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# The Osmium−Silicon Triple Bond: Synthesis, Characterization, and Reactivity of an Osmium Silylyne Complex

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*Supporting Information*

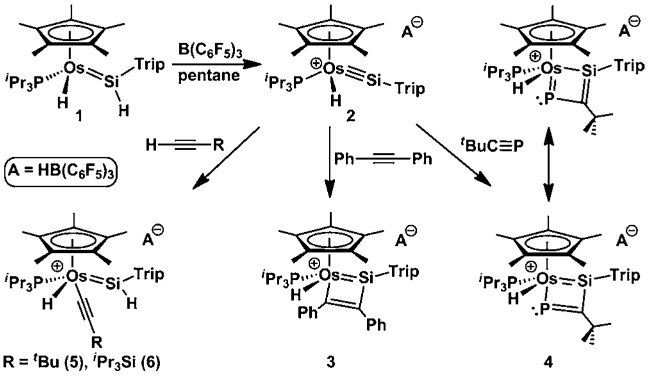
**ABSTRACT:** The first silylyne complex of a metal beyond group 6, [Cp*($^i$Pr$_3$P)(H)Os≡Si(Trip)][HB(C$_6$F$_5$)$_3$], was prepared by a new synthetic route involving hydride abstraction from silicon. NMR and DFT computations support the presence of a silylyne ligand, and NBO and ETS-NOCV analysis revealed the nature of this Os−Si interaction as a triple bond consisting of a covalent $\sigma$ bond and two strong $\pi$ back-donations. The discovery of this complex allowed observations of the first cycloadditions involving a silylyne complex, and terminal alkynes are shown to react *via* C−H bond additions across the Os≡Si bond.

Carbyne (or alkylidyne) complexes with formal metal−carbon triple bonds have been the focus of considerable fundamental research on structure, bonding, and reactivity, especially given the utility of such species in catalysis.[1] These investigations have heightened curiosity in related transition metal-group 14 congeners, which are expected to exhibit new and interesting reactivity patterns. The well-known instability of $\pi$ bonds involving these heavier elements[2] makes such metal−ylyne complexes of the type L$_n$M≡ER (E = Si, Ge, Sn, Pb) even more intriguing as synthetic targets. Power and co-workers reported the first successes along these lines, with preparation of the terminal germylyne complexes Cp(CO)$_n$M≡Ge[2,6-Ar$_2$-C$_6$H$_3$] ($n$ = 2, 3; M = Cr, Mo, W; Ar = Trip, 2,4,6-$^i$Pr$_3$C$_6$H$_2$; Mes, 2,4,6-Me$_3$C$_6$H$_2$), by direct reaction of anionic [Cp(CO)$_3$M]$^-$ complexes with stable ClGe[2,6-Ar$_2$-C$_6$H$_3$] species.[3] Filippou et al. also utilized halogermylene species to prepare the germylyne complexes X(P−P)$_2$M≡Ge($\eta^1$-Cp*) (X = Cl, Br, I; M = Mo, W; P−P = Ph$_2$PCH$_2$CH$_2$PPh$_2$, Et$_2$PCH$_2$CH$_2$PEt$_2$), and X(PMe$_3$)$_4$Mo≡Ge(2,6-C$_6$H$_3$-Trip$_2$) *via* oxidative additions of a Ge−X bond.[4] Similar approaches have been used to generate analogous stannylyne complexes.[5] Consistent with the lower stability and availability of low-valent silicon starting materials, the analogous silylyne complexes have proven more elusive. The first silylyne complex, [Cp*(dmpe)(H)Mo≡SiMes][B(C$_6$F$_5$)$_4$], was obtained in this laboratory by abstraction of chloride from the corresponding silylene complex Cp*(dmpe)(H)Mo=Si(Cl)-Mes. This complex features a linear Mo−Si−C arrangement and a weak Si···H interaction ($^2J_{\mathrm{SiH}}$ 15 Hz).[6] More recently, Filippou and co-workers have reported the neutral silylyne Cp(CO)$_3$MoSi(2,6-Trip$_2$-C$_6$H$_3$) from a base-stabilized halosilylene adduct.[7]

