1.92 (vt $J_{\rm HH'} \approx J_{\rm H'P} \approx$ 7.0 Hz, 1 H, CHH'Ph), 1.26 (s, 3 H, SiCH_3). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 150.0, 149.9, 149.6, 149.3, 145.1, 140.4, 139.8, 138.1, 137.72, 137.66, 135.0, 134.1, 134.0, 129.5 ($^{1}J_{\rm CP}$ = 50 Hz), 128.53, 128.50 ($J_{\rm CP}$ = 2 Hz), 127.0, 126.9, 128.5, 123.6, 120.0 ($J_{\rm CP}$ = 6 Hz), 114.2 (aryl carbons), 35.4 ($^{2}J_{\rm CP}$ = 36 Hz, IrCH$_2$Ph), 6.1 (SiCH$_3$). ^{29}Si{^{1}H} NMR (C_6D_6, 99 MHz): δ −18.6 (d, $^{2}J_{\rm SiP}$ = 3 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ 38.3 (s). Anal. Calcd (%) for $C_{44}H_{37}N_2SiPClIr$: C, 60.02, H, 4.24, N, 3.18. Found: C, 59.63, H, 4.21, N, 2.80.

(NSiN)Ir(H)Cl(PMe$_3$) (13). To a 10 mL THF solution of (NSiN)Ir(H)Cl(coe) (0.27 g, 0.48 mmol) was slowly added a 5 mL THF solution of PMe$_3$ (55 μL, 0.53 mmol). After stirring for 12 h, the reaction solution was evaporated to dryness. The remaining yellow residue was then dissolved in 10 mL of THF and filtered through Celite. The resulting solution was concentrated to a volume of approximately 3 mL. Cooling the THF solution to −30 °C produced a yellow, crystalline solid in 67% yield (0.17 g, 0.32 mmol). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 10.71 (m, 1 H, ArH), 10.36 (m, 1 H, ArH), 8.11 (m, 4 H, ArH), 7.65 (d $J_{\rm HH}$ = 14 Hz, of d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 1.5 Hz, 2 H, ArH), 7.49 (m, 2 H, ArH), 7.38 (d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 5.0 Hz, 1 H, ArH), 7.32 (d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 5.0 Hz, 1 H, ArH), 1.30 (d $J_{\rm HP}$ = 10 Hz, 9 H, P(CH_3)$_3$), 1.15 (s, 3 H, SiCH_3), −19.6 (d $^{2}J_{\rm HP}$ = 22 Hz, 1 H, IrH). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125 MHz): δ 155.1, 154.6, 153.8, 152.2, 149.3, 148.3, 137.6, 137.5, 134.8, 134.5, 129.4, 129.3 (d $J_{\rm CP}$ = 1.2 Hz), 128.1, 128.0, 127.5, 127.4, 122.2, 122.1 (d $J_{\rm CP}$ = 2.4 Hz) (aryl carbons), 19.1 (d $J_{\rm CP}$ = 40 Hz, PCH$_3$), −4.4 (SiCH$_3$). ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, 99 MHz): δ 0.85 ($^{2}J_{\rm SiP}$ = 13 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 162 MHz): δ −40.3 (s). Anal. Calcd (%) for $C_{22}H_{25}N_2SiPIrCl$: C, 43.73, H, 4.17, N, 4.64. Found: C, 43.82, H, 4.21, N, 4.49. IR (cm^{-1}): $\nu_{\rm IrH}$ 2105.

