Activations of Silanes with $[PhB(CH_2PPh_2)_3]Ir(H)(\eta^3-C_8H_{13})$. Formation of Iridium Silvlene Complexes via the Extrusion of Silvlenes from Secondary Silanes R₂SiH₂

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The abstraction of methide from $(Me_3P)_3Ir(SiHMes_2)(Me)(H)$ (1) with $B(C_6F_5)_3$ gave the silylene complex $[fac-(Me_3P)_3(H)_2Ir(SiMes_2)][MeB(C_6F_5)_3]$ (2) via 1,2-hydrogen migration. Secondary silanes (H₂SiR₂) reacted with [PhBP₃]Ir(H)(η^3 -C₈H₁₃) (**3**) (where [PhBP₃] = $PhB(CH_2PPh_2)_3^{-})$ to give silvlene complexes of the type $[PhBP_3](H)_2Ir=SiR_2$ (R = 2,4,6trimethylphenyl (Mes), 4a; R = Ph, 4b; R = Et, 4c; R = Me, 4d), with loss of cyclooctene. Analogously, the germylene complex [PhBP₃](H)₂Ir=GeMes₂ was obtained via the reaction of **3** with Mes₂GeH₂. Primary silanes (H₃SiR) reacted with **3** to give $[PhBP_3](H)_2Ir=Si(R)$ - $(c-C_8H_{15})$ (R = Mes, **8a**; R = 2,4,6-triisopropylphenyl (Trip), **8b**) via an intermediate silylene complex with an Si-H bond, [PhBP₃](H)₂Ir=Si(R)(H). With tertiary silanes (R₃SiH), silylcapped trihydride complexes of the type $[PhBP_3]IrH_3(SiR_3)$ (R = Et, **7a**; R = Me, **7b**) and 1,3-cyclooctadiene were produced. The mechanisms of these processes are discussed.

Introduction

Transition-metal silylene chemistry has evolved significantly since the first silylene complexes were reported in 1990.¹ This class of compounds is important to the development of organosilicon chemistry, as numerous reactions of organosilanes are thought to occur via intermediate silylene complexes.²⁻⁷ Furthermore, since carbene complexes are useful in organic synthesis, it is possible that analogous silylene complexes may be valuable as catalysts and synthetic intermediates in organosilicon chemistry.

Synthetic approaches to silylene complexes include triflate^{1,8-11} or chloride¹² abstraction from silicon to yield cationic complexes of the type $L_n M = SiR_2^+$ (eq 1), the coordination of free silvlenes (as stable diamide compounds^{13–17} or as generated photochemically¹⁸) to tran-

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sition metals (eq 2), and the induced migration of H from Si to Pt upon abstraction of Me⁻ from (dippe)Pt(Me)-(SiHMes₂) (eq 3; dippe = ${}^{i}Pr_{2}PCH_{2}CH_{2}P^{i}Pr_{2}$, Mes = 2,4,6-trimethylphenyl).¹⁹ The last process, based on 1,2migration, is of interest because silvlene-containing intermediates produced in this way have often been proposed to account for rearrangements in metal silyl complexes.^{2-7,20-30} In addition, the participation of silvlene complexes in catalytic cycles would seem to require a two-step activation of the silane substrate, involving initial oxidative addition of the silane followed by a 1,2-migration to produce the silylene ligand (eq 4).

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Given the potential for 1,2-migrations to produce reactive silvlene complexes that may mediate new chemical transformations, we have sought to develop reaction systems for which this migration is facile. One approach is based on extension of the induced-migration method used to form the four-coordinate Pt(II) silylene complex shown in eq 3 to other metal systems and coordination geometries. An initial goal targeted migrations that would generate stable octahedral complexes, and for this purpose we have focused on d⁶ Ir(III). In related work, it has been shown that addition of H₂-SiMes₂ to $Cp^*(PMe_3)$ IrMe(OTf) (where $OTf = OSO_2CF_3$) produces the silylene complex [Cp*(PMe₃)(H)Ir=SiMes₂]-[OTf], and mechanistic studies suggested that this transformation occurs via 1,2-migration of hydrogen in the intermediate [Cp*(PMe₃)IrSiHMes₂][OTf].³¹

In this contribution we describe migrations that produce octahedral iridium silylene complexes and a general chemical process that involves the facile extrusion of silylenes and germylenes from secondary silanes and germanes (R_2EH_2 : E = Si, Ge). As discussed below, this chemistry appears to involve 1,2-migrations between iridium and silicon (or germanium). Some of these results have been communicated previously.³² Extrusions of this general type are potentially useful in catalysis and have been identified in a few other cases. For example, extrusions of carbenes from organic substrates have been observed at electron-rich metal centers.³³⁻⁴¹ In addition, the extrusion of a germylene from a germane^{42,43} has been reported by Banaszak Holl.

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Results and Discussion

An Iridium Silylene Complex via 1,2-Hydrogen Migration. Our strategy for the generation of iridium silvlene complexes via migration chemistry targeted a 5-coordinate, 16-electron Ir-SiHR₂ derivative. It was envisioned that such a species might be available by methide abstraction, and a suitable starting material proved to be $(Me_3P)_3Ir(SiHMes_2)(Me)(H)$ (1), prepared by addition of Mes₂SiH₂ to (Me₃P)₄IrMe.⁴⁴ Upon addition of $B(C_6F_5)_3$ to 1 in CH_2Cl_2 , the reaction solution changed from colorless to yellow, and NMR spectroscopy indicated quantitative formation of a new product (2). For **2**, a resonance attributed to $H_3C-B(C_6F_5)_3$ (δ 0.52) and an IrH resonance which is integrated as two hydrogens $(\delta -11.02, {}^{2}J_{\text{HP(trans)}} = 84 \text{ Hz})$ were observed. This suggested that abstraction of Me⁻ had occurred, followed by a 1,2-H migration from silicon to iridium to form the silvlene complex [fac-(Me₃P)₃(H)₂Ir(SiMes₂)]- $[MeB(C_6F_5)_3]$ (2; eq 5). This was verified by the ²⁹Si-

{¹H} NMR spectrum of **2**, which contains a large downfield chemical shift (δ 241, dt, ${}^{2}J_{SiP(trans)} = 172$ Hz, ${}^{2}J_{SiP(cis)} = 4$ Hz), characteristic of sp²-hybridized silicon.^{1,8–12,18,19} Presumably Me[–] abstraction generated the unsaturated, five-coordinate intermediate [*fac*-(Me₃P)₃-(H)Ir(SiHMes₂)][MeB(C₆F₅)₃], prior to 1,2-H migration to form the coordinatively saturated silylene complex. Formation of the silylene complex upon addition of B(C₆F₅)₃ is rapid (<5 min), and no intermediates were observed at room temperature when the reaction was monitored by ³¹P NMR spectroscopy.

Although analytically pure **2** was easily obtained in powder form by removing the CH_2Cl_2 used in its preparation, we have been unable to crystallize it under a variety of conditions. In general, we have found that crystallizations are often problematic for ionic complexes such as **2**, which contain a fluorocarbon-based anion, $MeB(C_6F_5)_3^-$, and a hydrocarbon-based cation. In an effort to obtain a neutral analogue of **2**, we studied the reactivity of hydrosilanes in a related iridium system based on $[PhBP_3]Ir(H)(\eta^3-C_8H_{13})^{32}$ (**3**), where $[PhBP_3]$ = $PhB(CH_2PPh_2)_3^-$. This complex contains three facially

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Scheme 1



Table 1. ²⁹Si NMR Shifts for the Silylene Complexes [PhBP₃](H)₂Ir=SiR₂

R ₂	29 Si NMR, δ	R_2	$^{29}{\rm Si}$ NMR, δ
Mes ₂ Ph ₂	241 327	Me ₂ Mes(C ₈ H ₁₅)	311 274
Et_2	307	$Trip(C_8H_{15})$	317

coordinated phosphines but is zwitterionic, with a borate incorporated into the ligand backbone.