Despite recent progress in the isolation and characterization, including recent computational studies[8] on metal−ylyne complexes of the heavier group 14 elements, synthetic control of structure and bonding in such compounds remains quite challenging. This is emphasized by the facts that known complexes of this type generally require an exceptionally bulky substituent and all of them feature a group 6 metal (Cr, Mo, or W). In this contribution, the first ylyne complex of a nongroup 6 metal, and a rare example of a silylyne complex, is reported. This complex, [Cp*($^i$Pr$_3$P)(H)Os≡Si(Trip)][HB(C$_6$F$_5$)$_3$], was obtained using the readily available primary silane (Trip)SiH$_3$ as the silicon-based starting material. Significantly, this complex represents the first L$_n$M≡ER species to exhibit alkyne cyclization reactivity, akin to that observed for carbyne species.[1]

Initial efforts to generate a group 8 silylyne complex focused on a strategy related to that used to obtain [Cp*(dmpe)(H)-Mo≡SiMes]$^+$,[6] namely abstraction of an anionic substituent from a neutral silylene ligand. Thus, reaction of a bromobenzene solution of Cp*($^i$Pr$_3$P)(H)Os=SiH(Trip)[9] (**1**) with the Lewis acid B(C$_6$F$_5$)$_3$ immediately resulted in a color change from bright orange to ruby red, and formation of [Cp*($^i$Pr$_3$P)(H)Os≡Si(Trip)][HB(C$_6$F$_5$)$_3$] (**2**), as indicated by multinuclear ($^1$H, $^{11}$B, $^{13}$C, $^{19}$F, $^{29}$Si, $^{31}$P) NMR spectroscopy (Scheme 1).

**Scheme 1. Synthesis and Reactivity of Osmium Silylyne 2**



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Complex **2** was isolated as a thermally sensitive ($t_{1/2} \approx 30$ min in $d_5$-bromobenzene at ambient temperature) solid in 67% yield. It exhibits a $^{29}$Si NMR resonance at $\delta$ 321 that is shifted downfield by 92 ppm relative to the resonance for silylene **1**. This value agrees well with that obtained computationally for the optimized structure of complex **2** ($\delta$ 309). The conversion of **1** to **2** is also accompanied by the disappearance of the Os−H and Si−H $^1$H NMR resonances for **1**, and appearance of a characteristic, hydridic doublet at $\delta$ −14.5 (1H, $^2J_{HP}$ = 29 Hz) and a broad signal at $\delta$ 4.39 (1H) attributed to Os−H and B−H signals, respectively, for silylyne **2**. Attempts to measure the $^2J_{SiH}$ value using variable temperature one- and two-dimensional NMR experiments were unsuccessful. Furthermore, $^2J_{SiH}$ is computed to be only 7.4 Hz, confirming an extremely weak OsH···Si interaction. Spectroscopic features of the $HB(C_6F_5)_3^-$ anion, specifically the upfield $^{11}$B NMR resonance at $\delta$ −25 in combination with a $\Delta\delta_{m,p}$ value of 2.6 ppm for the $^{19}$F NMR shifts, indicate that the anion is weakly coordinating.[10] In addition, low temperature NMR studies failed to reveal evidence for Si−H or Si−F contacts. Thus, extensive solution NMR data characterize **2** as a terminal silylyne complex as shown in Scheme 1, and this is supported by DFT calculations.[11]

In an effort to more firmly establish the bonding mode for the hydride ligand in complex **2**, calculations at the DFT TPSS[12] level were undertaken. The two extreme structures **2** and **2′** with the hydrogen located at the osmium and silicon atoms, respectively, and the transition state having a bridging hydrogen atom (**TS**) were examined (Scheme 2). The results in Table 1 show that **2′** is 14.8 kcal mol$^{-1}$ higher in energy ($\Delta G$) than **2** and that it can easily transform to **2** through the bridging hydride transition state (**TS**), with a free-energy barrier of only 5.5 kcal mol$^{-1}$. Furthermore, the computed $^{29}$Si NMR resonance of **2′** ($\delta$ 282) does not match the experimental value. Thus, **2** is the exclusive product formed in the hydride abstraction reaction.

**Scheme 2. Structural Models for 2**

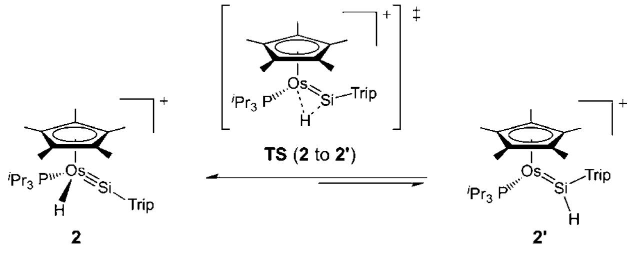


**Table 1. Selected Bond Lengths (Å), Bond Angle (deg), and Solvated Free Energies (kcal mol$^{-1}$)**

| | $\Delta G$ | Os−Si | Os−H | Si−H | Os−Si−C |
|---|---|---|---|---|---|
| **2** | 0.0 | 2.176 | 1.635 | 2.760 | 168.0 |
| **TS** | 20.3 | 2.254 | 2.487 | 1.550 | 165.0 |
| **2′** | 14.8 | 2.303 | 3.298 | 1.499 | 135.4 |