[(κ^2-NSiN)Ir(H)(PMe$_3$)$_3$][Cl] (14). To a 20 mL CH$_2$Cl$_2$ solution of (NSiN)Ir(H)Cl(coe) (0.11 g, 0.20 mmol) was added neat PMe$_3$ (0.21 μL, 2.0 mmol). After 8 h of stirring at room temperature, the solution was evaporated to dryness under vacuum. The remaining yellow residue was dissolved in approximately 8 mL of CH$_2$Cl$_2$, and the resulting solution was filtered through Celite and concentrated to 2 mL. Layering this solution with ca. 6 mL of pentane at room temperature afforded a yellow, crystalline product in 81% yield (0.12 g, 0.16 mmol). ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 9.86 (m, 1 H, ArH), 8.54 (m, 1 H, ArH), 8.47 (d $J_{\rm HH}$ = 8.0 Hz, 1 H, ArH), 8.07 (d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 1.5 Hz, 1 H, ArH), 7.85 (d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 5.0 Hz, 1 H, ArH), 7.79 (m, 2 H, ArH), 7.64 (d $J_{\rm HH}$ = 8.0 Hz, 1 H, ArH), 7.56 (m, 1 H, ArH), 7.30 (d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 4.0 Hz, 1 H, ArH), 7.06 (d $J_{\rm HH}$ = 7.5 Hz, 1 H, ArH), 1.99 (d $^{2}J_{\rm HP}$ = 9.5 Hz, 9 H, P(CH_3)$_3$), 1.54 (d $^{2}J_{\rm HP'}$ = 8.0 Hz, 9 H, P′(CH_3)$_3$), 1.40 (d $^{3}J_{\rm HP''}$ = 2.5 Hz, 3 H, SiCH_3), 1.06 (d $^{2}J_{\rm HP''}$ = 8.5 Hz, 9 H, P″(CH_3)$_3$), −10.9 (m, 1 H, IrH). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 125 MHz): δ 163.6 (m), 157.4, 154.9, 154.6, 153.7, 151.9, 148.1, 139.9, 137.8, 136.6, 135.6 (d $J_{\rm CP}$ = 2.2 Hz), 128.6, 128.4, 128.2, 127.8, 126.2, 1213.3 (br m), 121.0 (aryl carbons), 24.7 (m, P(CH$_3$)$_3$), 21.5 (d $^{2}J_{\rm CP}$ = 24 Hz, of d $^{3}J_{\rm CP}$ = 1.9 Hz, P′(CH$_3$)$_3$), 19.3 (d $^{2}J_{\rm CP}$ = 16 Hz, of d $^{3}J_{\rm CP}$ = 4.0 Hz, P″(CH$_3$)$_3$), 6.7 (m, SiCH$_3$). ^{29}Si{^{1}H} NMR (CD$_2$Cl$_2$, 99 MHz): δ −6.0 (m). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 202.5 MHz): δ −50.9 (d $^{2}J_{\rm PP'}$ = 20 Hz, of d $^{2}J_{\rm CP''}$ = 10 Hz), −51.2 (br m), −51.6 (br m). Anal. Calcd (%) for $C_{28}H_{43}N_2SiP_3IrCl$: C, 43.69, H, 5.63, N, 3.64. Found: C, 43.74, H, 5.55, N, 3.62. IR (cm^{-1}): $\nu_{\rm IrH}$ 2022.