Silylene Extrusion from Secondary Silanes. Complex **3** reacts with secondary silanes (H_2SiR_2 , with R = Mes, Ph, Et, Me) in benzene to give silylene dihydride complexes of the type [PhBP₃](H)₂Ir=SiR₂ (eq 6: R = Mes, **4a**; R = Ph, **4b**; R = Et, **4c**; R = Me, **4d**), with concomitant loss of cyclooctene (COE). Formation of the



silylene complex was confirmed by ²⁹Si{¹H} NMR spectroscopy, as all the complexes exhibit resonances downfield of 200 ppm (Table 1). The required reaction conditions varied depending on the steric bulk of the silane. For example, in benzene- d_6 , formation of [Ph-BP₃](H)₂Ir=SiMes₂ required heating at 95 °C for 24 h while [PhBP₃](H)₂Ir=SiMe₂ formed after heating at 80 °C for 2 min. Furthermore, formation of the silylene complex is nearly complete in each case (>85% by NMR spectroscopy). This transformation is exceptional in that the direct conversion of secondary silanes to silylene complexes was previously unknown.



Figure 1. ORTEP diagram of [PhBP₃](H)₂Ir=SiMes₂ (4a).

Interestingly, the related parent allyl complex [PhBP₃]-Ir(H)(η^3 -C₃H₅)⁴⁵ did not react with R₂SiH₂ (R = Mes, Et, or Me) under forcing conditions (benzene- d_6 , 80 °C, 1 week). The inertness of this complex relative to **3** may reflect a reduced tendency for it to undergo a change in hapticity (η^3 to η^1 ; Scheme 1) which would allow oxidative addition to the metal center. It is also noteworthy that the related complexes TpIr(H)(η^3 -C₈H₁₃)⁴⁶ and Tp^{Me₂Ir(H)(η^3 -C₄H₇)⁴⁶ (where Tp = hydridotris-(pyrazolyl)borate and Tp^{Me₂} = hydridotris(3,5-dimethylpyrazolyl)borate), which are less electron-rich and less sterically demanding than **3**,⁴⁵ fail to react with H₂-SiMes₂ (benzene- d_6 , 92 °C, 24 h).}

The dimesitylsilylene complex $[PhBP_3](H)_2Ir=SiMes_2$ (4a) was precipitated by the addition of pentane to a toluene solution of 4a (67% yield). The molecular structure of 4a (Figure 1) features a dimesitylsilylene ligand which is planar at silicon (sum of the angles about Si 359.0(6)°). Notably, the Ir=Si bond distance of 2.260(3) Å is 5% shorter than the average of previously observed Ir-Si distances (2.39 Å).⁴⁷ The [PhBP₃] ligand is facially coordinated to iridium with P-Ir-P angles

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	4a	5	6
empirical formula	C ₇₂ H ₇₁ BP ₃ IrOSi	C47H49BP3IrOSi2	C ₇₅ H ₇₅ BP ₃ IrGe
fw	1268.39	1837.76	1344.99
cryst size (mm)	0.05 imes 0.21 imes 0.30	0.12 imes 0.10 imes 0.02	$0.34 \times 0.10 \times 0.03$
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P\overline{1}$
a (Å)	11.5877(2)	15.956(1)	13.2680(7)
b (Å)	19.6433(2)	28.838(2)	14.1823(7)
<i>c</i> (Å)	27.2469(5)	18.279(1)	19.105(1)
α (deg)	90	90	88.229(1)
β (deg)	91.569(1)	92.025(1)	73.711(2)
γ (deg)	90	90	66.383(2)
$V(Å^3)$	6199.6(2)	8406(2)	3148.1(3)
orientation rflns: no., 2θ range (deg)	6753, 3.0 - 45.0	4517, 3.0-46.0	2730, 3.0-46.0
Ζ	4	8	2
D_{calcd} (g/cm ³)	1.359	1.552	1.269
diffractometer		SMART	
radiation	Μο Κα (λ	= 0.710 69 Å), graphite mono	chromated
temp (K)	167(1)	140(1)	155(1)
scan type	ω (0.3° per frame)		
scan rate (s/frame)	10.0		
data collected, $2\theta_{\max}$ (deg)	49.4	51.2	51.3
no. of rflns measd			
total	10 766	38 028	15 973
unique	5890	14 426	10 012
$R_{ m int}$	0.075	0.100	0.062
structure soln		direct methods (SIR92)	
no. of obsd data $(I > 3\sigma(I))$	5890	4956	4392
no. of params refined	665	534	350
final residuals: R ; R_w ; R_{all}^a	0.047; 0.049; 0.106	0.034; 0.032; 0.034	0.041; 0.040; 0.111
goodness of fit indicator ^b	1.54	0.82	0.89
max. shift/error final cycle	0.04	0.08	0.01
max and min peaks, final diff map (e/ų)	1.63, -1.15	0.97, -0.63	1.27, -0.88

 $^{a}R = \sum ||F_{0}| - |F_{c}||/\sum |F_{0}|; R_{w} = \sum w(|F_{0}| - |F_{c}|)^{2}/\sum wF_{0}^{2}|^{1/2}. {}^{b}$ Goodness of fit = $[\sum w(|F_{0}| - |F_{c}|)^{2}/(N_{observes} - N_{params})]^{1/2}.$

Table 3. Selected Bond Distances (Å) and
Angles (deg) for 4a

(a) Bond Distances					
Ir1-P1	2.345(3)	Ir1-P3	2.408(2)		
Ir1-P2	2.329(3)	Ir1-Si1	2.260(3)		
(b) Bond Angles					
P1-Ir1-P2	90.84(9)	PI-Ir1-Si1	141.5(1)		
P1-Ir1-P3	89.11(8)	P2-Ir1-Si1	120.9(1)		
P2-Ir1-P3	86.17(9)	P3-Ir1-Si1	112.32(9)		



Figure 2. ORTEP diagram of $\{[PhBP_3](H)_3IrSiMe_2\}_2O(5)$.

of $86-91^{\circ}$, but otherwise the iridium center is distorted from ideal octahedral geometry. Significant steric interactions between dimesitylsilylene and the bulky [PhBP₃] ligand presumably give rise to the Si–Ir–P angles of 141.5(1), 120.9(1), and 112.3(1)° (vs 180, 90, and 90° for an ideal octahedron). Selected bond distances and angles for **4a** are listed in Table 3.

Except for **4a**, which possesses the most sterically demanding substituents at silicon, these silylene com-

plexes are thermally unstable. For **4b**-**4d**, removal of the solvent in vacuo resulted in significant decomposition (>50%) to mixtures of products. For [PhBP₃](H)₂-Ir=SiMe₂ (**4d**) an apparent hydrolysis product was observed when crystals were grown over several weeks from a toluene solution which had been layered with Et₂O. Analysis of these crystals by X-ray crystallography revealed the bimetallic complex {[PhBP₃](H)₃Ir(SiMe₂)}O (**5**, Figure 2 and Table 4), which is assumed to be the result of slow diffusion of adventitious water into the solution of **4d** (eq 7). Attempts to prepare **5** via the



stoichiometric addition of H_2O to **4d** in benzene- d_6 gave a mixture of products.

Germylene Extrusion from a Germane. Given the generality of the transformation shown in eq 6, we attempted to extend this method to the formation of germylene complexes from secondary germanes. The reaction of Mes₂GeH₂ with **3** (benzene, 83 °C, 36 h) gave



Figure 3. ORTEP diagram of [PhBP₃](H)₂Ir=GeMes₂ (6).