The optimized structure of **2** has some noteworthy characteristics (Figure 1). The Os−Si−C bond angle is 168.0°, a value which suggests that the Si atom has nearly *sp* hybridization. This angle is much larger than the computed value of 135.4° in **2′** (Table 1), where *sp*$^2$ hybridization would be expected. Furthermore, the computed Os−Si bond length in **2** is 2.176 Å, which is extremely short and contracted by 0.079 Å with respect to **1** (computed as 2.255 Å). This predicted decrease in bond length is slightly larger than the observed difference between the Mo−Si bond lengths in Cp*(dmpe)(H)Mo═Si(Cl)Mes (2.288(2) Å) and [Cp*(dmpe)(H)Mo≡SiMes][B($C_6F_5$)$_4$] (2.219(2) Å).[6] Structures of several known compounds that share the same Cp*($^i$Pr$_3$P)Os$^+$ fragment (Figure S1) were optimized to compare Os−Si bond lengths, and these results also suggest a bond order higher than two for the Os−Si bond in compound **2** (Table S1).

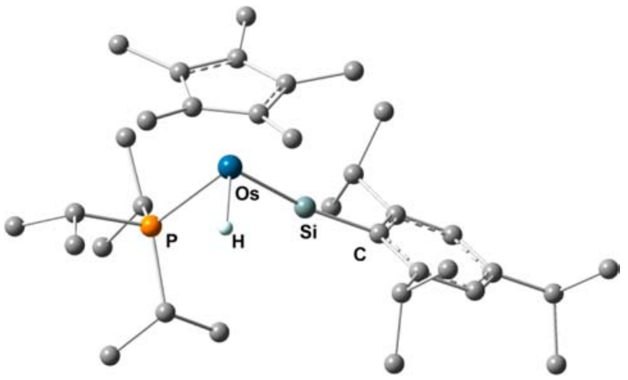


**Figure 1.** DFT optimized structure of **2**. All the hydrogen atoms are hidden except the hydride on the Os atom.

In order to understand the nature of this Os−Si bond, natural bond orbital (NBO) analysis[13] was performed. The three strongest interactions between Os and Si consist of one $\sigma$ bond and two $\pi$ bonds (Figure 2 and Table S2). The $\sigma$ bond has 43% osmium and 57% silicon character, so it is slightly polarized toward the silicon atom. The osmium component contains 43% *s* and 57% *d* orbital character, and the silicon component is composed by 55% *s* and 45% *p* orbital character, providing additional evidence for *sp* hybridization on silicon. With the default NBO parameters, both $\pi$ bonds are characterized as donor−acceptor interactions (Table S2), i.e. back-donations from doubly occupied Os *d* orbitals to empty Si *p* orbitals. The polarization of this bond gives rise to a highly electrophilic silicon atom with an NPA (natural population analysis) charge of 1.14. In order to obtain a more quantitative understanding about the energetics of this bonding interaction, a combination of the extended transition state (ETS)[14] energy decomposition scheme and the natural orbital for chemical valence (NOCV)[15] density decomposition approach was employed to study the interactions between the two closed shell fragments: Cp*($^i$Pr$_3$P)(H)Os and [Si(Trip)]$^+$.[16] In the ETS decomposition scheme the two attractive interactions, the covalent interaction (also known as orbital interaction, −168.5 kcal/mol) and the electrostatic interaction (−166.1 kcal/mol), have nearly equal contributions; these attractive interactions are offset by a large Pauli repulsion (206.5 kcal/mol) (Table S3). The NOCV analysis suggests strong $\pi$ contributions to the overall orbital interactions. Such strong $\pi$ interactions are consistent with the short Os−Si bond. The high reactivity of this bond may reflect ease of polarization of the Os−Si $\pi$ bonds from nearly covalent to donor−acceptor interactions. Detailed computational studies on the reactivity of **2** are underway.