(κ^1-NSiN)Ir(H)(Me)(PMe$_3$)$_3$ (15). A 10 mL C_6H_6 solution of Qn$_2$SiHMe (0.059 g, 0.20 mmol) was added dropwise to a 5 mL C_6H_6 solution of (PMe$_3$)$_4$IrMe (0.10 g, 0.20 mmol) at room temperature. The red reaction mixture was allowed to stir at room temperature for 8 h before all volatiles were removed under vacuum, leaving an oily, orange-red residue. This residue was dissolved in approximately 8 mL of diethyl ether and filtered through a glass fiber filter. The red diethyl ether solution was concentrated to 1 mL and cooled to −30 °C for several days. An orange, crystalline solid was obtained in 71% yield (0.10 g, 0.14 mmol). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.73−8.64 (m, 3 H, ArH), 8.52 (d $J_{\rm HH}$ = 7.2 Hz, of d $J_{\rm HH}$ = 1.2 Hz, 1 H, ArH), 7.65 (d $J_{\rm HH}$ = 8.0 Hz, 2 H, ArH), 7.46 (m, 2 H, ArH), 7.38 (t $J_{\rm HH}$ = 7.2 Hz, 1 H, ArH), 7.25 (t $J_{\rm HH}$ = 7.2 Hz, 1 H, ArH), 6.81 (d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 4.0 Hz, 1 H, ArH), 6.77 (d $J_{\rm HH}$ = 8.0 Hz, of d $J_{\rm HH}$ = 4.0 Hz, 1 H, ArH), 1.89 (d $^{2}J_{\rm HP}$ = 2.4 Hz, 3 H, SiCH_3), 1.28 (d $^{2}J_{\rm HP}$ = 7.2 Hz, 9 H, P(CH$_3$)$_3$), 1.15 (d $^{2}J_{\rm HP'}$ = 7.2 Hz, 9 H, P′(CH$_3$)$_3$), 1.08 (d $^{3}J_{\rm HP''}$ = 7.6 Hz, 9 H, P″(CH$_3$)$_3$), 0.247 (m, 3 H, IrCH_3), −11.3 (d $^{2}J_{\rm HP'}$ = 131 Hz, of vt $^{2}J_{\rm HP} \approx$ 17 Hz, 1 H, IrH). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 153.8, 153.6, 146.8, 146.7, 139.5, 138.9, 136.1, 135.9, 128.73, 128.71, 126.71, 126.67, 126.0, 125.9, 119.6, 119.2 (aryl carbons), 25.04 (d $^{2}J_{\rm CP}$ = 28 Hz, of t $^{3}J_{\rm CP}$ = 4.2 Hz, P(CH$_3$)$_3$), 21.2 (d $^{2}J_{\rm CP}$ = 23 Hz, of d $^{3}J_{\rm CP}$ = 3.2 Hz, of d $^{3}J_{\rm CP}$ = 2.0 Hz, P′(CH$_3$)$_3$), 20.5 (d $^{2}J_{\rm CP}$ = 25 Hz, of d $^{3}J_{\rm CP}$ = 5.7 Hz, of d $^{3}J_{\rm CP}$ = 2.6 Hz, P″(CH$_3$)$_3$), 8.23 (m, SiCH$_3$). ^{29}Si{^{1}H} NMR (C_6D_6, 99 MHz): δ −9.4 (m). ^{31}P{^{1}H} NMR (C_6D_6, 162 MHz): δ −59.6 (br m), −60.6 (d $^{2}J_{\rm PP'}$ = 17 Hz), −62.7 (d $^{2}J_{\rm PP'}$ = 17 Hz). Anal. Calcd (%) for $C_{29}H_{46}N_2SiP_3Ir$: C, 47.33, H, 6.30, N, 3.81. Found: C, 47.69, H, 6.60, N, 3.78. IR (cm^{-1}): $\nu_{\rm IrH}$ 2027 (br m).

(NSiN)Ir(H)(OTf)(PPh$_3$) (16). (1) To an aluminum foil-covered 100 mL Schlenk flask equipped with a stir bar were added AgOTf (0.070 g, 0.27 mmol) and (NSiN)Ir(H)(Cl)(PPh$_3$) (0.20 g, 0.26 mmol). To this, 15 mL of THF was added, and the reaction mixture was stirred at ambient temperature for 12 h. Then, the reaction mixture was filtered through Celite, and the resulting yellow solution was evaporated to dryness *in vacuo*. Recrystallization of the product in 5 mL of C_6H_6 with a small amount of THF (0.5 mL) afforded a yellow, crystalline solid in 68% yield (0.16 g, 0.18 mmol).