Table 4.	Selected Bond Distances (Å) and
	Angles (deg) for 5

(a) Bond Distances					
Ir1-P1	2.353(3)	Ir1-Si1	2.408(4)		
Ir1–P2	2.358(3)	Si1-01	1.637(8)		
Ir1–P3	2.358(3)	Si2-01	1.646(8)		
(b) Bond Angles					
P1-Ir1-Si1	133.4(1)	P3-Ir2-Si2	124.8(1)		
P2-Ir1-Si1	117.3(1)	P4-Ir2-Si2	125.8(1)		
P3-Ir1-Si1	124.8(1)	P5-Ir2-Si2	126.6(1)		
Ir1-Si1-O1	112.8(3)	Ir2-Si2-O1	111.9(3)		
Si1-01-Si2	148.6(6)				

Table 5. Selected Bond Distances (Å) and
Angles (deg) for 6

(a) Bond Distances					
Ir1-P1	2.362(3)	Ir1–P3	2.310(3)		
Ir1–P2	2.329(3)	Ir1–Ge1	2.339(1)		
(b) Bond Angles					
P1-Ir1-P2	91.9(1)	P1–Ir1–Ge1	111.02(7)		
P1-Ir1-P3	88.1(1)	P2-Ir1-Ge1	113.59(8)		
P2-Ir1-P3	90.2(1)	P3-Ir1-Ge1	147.96(8)		

[PhBP₃](H)₂Ir=GeMes₂ (**6**), which was isolated in 76% yield. Like the analogous silylene complexes, the ³¹P-{¹H} NMR spectrum of **6** consists of two coupled resonances (benzene- d_6 , δ 6.12, 3.61, ² J_{PP} = 19 Hz), and the ¹H NMR spectrum features an IrH resonance (δ -9.68, dm, ² $J_{HPtrans}$ = 83 Hz) which is integrated as two hydrogens. Complex **3** did not give analogous stannylene or carbene complexes upon addition of secondary stannanes or alkanes; H₂CR₂ (R = Ph, Mes) failed to react with **3** in benzene- d_6 after heating at 95 °C for 2 weeks, and Mes₂SnH₂ reacted immediately with **3** in benzene- d_6 at room temperature to give a variety of iridium products, H₂, and several Sn-H-containing compounds (by ¹H NMR spectroscopy).

X-ray-quality crystals of **6** were grown via the slow evaporation of a benzene- d_6 solution; an ORTEP diagram is shown in Figure 3, and selected bond distances and angles are given in Table 5. Germylene complex **6** is structurally similar to its silylene analogue (**4a**). The dimesitylgermylene substituent is bent away from the bulky [PhBP₃] phosphine groups, resulting in Ge–Ir–P angles of 147.96(8), 113.59(8), and 111.02(7)°. The germanium coordination plane (Ir, Ge, C, C) is nearly trigonal planar, with the sum of the angles about Ge being 355.7(6)°, and the Ir=Ge bond distance is 2.339-(1) Å. The only other crystallographically characterized complexes containing Ge–Ir bonds are $(Ph_3P)_2(CO)(H)_2$ -IrGeMe $_3{}^{48}$ and the germylene complexes ${\bf A}$ and ${\bf B}.{}^{49}$



Among these structures, the Ge–Ir distances range from 2.32 to 2.47 Å, with the shorter distances corresponding to germylene–iridium contacts.

Mechanistic Considerations for Silylene Extrusion from Secondary Silanes. Two possible mechanisms for silylene (or germylene) formation from the reactions of H₂SiR₂ (or H₂GeR₂) with [PhBP₃]Ir(H)(η^3 - C_8H_{13}) are shown in Scheme 1. In path A, an η^1 -allyl complex is in equilibrium with an η^2 -COE complex, and addition of an Si-H bond followed by loss of cyclooctene would yield the 16-electron silvl intermediate **D**. This unsaturated intermediate would then undergo 1,2-H migration to form the observed silvlene product, in which iridium is coordinatively and electronically saturated. Alternatively, as shown in path B, 3 could be in equilibrium with an η^1 -allyl complex, which then undergoes oxidative addition of H_2SiR_2 to give an Ir(V)intermediate (C). From this intermediate, reductive elimination of COE and 1,2-H migration would produce the final product.

In an effort to determine which mechanism is operative, the reaction of **3** with D_2SiMes_2 was monitored by NMR spectroscopy. While path A would yield a product with two iridium deuterides, $[PhBP_3](D)_2Ir=SiMes_2$, path B would give a mixture of deuteride and hydride ligands in the iridium product, with some of the deuterium label being incorporated into cyclooctene. To our surprise, this labeling study did not lead to products consistent with path A or B but instead revealed the presence of a $[PhBP_3]$ ligand metalation process.

During the course of a reaction of D_2SiMes_2 with **3** (benzene, 80 °C, 3 h) the deuterium label was incorporated into the ortho position of the *P*-phenyl substituent of [PhBP₃] as well as various positions of the C_8H_{13} ring of **3** prior to product formation (by ¹H, ²H{¹H}, and ³¹P-{¹H} NMR spectroscopy). This observation indicates that silane addition to [PhBP₃]Ir(H)(η^3 - C_8H_{13}) is reversible (D_2SiMes_2 is converted to H_2SiMes_2 prior to formation of the silylene complex), that ortho metalation of the ligand *P*-phenyl groups is a rapid, reversible process,

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and that exchange of iridium-bound and cyclooctenylbound hydrogens occurs rapidly (eq 8).⁵⁰ The metalation



 $[PhBP_3-d_n]Ir=SiMes_2$ (8)

process is consistent with our recent observation of the ortho-metalation product $\{PhB[(CH_2PPh_2)_2(CH_2PPh-C_6H_4)]\}$ Ir(H)(PMe₃), which forms upon addition of PMe₃

 C_6H_4)] $_1$ r(H)(PMe_3), which forms upon addition of PMe_3 to **3**.⁴⁵

We have observed evidence to suggest that the hydride ligands readily migrate back to silicon. For example, the addition of excess CO to **4a** (benzene- d_6 , 92 °C, 24 h) produced Mes₂SiH₂ and [PhBP₃]Ir(CO)₂ (quantitative by ³¹P{¹H} NMR spectroscopy). Additionally, a C–H activation process was observed upon reaction of propene with **4a** (1 atm, benzene- d_6 , 80 °C). After 7 days at 80 °C, 40% conversion to Mes₂SiH₂ and [PhBP₃]Ir(H)(η^3 -C₃H₅) was observed (eq 9). This first



example of a C–H activation by a transition silylene complex suggests that silylene complexes derived from [PhBP₃]Ir may possess a rich reaction chemistry.

Activation of Tertiary Silanes. Both mechanisms in Scheme 1 involve a rearrangement of the 16-electron silvl intermediate **D** to an 18-electron silvlene species via 1,2-H migration from silicon to iridium. This migration should be less favorable for substituents other than H, and thus we studied the reactions of tertiary silanes (HSiR₃) with [PhBP₃]Ir(H)(η^3 -C₈H₁₃) (**3**) in an effort to observe silvl complexes analogous to the proposed intermediates C and D. However, as described below, reactions of 3 with tertiary silanes are not analogous to those with secondary silanes. For example, thermolysis of **3** with 1 equiv of HSiEt₃ (benzene- d_6 , 60 °C, 20 h) led to formation of 1,3-cyclooctadiene (by GC/MS), and by ¹H NMR spectroscopy an IrH resonance which is integrated as three hydrogens (δ –10.6, $^{2}J_{\text{HP}}$ = 81 Hz) and a triethylsilyl substituent are observed. Additionally, the phosphine ligands are equivalent by ${}^{31}P{}^{1}H{}$ NMR spectroscopy (δ –3.81). These data are consistent with the symmetrical, silvl-capped Ir(V) species [PhBP₃]- $IrH_3(SiEt_3)$ (7a, eq 10). This reaction was quantitative by ¹H and ³¹P{¹H} NMR spectroscopy; the isolated yield of **7a** was 38%. It is interesting to note that, depending on reaction conditions, complex 3 may behave as a source of "[PhBP₃]Ir" (with elimination of COE as a

(50) Two reversible processes to account for this are feasible: insertion of COE into the Ir–H bond, or β -H elimination to form [PhBP₃]Ir(H)₂(COD), where COD = 1,3-cyclooctadiene.



Figure 4. ORTEP diagram of one of the two crystallographically independent molecules of [PhBP₃]IrH₃(SiMe₃) (**7b**). One of the phenyl groups on P2 has been omitted for clarity.



byproduct, as in the reactions with secondary silanes) or as a source of " $[PhBP_3]IrH_2$ " (with elimination of 1,3-COD, as in the reactions with tertiary silanes). This difference has also been observed in reactions of **3** with phosphines.⁴⁵ As yet, we do not fully understand the factors that influence this reactivity.