The mechanism by which **2** is generated may involve direct abstraction of the silylene hydrogen by B($C_6F_5$)$_3$, or abstraction of the osmium hydride ligand followed by $\alpha$-hydrogen

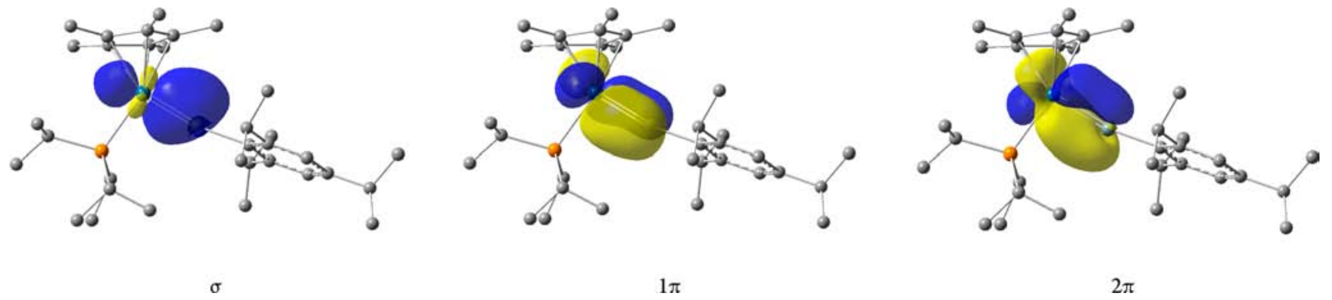


**Figure 2.** Three bonding interactions in compound **2** described by natural bond orbital analysis. 1*π* and 2*π* are back-donations from filled osmium *d* orbitals to empty silicon *p* orbitals.

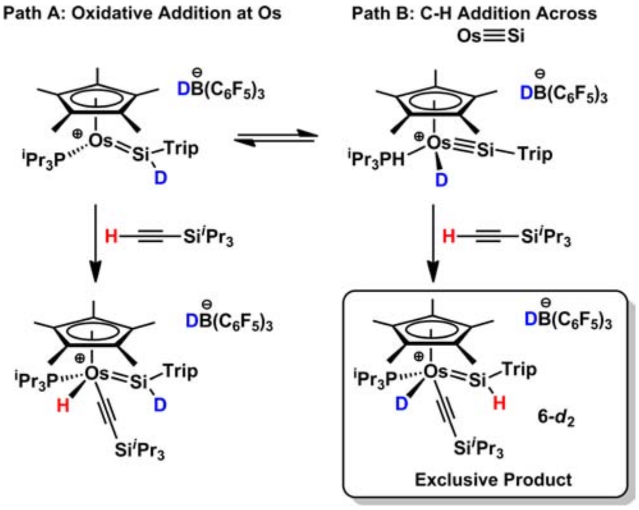
migration from silicon to osmium. It is not currently possible to distinguish between these mechanisms, but a possibly relevant observation is that, under comparable experimental conditions, there is no appreciable reaction between $B(C_6F_5)_3$ and $Cp^*(^iPr_3P)(H)Os{=}SiH(dmp)$ (dmp = 2,6-$Mes_2$-$C_6H_3$).[9] Given the much greater steric hindrance associated with the silicon center of the latter silylene complex (vs that for **1**), this result suggests that Si−H abstraction may be operative in the formation of **2**.

Since the thermal sensitivity of **2** precluded growth of X-ray quality crystals, reactivity studies were undertaken to confirm its identity. Treatment of a bromobenzene solution of silylyne **2** with diphenylacetylene afforded the unprecedented cycloaddition product, $[Cp^*(^iPr_3P)(H)Os{=}Si(Trip)(PhC{=}CPh)][HB(C_6F_5)_3]$ (**3**), as an analytically pure yellow powder in 88% yield (Scheme 1). Complex **3** exhibits an upfield-shifted $^{29}Si$ NMR silylene resonance at $\delta$ 110 (calculated: $\delta$ 102; see Supporting Information (SI)) and diagnostic quaternary signals at 164.3 ($^2J_{CP}$ = 13 Hz) and 197.5 ($^3J_{CP}$ = 3.1 Hz) in the $^{13}C\{^1H\}$ NMR spectrum assigned as $C_\alpha$ and $C_\beta$, respectively. Resonances in the $^1H$, $^{11}B$, and $^{19}F$ NMR spectra attributed to the $HB(C_6F_5)_3^-$ anion remained essentially unchanged from those of complex **2**. Unlike silylyne **2**, metallosilacyclobutadiene **3** is stable indefinitely under an inert atmosphere at low temperature. The cycloaddition does not appear to be reversible, as evidenced by the lack of reaction between **3** and either $^tBuCCH$ or $^iPr_3SiCCH$ (90 min in $d_5$-bromobenzene solution). Despite well documented examples of similar cycloadditions for carbyne complexes,[1] complex **3** represents the first example of addition of an alkyne across a M≡E functionality. Furthermore, direct cycloadditions of this type have rarely been observed for silylene complexes, but are of great interest in the context of metathesis reactivity.[17]