(2) Alternatively, **16** can be generated from addition of a 3 mL CH_2Cl_2 solution of PPh_3 (0.037 g, 0.16 mmol) to a 5 mL CH_2Cl_2 solution of **1** (0.12 g, 0.16 mmol). After 2 h of stirring at room temperature, the solution was evaporated to dryness under vacuum. Recrystallization from a solvent mixture of C_6H_6 and THF afforded **16** in 84% yield (0.12 g, 0.13 mmol). ^{1}H NMR (THF-d_8, 500 MHz): δ 10.04 (m, 1 H, ArH), 9.51 (d J_{HH} = 5.0 Hz, 1 H, ArH), 8.34 (d J_{HH} = 7.0 Hz, 1 H, ArH), 8.13 (d J_{HH} = 8.5 Hz, of d J_{HH} = 1.0 Hz, 1 H, ArH), 8.09 (d J_{HH} = 7.0 Hz, of d J_{HH} = 1.0 Hz, 1 H, ArH), 7.86 (d J_{HH} = 7.0 Hz, of d J_{HH} = 1.2 Hz, 1 H, ArH), 7.80 (d J_{HH} = 8.0 Hz, 1 H, ArH), 7.67 (m, 1 H, ArH), 7.52 (m, 2 H, ArH), 7.46−7.41 (m, 7 H, ArH), 7.29 (m, 1 H, ArH), 7.20 (m, 3 H, ArH), 7.12 (m, 6 H, ArH), 0.470 (s, 3 H, SiCH_3), −16.5 (d $^2J_{HP}$ = 19 Hz, 1 H, IrH). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 153.2, 153.0, 151.9, 151.8, 144.0, 143.5, 139.6, 139.1, 135.6 (J_{CP} = 3.8 Hz), 133.7 (J_{CP} = 10 Hz), 131.0 (J_{CP} = 2.5 Hz), 130.7 (J_{CP} = 58 Hz), 129.7, 129.5, 129.4, 129.3, 128.7 (J_{CP} = 11 Hz), 128.5, 128.2, 123.0, 122.9 (aryl carbons), −5.4 (SiCH_3). ^{19}F NMR (THF-d_8, 376.5 MHz): δ −77.8 (s). ^{29}Si{^{1}H} NMR (THF-d_8, 99 MHz): δ −6.1 (d, $^2J_{SiP}$ = 11 Hz). ^{31}P{^{1}H} NMR (THF-d_8, 162 MHz): δ 9.3 (br s). Anal. Calcd (%) for $C_{38}H_{31}N_2SiPO_3SF_3Ir$: C, 50.49, H, 3.46, N, 3.10. Found: C, 50.77, H, 3.48, N, 3.02. IR (cm^{-1}): ν_{IrH} 2120 (w).

X-ray Crystallography. General Considerations. The single-crystal X-ray analyses of compounds **2**, **5**, **14**, and **15** 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 (**2**), 15 s (**14**), or 30 s (**5** and **15**). Cell constants and an orientation matrix for data collection were obtained from a least-square refinement using the measured positions of reflections in the range $3.5° < 2\theta < 52.7°$. 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 the 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-square 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 diethyl ether solution of **2** at −30 °C.

For **5**. Crystals were grown by layering diethyl ether onto a dichloromethane solution of **5** at room temperature.

For **14**·CH_2Cl_2. Crystals were grown by layering pentane onto a dichloromethane solution of **14** at room temperature. One molecule of CH_2Cl_2 was found in the asymmetric unit cell. The Ir−H group could not be located in the difference Fourier map.

For **15**·0.5Et_2O. Crystals were grown from a concentrated diethyl ether solution of **15** at −30 °C. One-half molecule of Et_2O was found in the asymmetric unit cell with the oxygen atom on an inversion center. This molecule was modeled with a half-occupancy oxygen and two full-occupancy carbons. The other atoms of the diethyl ether molecule were generated using a full symmetry expansion. The Ir−H ligand was located in the difference Fourier map and positionally refined.

Acknowledgment. We thank Dr. Fred Hollander and Dr. Alan Oliver of the UC Berkeley CHEXRAY facility for assistance with X-ray crystallography, Dr. Urs Burckhardt, Dr. Rudi Nunlist, and Dr. Herman van Halbeek for implementation of ^{29}Si NMR experiments, and Dr. Ulla Andersen for carrying out mass spectrometry measurements. This work was supported by the National Science Foundation under Grant No. CHE-0649583.

Supporting Information Available: Text describing complete X-ray experimental details, ORTEP plots, and structural data for **2**, **5**, **14**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700494Q