Under an atmosphere of HSiMe₃ 3 reacts (benzene, 75 °C, 6 days) to give the corresponding trimethylsilyl product [PhBP₃]IrH₃(SiMe₃) (7b), which was isolated in 66% yield. The NMR data for 7b are quite similar to those of 7a, which suggests that the complexes are isostructural in solution. The solid-state structure of 7b was determined by X-ray crystallography (Figure 4) and confirms the geometry of this complex, which may be described as a distorted, silyl-capped octahedron. Two structurally similar molecules are in the asymmetric unit. In both molecules all P-Ir-P angles are approximately 90°, while the P–Ir–Si angles range from 119 to 129°. Selected bond distances and angles for 7b are given in Table 7. Overall, the coordination geometry for iridium is similar to that in the related complex Tp^{Me₂}IrH₃(SiEt₃).⁵¹ However, it contrasts with the structures of related Cp* complexes, including Cp*IrH₃(ER₃) (where $ER_3 = SiMe_3$, $SnMe_3$, $SnPh_3$)⁵² and $Cp*IrH_2$ -(SiEt₃)₂,⁵³ which may be described as four-legged piano stools.

⁽⁵¹⁾ Gutierrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Taboada, S.; Trujillo, M.; Carmona, E. *J. Am. Chem. Soc.* **1999**, *121*, 346.

Table 6. Crystallographic Data for 7b and	18	Sa
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	7b	8a
empirical formula	C48H50BP3IrSi	C ₆₂ H ₆₉ BP ₃ IrSi
fw	994.05	985.98
cryst size (mm)	$0.19 \times 0.16 \times 0.07$	$0.30\times0.25\times0.07$
cryst syst	triclinic	monoclinic
space group	<i>P</i> 1	$P2_{1}/c$
a (Å)	13.3907(3)	16.9431(4)
$b(\mathbf{A})$	17.3646(4)	14.9301(1)
<i>c</i> (Å)	20.4662(3)	21.3674(4)
α (deg)	65.825(1)	90
β (deg)	86.788(2)	99.521(1)
γ (deg)	89.680(2)	90
V (Å ³)	4333.9(2)	5330.7(2)
orientation rflns:	3923, 3.0-45.0	6301, 3.0-45.0
no., 2θ range (deg)		
Ζ	4	4
D_{calcd} (g/cm ³)	1.523	1.228
diffractometer	SM	ART
radiation	Mo K α (λ =	0.710 69 Å),
	graphite mo	nochromated
temp (K)	0 1	154(1)
scan type	ω (0.3 ° p	er frame)
scan rate (s/frame)	10).0
no. of data collected,		46.5
$2\theta_{\rm max}$ (deg)		
no. of rflns measd		
total	25 520	24 769
unique	14 104	7975
R _{int}	0.056	0.100
structure soln	direct meth	ods (SIR92)
no. of obsd data	5626	4387
$(I > 3\sigma(I))$		
no. of params refined	483	592
final residuals:	0.035; 0.035;	0.037; 0.038;
$R; R_w; R_{all}^a$	0.108	0.081
goodness of fit indicator ^b	0.84	1.34
max shift/error	0.00	0.01
final cycle		
max and min peaks.	1.47, -0.53	0.67, -0.39
final diff map ($e/Å^3$)	,	,

^a $R = \sum ||F_0| - |F_c|| / \sum |F_0|; R_w = [\sum w(|F_0| - |F_c|)^2 / \sum wF_0^2]^{1/2}.$ ^b Goodness of fit = $[\sum w(|F_0| - |F_c|)^2 / (N_{observes} - N_{params})]^{1/2}.$

Table 7. Selected Bond Distances (Å) andAngles (deg) for 7b

	-	-			
(a) Bond Distances					
Ir1-P1	2.367(3)	Ir1–P3	2.375(3)		
Ir1-P2	2.363(3)	Ir1-Si1	2.437(3)		
(b) Bond Angles					
P1-Ir1-P2	89.7(1)	P1-Ir1-Si1	128.5(1)		
P1–Ir1–P3	91.6(1)	P2-Ir1-Si1	128.1(1)		
P2–Ir1–P3	88.9(1)	P3-Ir1-Si1	118.7(1)		

Silylene Complexes Derived from Primary Silanes. Given the ease with which silylenes are extruded from secondary silanes using **3**, we sought to prepare complexes with a hydrogen substituent on the silylene ligand, $[PhBP_3](H)_2Ir=SiH(R)$, from the reaction of **3** with primary silanes. Such species are expected to be quite reactive, given the presence of a Si-H bond and the relatively low steric protection for the silylene center. Recently a silylene complex of this type, $[(Et_3P)_3(H)_2Ir=SiH(C_6H_3Mes_2-2,6)][B(C_6F_5)]$, was reported.⁵⁴

The reaction of MesSiH₃ with **3** (benzene- d_6 , 25 °C, 24 h) did in fact cleanly produce a new species with a



Figure 5. ORTEP diagram of $[PhBP_3](H)_2Ir=Si(Mes)(c-C_8H_{15})$ (**8a**). The cyclooctyl ring bound to silicon is highly disordered, and several partial-occupancy carbon atoms are displayed.

Table 8. Selected Bond Distances (Å) and
Angles (deg) for 8a

(a) Bond Distances					
2.377(2)	Ir1–P3	2.328(2)			
2.333(2)	Ir1-Si1	2.250(3)			
(b) Bond Angles					
87.98(8)	P1-Ir1-Si1	115.3(1)			
88.51(8)	P2-Ir1-Si1	140.7(1)			
90.43(8)	P3-Ir1-Si1	119.7(1)			
	(a) Bond 2.377(2) 2.333(2) (b) Bond 87.98(8) 88.51(8) 90.43(8)	(a) Bond Distances 2.377(2) Ir1-P3 2.333(2) Ir1-Si1 (b) Bond Angles 87.98(8) P1-Ir1-Si1 88.51(8) P2-Ir1-Si1 90.43(8) P3-Ir1-Si1			

Scheme 2



²⁹Si{¹H} NMR shift of δ 274, consistent with the formation of a silylene complex. However, by ¹H NMR spectroscopy no resonances consistent with COE or the presence of a Si-H bond were observed. Instead, several methylene resonances (δ 1.73–2.03) were observed, suggesting the possibility of a cyclooctyl substituent on silicon and a silylene complex of the type [PhBP₃](H)₂-Ir=Si(Mes)(*c*-C₈H₁₅) (**8a**). Such a product could result (formally) from the hydrosilylation of COE by the anticipated silylene complex, [PhBP₃](H)₂Ir=SiH(Mes).

An X-ray diffraction study of complex **8a** confirmed its structure (Figure 5), which is similar to that of **4a**. The Ir=Si bond distance of 2.250(3) Å is the shortest Ir-Si contact reported to date.⁵⁵ The geometry at iridium is a distorted octahedron, with P-Ir-P angles ranging from 88 to 90° and P-Ir-Si angles of 140.7(1),

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 $[\]left(55\right)$ Based on a search of the Cambridge Structural Database, April 2002.

Scheme 3



119.7(1), and $115.3(1)^{\circ}$. Significantly, the crystallographic data are consistent with the presence of a cyclooctyl substituent on the silylene moiety, which confirms that activation of all three Si-H bonds of MesSiH₃ has taken place. Additional bond distances and angles for **8a** are listed in Table 8.