A related cycloaddition was observed upon reaction of **2** with 1 equiv of the phosphaalkyne $^tBuCP$[18] in bromobenzene solution, to cleanly produce the orange complex $[Cp^*(^iPr_3P)(H)Os{=}Si(Trip)(P{=}C^tBu)][HB(C_6F_5)_3]$ (**4**), as determined by multinuclear NMR spectroscopy. Upon washing with pentane, complex **4** was isolated as an analytically pure, orange powder in 77% yield. Diagnostic resonances in the $^{29}Si$, $^{31}P$, and $^{13}C$ NMR spectra at $\delta$ 82, 516, and 278 for the silicon, phosphorus, and carbon ring atoms, respectively, suggest that **4** is best described by a resonance structure containing osmium phosphinidene[19] (Os=P) and silene[20] (Si=C) moieties (Scheme 1). Notably, this interpretation agrees well with computations that predict $^{29}Si$, $^{31}P$, and $^{13}C$ NMR chemical shifts for complex **4** (96, 527, and 298 ppm, respectively). This reactivity suggests that silylyne complexes similar to **2** might provide useful routes to other triply bonded species (e.g., alkylidyne and phosphinidene complexes). As with complex **3**, $^{11}B$ and $^{19}F$ NMR spectra indicate that the $HB(C_6F_5)_3^-$ anion of **4** remains intact and weakly coordinating.

Interestingly, terminal alkynes exhibit a different mode of reactivity toward **2**, involving C−H addition across the Os≡Si triple bond. Thus, addition of RC≡CH to **2** afforded the new silylene complexes $[Cp^*(^iPr_3P)(H)(RC{\equiv}C)Os{=}SiH(Trip)][HB(C_6F_5)_3]$ (**5**, R = $^tBu$; **6**, R = $^iPr_3Si$), identified by $^1H$, $^{11}B$, $^{19}F$, and $^{31}P$ NMR spectroscopy (Scheme 1). Silylene complexes **5** and **6** exhibit characteristic downfield Si−H resonances in the $^1H$ NMR spectra, at $\delta$ 9.5 and 11.6, respectively. These unusual C−H activations might be envisioned as proceeding by two possible mechanisms (Scheme 3): (1) hydrogen migration from osmium to silicon followed by C−H oxidative addition at Os (Path A) or (2) direct C−H addition across the Os≡Si bond (Path B). To distinguish between these pathways, a deuterium-labeling experiment was performed. Treatment of a $d_5$-bromobenzene solution of $[Cp^*(^iPr_3P)(D)Os{\equiv}SiTrip]$ $[DB(C_6F_5)_3]$ (**2-*d*₂**) with 1 equiv of $^iPr_3SiCCH$ afforded $[Cp^*(^iPr_3P)(D)(^iPr_3C{\equiv}C)Os{=}SiH(Trip)][DB(C_6F_5)_3]$ (**6-*d*₂**) as the exclusive product, thereby confirming that path B is the operative mechanism. No OsD/SiH or SiH/BD exchange was observed after 6 h at ambient temperature.

**Scheme 3. Mechanism of Formation of Complex 6**



In summary, a new route to a transition metal silylyne complex, involving hydride abstraction from silicon, has been established. NMR and DFT computations helped to validate the proposed structure of this complex. Unlike previous examples of complexes with triple bonds between a transition metal and a heavy group 14 element, the new silylyne complex does not feature a group 6 transition metal center. NBO and ETS-NOCV analysis revealed the nature of this Os−Si bond as a triple bond consisting of a covalent $\sigma$ bond and two strong $\pi$ back-donations. Significantly, the discovery of complex **2** has allowed the exploration of new reactivity for a metal−silicon triple bond. In particular, the observed additions of multiple bonds, and C−H bonds, across the Os$\equiv$Si bond would seem to portend a rich and varied chemical reactivity for $L_nM{\equiv}ER$ species and the possibility of new chemical structures and previously unobserved transformations of fundamental significance. This work is also an excellent demonstration of close interplays between experiment and theory in studying novel compounds.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Detailed experimental procedure, NMR spectra, computational details, and coordinates of important molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interests.