In a reaction of the more sterically congested 2,4,6triisopropylphenylsilane (TripSiH₃) with 3 (toluene, room temperature, 2.5 days), an intermediate was observed in the course of an analogous triple Si-H bond activation. As in the case above, a cyclooctylsilylene complex, $[PhBP_3](H)_2Ir=Si(Trip)(c-C_8H_{15})$ (8b), is the final product with a ²⁹Si{¹H} NMR resonance of δ 317. However, when the reaction was monitored by NMR spectroscopy, intermediate formation of COE and a species consistent with [PhBP₃](H)₂Ir=SiH(Trip) (9) was observed (Scheme 2). The concentration of 9 did not build up significantly (<20%), but it was observed in the presence of COE and was completely converted to 8b once all of the COE had been consumed. For 9, two coupled resonances are observed by ³¹P{¹H} NMR spectroscopy (δ 2.87 and 1.86, ${}^{2}J_{PP} = 18$ Hz). The ${}^{1}H$ NMR spectrum for silylene 9 features an IrH resonance at δ –9.34 (²*J*_{HPtrans} = 75 Hz) and, significantly, a SiH resonance at δ 11.16 (³*J*_{HP} = 20 Hz). This downfield shift for the silylene SiH is consistent with [(Et₃P)₃(H)₂Ir= SiH(C₆H₃Mes₂-2,6)][B(C₆F₅)]⁵⁴ and other SiH silylene complexes prepared in our group⁵⁶ and is reminiscent of the downfield ¹H NMR shifts that have been observed for hydrogen-substituted carbene complexes of the type L_nM=CHR.^{57,58}

As outlined in Scheme 3, there are three mechanisms whereby the intermediate [PhBP₃](H)₂Ir=SiH(Trip) (9) can react with COE to give the final product [PhBP₃](H)₂-Ir=SiH(Trip) (8b). First, 1,2-H migration from silicon to iridium followed by COE coordination, and migratory insertion would generate five-coordinate [PhBP₃]Ir(c-C₈H₁₅)(SiH₂Trip) (E). Intermediate E could undergo reductive elimination to give H₂Si(Trip)(c-C₈H₁₅) and "[PhBP₃]Ir",⁵⁹ which could then form the product silylene complex 9 via double Si-H activation. Alternatively, intermediate E could undergo a series of 1,2migrations to give silvlene complex F and silvl complex G prior to product formation. Finally, silylene complex **9** could undergo 2 + 2 cycloaddition to give the iridasilacycle H; C-H reductive elimination would then generate $[PhBP_3](H)Ir(c-C_8H_{15})(SiHTrip)$ (G), and a 1,2migration would yield **8b**. Although no 2 + 2 cycloadditions between alkenes and silylene complexes have been reported, products apparently derived from alkyne cycloaddition with silylene complexes have been observed.^{2,3,60-65}

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Conclusion

In the study described here, migration chemistry in iridium silyl complexes was exploited to produce stable, isolable silvlene complexes. The synthetic routes employed have targeted silvlene complexes with the most stable coordination geometry for Ir(III), which is designed to form via 1,2-H migration in a reactive, 5-coordinate intermediate. The viability of this approach was first demonstrated by a reaction scheme that appears to generate the 16-electron intermediate (Me₃P)₃-(H)Ir–SiHMes₂⁺, which rapidly converts to the 6-coordinate silvlene complex $(Me_3P)_3(H)_2Ir=SiMes_2^+$ (2). This result, along with those reported earlier for the platinum system of eq 3,19 emphasizes the importance of changes in the metal's coordination geometry in influencing migration chemistry. Evidently, 1,2-migrations are not favored in square-planar Pt(II) silyl complexes^{18,19} or in octahedral Rh(III) silyl complexes.⁶⁶ However, reaction schemes that produce less stable coordination geometries (e.g., 3-coordinate Pt(II) or 5-coordinate Ir(III)) can lead to migrations of this type. Such low-coordinate intermediate species may result from ligand abstractions, as reported here and elsewhere,^{19,31} but may also form via ligand dissociation processes. This latter possibility is yet to be demonstrated, however.

Further development of this migration chemistry might lead to useful catalytic transformations involving reactive silvlene complexes as intermediates. Significant progress in this direction has been made with identification of reactions that involve the facile extrusion of silvlene ligands from simple secondary and primary silanes. Notably, this chemistry resulted from investigation of a new iridium-based fragment involving the anionic triphosphine ligand [PhBP₃]. With development of new chemical transformations for silvlene complexes, it may prove possible to design catalytic cycles that involve silvlene extrusions. In this context, it is worth noting the propene reaction of eq 9, which represents the first example of a C-H activation mediated by a transition metal silvlene complex. Currently, the mechanism of this conversion is not known. Future efforts will address this issue and the reactivity of silvlene complexes toward various organic compounds.

Experimental Section

General Considerations. All experiments were performed under dry nitrogen using standard Schlenk or drybox techniques. Solvents were distilled under nitrogen from sodium benzophenone ketyl, and dichloromethane was distilled from CaH₂. To remove olefin impurities, pentane and benzene were pretreated with concentrated H₂SO₄, 0.5 N KMnO₄ in 3 M H₂-SO₄, NaHCO₃, and then anhydrous MgSO₄. Benzene-*d*₆ and THF-*d*₈ were distilled from Na/K alloy. Other chemicals were obtained from commercial suppliers and were used as received. [PhBP₃]Ir(η^3 -C₈H₁₃)(H),³² (PMe₃)₄IrMe,⁴⁴ Mes₂SiH₂,⁶⁷ and Mes₂-GeH₂⁶⁸ were prepared according to literature procedures. TripSiH₃ was prepared by reaction of TripSiCl₃⁶⁹ with LiAlH₄. Elemental analyses were performed by the Microanalytical Laboratory in the College of Chemistry at the University of California, Berkeley. FT-infrared spectra were recorded on a Mattson FTIR 3000 instrument.

NMR Measurements. Routine ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR spectra were recorded at 298 K on a Bruker DRX-500 instrument equipped with a 5 mm broad band probe and operating at 500.13 MHz (¹H), 125.77 MHz (¹³C), 99.36 MHz (²⁹Si), and 202.45 MHz (³¹P). The ²⁹Si NMR data were obtained using ¹H-²⁹Si HMQC experiments. Chemical shifts are reported in ppm downfield from internal SiMe₄ (¹H, ¹³C, ²⁹Si), and external 85% H₃PO₄ (³¹P); coupling constants are given in Hz. Bruker XWINNMR software was used for all processing.

X-ray Crystallography. General Considerations. The single-crystal analyses were carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements were made on a Bruker SMART CCD area detector with graphitemonochromated Mo K α radiation ($\lambda = 0.710$ 69 Å). Data were integrated by the program SAINT, corrected for Lorentz and polarization effects, and analyzed for agreement and possible absorption using XPREP. Empirical absorption corrections were made using SADABS. Structures were solved by direct methods and expanded using Fourier techniques. The quantity minimized by the least-squares program was $\sum W(|F_0| - |F_c|)$,⁷⁰ where *w* is the weight of a given observation. The analytical forms of the scattering factor tables for the neutral atoms were used, and all scattering factors were corrected for both the real and the imaginary components of anomalous dispersion. All calculations were performed using the teXsan crystallographic software package. Selected crystal and structure refinement data are summarized in Tables 2 and 6. All crystals were mounted on a glass fiber using Paratone N hydrocarbon oil.

Considerations for 4a. Crystallization via slow diffusion of pentane into a toluene/THF solution of **4a** provided X-rayquality crystals. The molecule packs in the unit cell with one moderately well-defined molecule of toluene and a poorly defined mass of electron density that might correspond to one tetrahydrofuran per two molecules of **4a**. This was assumed in determining the unit cell contents for the purposes of calculating F_{000} and the density. The model for the disordered solvent was five half-occupancy carbon atoms, since there was no way to assign one of them as a likely oxygen atom. All non-hydrogen atoms were refined anisotropically, except for boron and the carbon atoms of the solvent molecule. Hydrogen atom positions were calculated but not refined.

Considerations for 5. Crystals suitable for X-ray diffraction studies were grown over several days from a toluene solution that had been layered with ether. There are two unique molecules (which are structurally similar) in the asymmetric unit. The iridium, phosphorus, and silicon atoms were refined anisotropically. Methylene (CH_2) and methyl (CH_3) carbon atoms were refined anisotropically, while the phenyl (CH) carbon atoms were refined isotropically, and the hydrogen atom positions were calculated but not refined.

Considerations for 6. Crystals suitable for X-ray diffraction studies were grown over several days by the slow evaporation of a benzene solution of **6**. The iridium, phosphorus, and germanium atoms were refined anisotropically, the carbon and boron atoms were refined isotropically, and all hydrogen positions were calculated but not refined.