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## ■ REFERENCES

(1) (a) Bunz, U. H. F. *Acc. Chem. Res.* **2001**, *34*, 998. (b) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (c) Furstner, A.; Davies, P. W. *Chem. Commun.* **2005**, 2307. (d) Schrock, R. R.; Czekelius, C. *Adv. Synth. Catal.* **2007**, *349*, 55. (e) Zhang, W.; Moore, J. S. *Adv. Synth. Catal.* **2007**, *349*, 93. (f) Wu, X.; Tamm, M. *Beilstein J. Org. Chem.* **2011**, *7*, 82. (g) Heppekausen, J.; Stade, R.; Kondoh, A.; Seidel, G.; Goddard, R.; Fürstner, A. *Chem.—Eur. J.* **2012**, *18*, 10281.

(2) (a) Jutzi, P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 232. (b) Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529. (c) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (d) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (e) Waterman, R.; Hayes, P. G.; Tilley, T. D. *Acc. Chem. Res.* **2007**, *40*, 712.

(3) (a) Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 11966. (b) Pu, L.; Twamley, B.; Haubrich, S. T.; Olmstead, M. M.; Mork, B. V.; Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 650.

(4) (a) Filippou, A. C.; Philippopoulos, A. I.; Portius, P.; Neumann, D. U. *Angew. Chem., Int. Ed.* **2000**, *39*, 2778. (b) Filippou, A. C.; Portius, P.; Philippopoulos, A. I. *Organometallics* **2002**, *21*, 653. (c) Filippou, A. C.; Schnakenburg, G.; Philippopoulos, A. I.; Weidemann, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 5979. (d) Filippou, A. C.; Weidemann, N.; Philippopoulos, A. I.; Schnakenburg, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 5987.

(5) (a) Filippou, A. C.; Philippopoulos, A. I.; Schnakenburg, G. *Organometallics* **2003**, *22*, 3339. (b) Filippou, A. C.; Portius, P.; Philippopoulos, A. I.; Rohde, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 445.

(6) Mork, B. V.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 357.

(7) Filippou, A. C.; Chernov, O.; Stumpf, K. W.; Schnakenburg, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 3296.

(8) (a) Pandey, K. K.; Lein, M.; Frenking, G. *J. Am. Chem. Soc.* **2003**, *125*, 1660. (b) Filippou, A. C.; Rohde, H.; Schnakenburg, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2243. (c) Pandey, K. K.; Lledós, A. *Inorg. Chem.* **2009**, *48*, 2748. (d) Pandey, K. K.; Patidar, P.; Power, P. P. *Inorg. Chem.* **2011**, *50*, 7080.

(9) Hayes, P. G.; Beddie, C.; Hall, M. B.; Waterman, R.; Tilley, T. D. *J. Am. Chem. Soc.* **2006**, *128*, 428.

(10) Horton, A. D. *Organometallics* **1996**, *15*, 2675.

(11) Frisch, M. J., et al. *Gaussian 09*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2009. Please refer to the SI for the full citation.

(12) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(13) NBO 5.9 was used in this work. Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.9*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 2011; http://www.chem.wisc.edu/~nbo5.

(14) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

(15) (a) Mitoraj, M. P.; Michalak, A.; Ziegler, T. *J. Chem. Theory Comput.* **2009**, *5*, 962. (b) Mitoraj, M.; Michalak, A. *J. Mol. Model.* **2007**, *13*, 347. (c) Michalak, A.; Mitoraj, M.; Ziegler, T. *J. Phys. Chem. A* **2008**, *112*, 1933.

(16) ETS-NOCV calculations were performed by the ADF2012 program. (a) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391−403. (b) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931−967. (c) *ADF2012*; SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com. A full list of authors and contributors can be found in the SI.

(17) (a) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1997**, *119*, 11236. (b) Lee, V. Y.; Aoki, S.; Yokoyama, T.; Horiguchi, S.; Sekiguchi, A.; Gornitzka, H.; Guo, J.-D.; Nagase, S. *J. Am. Chem. Soc.* **2013**, *135*, 2987.

(18) Figueroa, J. S.; Cummins, C. C. *J. Am. Chem. Soc.* **2004**, *126*, 13916.

(19) Rosenberg, L. *Coord. Chem. Rev.* **2012**, *256*, 606.

(20) Ottosson, H.; Eklöf, A. M. *Coord. Chem. Rev.* **2008**, *252*, 1287.