Considerations for 7b. Crystals suitable for X-ray diffraction studies were grown over several days by the slow cooling of a toluene/ether solution to -35 °C. The iridium, phosphorus, and silicon atoms were refined anisotropically, the carbon and boron atoms were refined isotropically, and all hydrogen positions were calculated but not refined.

Considerations for 8a. Crystals suitable for X-ray diffraction were grown over several days by the slow cooling of a toluene solution to -35 °C. The iridium, phosphorus, silicon,

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and carbon atoms were refined anisotropically, with the exception of the carbon atoms of the disordered cyclooctyl ring. The cyclooctyl ring was modeled as 14 partial-occupancy carbon atoms. The positions and occupancies of these carbon atoms were refined, while the $B_{\rm iso}$ value for each atom was fixed at 9.5. The sum of the occupancies for these carbon atoms is 8. The boron atom was refined isotropically, and the hydrogen atom positions were calculated but not refined.

fac-(Me₃P)₃Ir(SiHMes₂)(Me)(H) (1). A Schlenk tube containing a magnetic stir bar was charged with (Me₃P)₄IrMe (0.658 g, 1.29 mmol) and H₂SiMes₂ (0.368 g, 1.37 mmol). Diethyl ether (20 mL) was added, and the resulting reaction solution was stirred rapidly. After 2-3 min 1 began to precipitate. The mixture was stirred for 7.5 h, filtered, and evaporated to dryness to give 0.558 g of analytically pure 1. The filtrate was concentrated slightly and stored for 3 days at room temperature. An additional 0.104 g of crystalline 1 was then isolated by filtration (total yield 73%). ¹H NMR (benzene- d_6): δ 6.85 (s, 4 H, aryl), 5.93 (m, 1 H, SiH), 2.89 (br s, 12 H, ortho 2,4,6-Me₃C₆H₂), 2.21 (s, 6 H, para 2,4,6-Me₃C₆H₂), 1.14 (d, $J_{HP} = 70$ Hz, 9 H, PMe₃), 1.11 (d, $J_{HP} = 76$ Hz, 9 H, PMe₃), 1.06 (d, J_{HP} = 71 Hz, 9 H, PMe₃), 0.09 (m, 3 H, IrMe), -11.47 (dt, ${}^{2}J_{\text{HP(trans)}} = 128$ Hz, ${}^{2}J_{\text{HP(cis)}} = 17$ Hz, 1 H, IrH). ³¹P{¹H} NMR (benzene- d_6): δ -63.3 (dd, ² J_{PP} = 19 Hz, ² J_{PP} = 14 Hz), -64.1 (dd, ${}^{2}J_{PP} = 19$ Hz, ${}^{2}J_{PP} = 14$ Hz), -64.7 (br). ²⁹Si{¹H} NMR (benzene- d_6): δ –46.7 (d, ¹ J_{SiH} = 151 Hz). ¹³C-{¹H} NMR (toluene- d_8): δ 144.1 (Si-C), 135.1 (aryl), 134.6 $(2,4,6-Me_3C_6H_2), 129.1 (2,4,6-Me_3C_6H_2), 24.8 (2,4,6-Me_3C_6H_2),$ 20.7 (2,4,6- $Me_3C_6H_2$), 23.0 (dm, ${}^1J_{CP} = 28$ Hz, P Me_3), 21.2 (dm, ${}^{1}J_{CP} = 27$ Hz, PMe₃), 17.8 (dm, ${}^{1}J_{CP} = 29$ Hz, PMe₃). IR (Nujol, cm⁻¹): 2133 m (IrH), 2075 m (SiH). Anal. Calcd for C₂₈H₅₄-IrP₃Si: C, 47.77; H, 7.73. Found: C, 47.44; H, 7.53. Mp: 124-127 °C.

 $[fac-(Me_3P)_3(H)_2Ir=SiMes_2][MeB(C_6F_5)_3]$ (2). A CH₂Cl₂ solution (10 mL) of $B(C_6F_5)_3$ (0.314 g, 6.13 mmol) was added via cannula to 1 (0.428 g, 6.08 mmol) in CH₂Cl₂ (10 mL) to give a yellow solution, which was stirred for 5 min. Removal of solvent under reduced pressure resulted in formation of a yellow powder which was analytically pure. Yield: 0.652 g (88%). ¹H NMR (CD₂Cl₂): δ 6.85 (s, 4 H, 2,4,6-Me₃C₆H₂), 2.53 (s, 12 H, ortho 2,4,6-Me₃C₆H₂), 2.28 (s, 6 H, para 2,4,6- $Me_3C_6H_2$), 1.78 (d, ${}^2J_{HP} = 9$ Hz, 9 H, PMe_3 [trans to SiMes₂]), 1.62 (d, ${}^{2}J_{HP} = 8$ Hz, 18 H, PMe₃), 0.52 (br, 3 H, B-Me), -11.02 (dm, ${}^{2}J_{\text{HP(trans)}} = 84$ Hz, 2 H, IrH). ${}^{31}P{}^{1}H}$ NMR (CD₂Cl₂): δ -63.0 (m), -63.8 (m), -64.4 (m). ²⁹Si{¹H} NMR (CD₂Cl₂): δ 254.1 (d, ${}^{2}J_{SiP}$ = 168 Hz). ${}^{13}C{}^{1}H$ NMR (CD₂Cl₂): δ 149.9 (aryl), 148.0 (aryl), 135.8 (m, C-F), 145.3 (Si-C), 141.8 (aryl), 140.0 (aryl), 129.9 (Mes aryl), 24.88 (dm, ${}^{1}J_{CP} = 30 \text{ Hz P}Me_{3}$), 24.5 (ortho 2,4,6-Me₃C₆H₂), 23.7 (m, PMe₃), 21.3 (para 2,4,6-Me₃C₆H₂). IR (Nujol, cm⁻¹): 2357 m (IrH). Anal. Calcd for C₄₆H₅₄BF₁₅IrP₃Si: C, 45.44; H, 4.48. Found: C, 45.38; H, 4.29. Mp: 64-69 °C dec.

[PhBP₃](H)₂Ir=SiMes₂ (4a). [PhBP₃]Ir(η^3 -C₈H₁₃)(H) (0.225 g, 0.228 mmol) was dissolved in benzene (5 mL). This solution was then transferred into a vessel containing dimesitylsilane, H₂SiMes₂ (0.0611 g, 0.228 mmol). The resulting colorless, homogeneous solution was then warmed to 95 °C, and it gradually turned yellow within 4-5 h. After 24 h the volatile materials were removed under reduced pressure. Extraction with toluene (5 mL) and filtration removed a light yellow precipitate and afforded a deep yellow filtrate. This filtrate, which was dried in vacuo, contained yellow 4a (0.221 g) as the only product identified by ¹H and ³¹P{¹H} NMR spectroscopy. High-yield crystallization of this crude powder was difficult. However, analytically and spectroscopically pure material was precipitated via pentane addition to a toluene solution of 4a, yielding 0.176 g (67%). A crystal suitable for an X-ray diffraction study was obtained by slow diffusion of pentane into a toluene/THF mixture (10:1) at 25 °C. ¹H NMR (benzene- d_6): δ 8.10–6.7 (m, 35 H, PhBP₃ aryl), 6.63 (s, 2 H, 2,4,6-Me₃C₆H₂), 2.50 (s, 12 H, ortho 2,4,6-Me₃C₆H₂), 2.08 (s, 6

H, para 2,4,6-*Me*₃C₆H₂), 1.93 (m, 4 H, PhB(CH'₂PPh₂)(*CH*₂-PPh₂)₂), 1.83 (m, 2 H, PhB(*CH*'₂PPh₂)(*CH*₂PPh₂)₂), -9.47 (m, ²J_{HP}(trans) = 70 Hz, 2 H, Ir*H*). ²⁹Si{¹H} NMR (benzene-*d*₆): δ 241.2 (dt, ²J_{SiP}(trans) = 172.4 Hz, ²J_{SiP}(cis) = 4 Hz). ³¹P{¹H} NMR (benzene-*d*₆): δ 3.44 (t, *J*_{PP} = 18 Hz), 2.24 (d, *J*_{PP} = 18 Hz). ¹³C{¹H} NMR (THF-*d*₈): δ 140.5 (aryl), 139.7 (aryl), 133.2 (aryl), 133.1 (aryl), 132.6 (aryl), 132.4 (aryl), 129.8 (aryl), 129.2 (aryl), 129.1 (aryl), 128.9 (aryl), 124.5 (aryl), 24.5 (ortho 2,4,6-Me₃C₆H₂), 21.4 (para 2,4,6-Me₃C₆H₂), 18.0 (br, BCH₂P). IR (Nujol, cm⁻¹): 3055 m, 2958 m, 2923 m, 2122 m, 2060 m (IrH), 1064 w, 1482 m, 1417 s, 1262 w, 1159 m, 1096 s, 1027 m, 924 m, 862 w, 803 w, 740 m, 697 s, 517 m. Anal. Calcd for C₆₃H₆₅-BIrP₃Si: C, 66.01; H, 5.72. Found: C, 65.76; H, 5.90.

Observations of [PhBP₃](H)₂Ir=SiR₂. For R = Ph (4b). An NMR tube containing a benzene- d_6 solution of **3** (0.024 g, 0.024 mmol) and Ph₂SiH₂ (0.005 g, 0.03 mmol) was heated at 80 °C for 24 h. Analysis of the reaction mixture by ¹H, ³¹P-{¹H}, and ²⁹Si{¹H} NMR spectroscopy revealed nearly complete conversion (ca. 85%) to [PhBP₃](H)₂Ir=SiPh₂ and COE. ¹H NMR (benzene- d_6): δ 8.11, 7.98, 7.76, 7.66, 7.41, 7.05, 6.67, 6.65 (aryl), 1.97 (m, 4 H, PhB(CH'₂PPh₂)(CH₂PPh₂)₂), 1.85 (m, 2 H, PhB(CH'₂PPh₂)(CH₂PPh₂)₂), -9.46 (dm, ²J_{HP}(trans) = 75 Hz, 2 H, Ir*H*). ³¹P{¹H} NMR (benzene- d_6): δ 5.41 (d, ²J_{PP} = 19 Hz, 2 P, trans to H), 3.50 (t, ²J_{PP} = 19 Hz, 1 P, trans to Si). ²⁹Si{¹H} (benzene- d_6): δ 327.5.

For R = **Et (4c).** An NMR tube containing a benzene- d_6 solution of **3** (0.017 g, 0.017 mmol) and Et₂SiH₂ (0.005 g, 0.05 mmol) was allowed to sit at room temperature for 12 h. Analysis by ¹H, ³¹P{¹H}, and ²⁹Si{¹H}NMR spectroscopy revealed nearly complete conversion to [PhBP₃](H)₂Ir=SiEt₂ and COE. ¹H NMR (benzene- d_6): δ 8.13, 7.78, 7.68, 7.57, 7.43, 7.12, 7.00, 6.81 (aryl), 1.92 (m, 4 H, PhB(CH'₂PPh₂)(CH₂-PPh₂)₂), 1.80 (m, 2 H, PhB(CH'₂PPh₂)(CH₂PPh₂)₂), -10.13 (dm, ²J_{HP}(trans) = 76 Hz, 2 H, IrH). ³¹P{¹H} NMR (benzene- d_6): δ 6.23 (d, ²J_{PP} = 19 Hz, 2 P, trans to H), 2.21 (t, ²J_{PP} = 19 Hz, 1 P, trans to Si). ²⁹Si{¹H}(benzene- d_6): δ 307.4.

For R = **Me (4d).** A PTFE-capped NMR tube containing a benzene- d_6 solution of **3** (0.018 g, 0.018 mmol) was degassed by two freeze-pump-thaw cycles, and an atmosphere of Me₂-SiH₂ was introduced. The tube was then sealed, and the solution was heated at 80 °C for 2 min. Analysis by ¹H, ³¹P-{¹H}, and ²⁹Si{¹H} NMR spectroscopy revealed nearly complete conversion (ca. 90%) to [PhBP₃](H)₂Ir=SiMe₂ and COE. ¹H NMR (benzene- d_6): δ 7.71–6.76 (35 H, aryl), 0.35 (s, 9 H, Si Me_3), -10.17 (dm, ² J_{HP} (trans) = 69 Hz, 2 H, IrH). ³¹P{¹H} NMR (benzene- d_6): δ 4.76 (d, ² J_{PP} = 20 Hz, 2 P, trans to H), 2.59 (t, ² J_{PP} = 20 Hz, 1 P, trans to Si). ²⁹Si{¹H} (benzene- d_6): δ 311.2.

[PhBP₃](H)₂Ir=GeMes₂ (6). In a PTFE-sealed reaction vessel, a 4 mL benzene solution of $[PhBP_3]Ir(\eta^3-C_8H_{13})H(0.102)$ g, 0.103 mmol) and Mes₂GeH₂ (0.031 g, 0.099 mmol) was stirred at 83 °C for 36 h. The solvent was removed in vacuo to give a yellow oil, which was triturated with 4 mL of benzene to yield an orange powder. The powder was crystallized by layering a 2 mL toluene solution with 3 mL of Et₂O and storing at -35 °C; from this, yellow crystals were obtained (0.084 g, 76%). ¹H NMR (benzene-*d*₆): δ 8.01–6.73 (35 H, [PhBP₃] aryl), 6.66 (s, 4 H, ortho 2,4,6-Me₃C₆H₂), 2.54 (s, 12 H, ortho 2,4,6-Me₃C₆H₂), 2.15 (s, 6 H, para 2,4,6-Me₃C₆H₂), 1.89 (br, 2 H B(CH₂P)₂(CH'₂P')), 1.82 (br, 2 H B(CH₂P)₂(CH'₂P')), -9.68 (dm, $^{2}J_{\text{HP}} = 83 \text{ Hz}, 2 \text{ H}, \text{ Ir}H$). $^{31}P\{^{1}\text{H}\}$ NMR (benzene- d_{6}): δ 6.12 (t, ${}^{2}J_{PP} = 19$ Hz, 2 P, trans to H), 3.61 (d, ${}^{2}J_{PP} = 19$ Hz, 1 P, trans to Ge). ${}^{13}C{}^{1}H$ NMR (benzene- d_6): δ 138.8 (aryl), 133.2 (aryl), 132.3 (aryl), 131.9 (aryl), 129.8 (aryl), 129.7 (aryl), 128.5 (aryl), 127.3 (aryl), 125.6 (aryl), 124.2 (aryl), 23.1 (ortho 2,4,6-Me₃C₆H₂), 21.0 (para 2,4,6-Me₃C₆H₂), 17.6 (br, BCH₂P). IR (KBr, cm⁻¹): 3052 m, 2917 m, 2061 br m (IrH), 1618 m, 1434 s, 1330 s, 1090 s, 924 m, 812 s, 697 s. Anal. Calcd for C₆₃H₆₅-BIrP₃Ge: C, 63.55; H, 5.50. Found: C, 63.83; H, 5.67. Mp: 134-137 °C dec.

[PhBP₃]IrH₃(SiEt₃) (7a). In a PTFE-sealed reaction vessel, [PhBP₃]Ir(η^3 -C₈H₁₃)H (0.091 g, 0.092 mmol) and Et₃SiH (0.011 g, 0.092 mmol) were combined with 4 mL of benzene. The reaction mixture was stirred and heated at 50 °C for 2 days. Removal of the volatile materials yielded an oily solid, which was triturated with 4 mL of pentane to give a yellow solid (0.035 g, 38%). ¹H NMR (benzene- d_6): δ 8.23–6.84 (35 H, $[PhBP_3]$ aryl), 1.93 (br, 6 H, BC H_2P), 1.37 (q, J = 8 Hz, 6 H, SiC H_2 CH₃), 1.08 (t, J = 8 Hz, 9 H, SiCH₂C H_3), -11.0 (dm, $^{2}J_{\text{HP(trans)}} = 64$ Hz, 3 H, Ir*H*). $^{31}P\{^{1}H\}$ NMR (benzene-*d*₆): δ -5.52 (s). ¹³C{¹H} NMR (benzene- d_6): δ 140.1 (aryl), 133.3 (aryl), 132.7 (aryl), 129.4 (aryl), 129.1 (aryl), 128.3 (aryl), 124.9 (aryl), 17.5 (q, ${}^{3}J_{CP} = 2$ Hz, Si $CH_{2}CH_{3}$), 16.5 (br, B $CH_{2}P$), 9.2 (SiCH₂CH₃). IR (KBr, cm⁻¹): 3056 m, 2904 m, 2871 m, 2081 br m (IrH), 1482 m, 1434 s, 1159 w, 1091 s, 1002 w, 923 m, 891 w, 861 w, 738 s, 694 w, 516 s, 480 m. Anal. Calcd for C₅₁H₅₉SiBP₃: C, 61.50; H, 5.97. Found: C, 61.78; H, 6.00. Mp: 207-216 °C dec, 216-219 °C (melt).

[PhBP₃]IrH₃(SiMe₃) (7b). In a PTFE-sealed reaction vessel, a 4 mL benzene solution of $[PhBP_3]Ir(\eta^3-C_8H_{13})H$ (0.212 g, 0.214 mmol) was degassed by three freeze-pump-thaw cycles, and an atmosphere of Me₃SiH was introduced. The vessel was then placed in an oil bath maintained at 75 °C for 6 days, after which time the solvent was removed in vacuo. The resulting oil was washed with pentane $(3 \times 5 \text{ mL})$ to give a tan powder (0.135 g, 66%). ¹H NMR (benzene- d_6): δ 8.13 (d, J = 7 Hz, 2 H, aryl), 7.68 (t, J = 7 Hz, 2 H, aryl), 7.46 (m, 13) H, aryl), 6.78 (m, 18 H, aryl), 1.83 (m, 6 H, BCH₂P), 1.06 (s, 9 H, SiMe₃), -10.6 (dm, ${}^{2}J_{HP(trans)} = 81$ Hz, 3 H, IrH). ${}^{31}P{}^{1}H$ NMR (benzene- d_6): δ -3.81. ²⁹Si{¹H} NMR (benzene- d_6): δ -21.4. ¹³C{¹H} NMR (benzene-*d*₆): δ 140.1 (d, *J* = 50 Hz, aryl), 132.8 (s, aryl), 132.6 (m, aryl), 129.3 (s, aryl), 128.2 (m, aryl), 16.6 (br, B*C*H₂P), 16.4 (q, ${}^{3}J_{CP} = 3$ Hz). IR (KBr, cm⁻¹): 3055 m, 2941 w, 2889 w, 2091 br m (IrH), 1483 m, 1433 s, 1259 m, 1159 m, 1092 s, 922 s, 827 s, 739 s, 694 s, 628 m. Anal. Calcd for C48H53BSiIrP3: C, 60.43; H, 5.60. Found: C, 60.11; H, 5.57. Mp: 191-197 °C dec, 213-220 °C (melt).

[PhBP₃](H)₂Ir=Si(Mes)(C₈H₁₅) (8a). A 1 mL benzene solution of MesSiH₃ was added to a 5 mL benzene solution of **3**, and the reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure to give a yellow oil. This was dissolved in 1 mL of THF, and slow diffusion of Et₂O at -35 °C yielded tan crystals of **8a** (0.158 g, 75%). ¹H NMR (benzene-*d*₆): δ 8.80–6.52 (35 H, aryl), 2.43 (br, 6 H, BC*H*₂P), 2.19 (s, 6 H, ortho 2,4,6-*Me*₃C₆H₂), 2.03 (s, 3 H, para 2,4,6-*Me*₃C₆H₂), 2.03–1.76 (m, 15 H, cyclooctyl), -10.00 (dm, ²*J*_{HP}(trans) = 76 Hz, 2 H, Ir*H*). ³¹P{¹H} NMR (benzene-*d*₆): δ 2.20 (t, ²*J*_{PP} = 19 Hz, 1 P, trans to Si), 1.41 (d, ²*J*_{PP} = 19 Hz, 2 P, trans to H). ²⁹Si{¹H} NMR (benzene-*d*₆): δ 274.2 (d, ²*J*_{SiP}(trans) = 158 Hz). ¹³C{¹H} NMR (benzene-*d*₆): 145.7 (aryl),

141.4 (aryl), 140.5 (aryl), 139.1 (aryl), 139.0 (aryl), 133.1 (aryl), 132.8 (aryl), 132.5 (aryl), 129.5 (aryl), 129.1 (aryl), 127.8 (aryl), 124.7 (aryl), 45.9 (d, ${}^3J_{CP} = 7$ Hz, Si*C*H assigned using a DEPT 90 experiment), 30.0 (cyclooctyl *C*H₂), 28.3 (cyclooctyl *C*H₂), 27.8 (cyclooctyl *C*H₂), 25.9 (cyclooctyl *C*H₂), 22.8 (ortho 2,4,6-*M*e₃C₆H₂), 21.5 (para 2,4,6-*M*e₃C₆H₂), 17.1 (br, B*C*H₂P). IR (KBr, cm⁻¹): 3055 m, 2917 s, 2851 m, 2090 m (IrH), 1482 m, 1433 s, 1159 w, 1091 s, 921 m, 890 w, 864 w, 790 w, 749 s, 738 s, 696 s, 518 s, 478 w, 421 w. Anal. Calcd for C₆₂H₆₉-SiBIrP₃: C, 65.42; H, 6.11. Found: C, 65.15; H, 6.31. Mp: 240–244 °C dec.

[PhBP₃](H)₂Ir=Si(Trip)(C₈H₁₅) (8b). A 4 mL toluene solution containing 3 (0.170 g, 0.172 mmol) and TripSiH₃ (0.040 g, 0.171 mmol) was stirred for 3 days. The reaction mixture was concentrated under reduced pressure to ca. 1.5 mL. The slow diffusion of pentane into the resulting toluene solution (room temperature) afforded yellow, crystalline 8b (0.097 g, 47%), which was isolated by filtration and washed with pentane (2 \times 1 mL). ¹H NMR (benzene- d_6): δ 8.18–6.68 (37 H, aryl), 3.67 (sept, J = 6 Hz, 2 H, ortho CHMe₂), 2.97 (sept, J = 6 Hz, 1 H, para CHMe₂), 2.38 (br, 6 H, BCH₂P), 2.03-1.76 (m, 15 H, cyclooctyl), 1.27 (d, J = 6 Hz, 12 H, ortho CHMe₂), 1.19 (d, J = 6 Hz, 6 H, para CHMe₂), -10.12 (dm, $^{2}J_{\text{HP}} = 71 \text{ Hz}, 2 \text{ H}, \text{ Ir}H$). $^{31}P{^{1}H} \text{ NMR}$ (benzene- d_{6}): $\delta 2.80$ (t, ${}^{2}J_{\rm PP}$ = 18 Hz, 1 P, trans to Si), 1.77 (d, ${}^{2}J_{\rm PP}$ = 18 Hz, 2 P, trans to H). ²⁹Si{¹H} NMR (benzene- d_6): δ 317.1. ¹³C{¹H} NMR (benzene-d₆): 151.4, 150.8, 141.7, 133.6, 132.7, 129.7, 126.0, 124.8, 124.6, 122.1, 121.8 (aryl), 39.2 (SiCH), 31.1 (cyclooctyl CH2), 29.8 (cyclooctyl CH2), 28.9 (cyclooctyl CH2), 26.9 (cyclooctyl CH₂), 22.9 (Trip Me), 21.8 (Trip Me), 18.3 (br, BCH₂P). IR (KBr, cm⁻¹): 3056 m, 2955 m, 2918 m, 2137 br m (IrH), 1482 m, 1434 s, 1159 w, 1089 s, 925 m, 863 w, 739 s, 695 s, 519 s, 482 m. Anal. Calcd for C₆₈H₈₁SiBIrSiP₃: C, 66.81; H, 6.68. Found: C, 66.95; H, 6.30. Mp: 189-193 dec.

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Supporting Information Available: Tables of crystal, data collection, and refinement parameters, bond distances and angles, and anisotropic displacement parameters for **4a**, **5**, **6**, **7b**, and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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