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New Cationic and Zwitterionic Cp*M(κ^2-P,S) Complexes (M = Rh, Ir): Divergent Reactivity Pathways Arising from Alternative Modes of Ancillary Ligand Participation in Substrate Activation

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Abstract: Treatment of 0.5 equiv of $[Cp^*IrCl_2]_2$ with 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene afforded Cp*Ir(Cl)(κ^2-3-P^{i}Pr$_2$-2-S-indene) (**1**) in 95% yield ($Cp^* = \eta^5$-C_5Me_5). Addition of AgOTf or $LiB(C_6F_5)_4 \cdot 2.5OEt_2$ to **1** gave [Cp*Ir(κ^2-3-P^{i}Pr$_2$-2-S-indene)]$^+$X$^-$ (**[2]$^+$X$^-$**; X = OTf, 78%; X = $B(C_6F_5)_4$, 82%), which represent the first examples of isolable coordinatively unsaturated [Cp′Ir(κ^2-P,S)]$^+$X$^-$ complexes. Exposure of **[2]$^+$OTf$^-$** to CO afforded **[2·CO]$^+$OTf$^-$** in 91% yield, while treatment of **[2]$^+$B(C$_6$F$_5$)$_4^-$** with PMe_3 generated **[2·PMe$_3$]$^+$B(C$_6$F$_5$)$_4^-$** in 94% yield. Treatment of **1** with K_2CO_3 in CH_3CN allowed for the isolation of the unusual adduct **3·CH$_3$CN** (41% isolated yield), in which the CH_3CN bridges the Lewis acidic Cp*Ir and Lewis basic indenide fragments of the targeted coordinatively unsaturated zwitterion Cp*Ir(κ^2-3-P^{i}Pr$_2$-2-S-indenide) (**3**). In contrast to the formation of **[2·CO]$^+$OTf$^-$**, exposure of **3·CH$_3$CN** to CO did not afford **3·CO**; instead, a clean 1:1 mixture of (κ^2-3-P^{i}Pr$_2$-2-S-indene)Ir(CO)$_2$ (**4**) and 1,2,3,4-tetramethylfulvene was generated. Treatment of **[2]$^+$OTf$^-$** with Ph_2SiH_2 resulted in the net loss of $Ph_2Si(OTf)H$ to give Cp*Ir(H)(κ^2-3-P^{i}Pr$_2$-2-S-indene) (**5**) in 44% yield. In contrast, treatment of **[2]$^+$B(C$_6$F$_5$)$_4^-$** with Ph_2SiH_2 or $PhSiH_3$ proceeded via H−Si addition across Ir−S to give the corresponding [Cp*Ir(H)(κ^2-3-P^{i}Pr$_2$-2-S(SiHPhX)-indene)]$^+$B(C$_6$F$_5$)$_4^-$ complexes **6a** (X = Ph, 68%) or **6b** (X = H, 77%), which feature a newly established S−Si linkage. Compound **6a** was observed to effect net C−O bond cleavage in diethyl ether with net loss of $Ph_2Si(OEt)H$, affording [Cp*Ir(H)(κ^2-3-P^{i}Pr$_2$-2-SEt-indene)]$^+$B(C$_6$F$_5$)$_4^-$ (**7**) in 77% yield. Furthermore, **6a** proved capable of transferring Ph_2SiH_2 to acetophenone, with concomitant regeneration of **[2]$^+$B(C$_6$F$_5$)$_4^-$**; however, **[2]$^+$X$^-$** did not prove to be effective ketone hydrosilylation catalysts. Treatment of 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene with 0.5 equiv of $[Cp^*RhCl_2]_2$ gave Cp*Rh(Cl)(κ^2-3-P^{i}Pr$_2$-2-S-indene) (**8**) in 94% yield. Combination of **8** and $LiB(C_6F_5)_4 \cdot 2.5Et_2O$ produced the coordinatively unsaturated cation [Cp*Rh(κ^2-3-P^{i}Pr$_2$-2-S-indene)]$^+$B(C$_6$F$_5$)$_4^-$ (**[9]$^+$B(C$_6$F$_5$)$_4^-$**), which was transformed into [Cp*Rh(H)(κ^2-3-P^{i}Pr$_2$-2-S(SiHPh$_2$)-indene)]$^+$B(C$_6$F$_5$)$_4^-$ (**10**) via net H−Si addition of Ph_2SiH_2 to Rh−S. Unlike **[2]$^+$X$^-$**, complex **[9]$^+$B(C$_6$F$_5$)$_4^-$** was shown to be an effective catalyst for ketone hydrosilylation. Treatment of **3·CH$_3$CN** with Ph_2SiH_2 resulted in the loss of CH_3CN, along with the formation of Cp*Ir(H)(κ^2-3-P^{i}Pr$_2$-2-S-(1-diphenylsilylindene)) (**11**) (64% isolated yield) as a mixture of diastereomers. The formation of **11** corresponds to heterolytic H−Si bond activation, involving net addition of H^- and Ph_2HSi^+ fragments to Ir and indenide in the unobserved zwitterion **3**. Crystallographic data are provided for **1**, **[2·CO]$^+$OTf$^-$**, **3·CH$_3$CN**, **7**, and **11**. Collectively, these results demonstrate the versatility of donor-functionalized indene ancillary ligands in allowing for the selection of divergent metal−ligand cooperativity pathways (simply by ancillary ligand deprotonation) in the activation of small molecule substrates.

Introduction

Coordinatively unsaturated platinum-group metal (PGM) complexes have long represented intriguing targets of inquiry, owing to their extraordinary propensity for stoichiometric and catalytic substrate activation.[1] In an effort to control metal-centered reactivity, the coordination of strategically constructed ancillary ligands principally intended to tune the steric and electronic properties of the metal coordination sphere has been exploited widely.[1] In moving beyond these more traditional design approaches, important reactivity breakthroughs have been achieved through the development of PGM complexes that can mediate challenging substrate transformations via cooperative metal−ligand interactions in which the ancillary ligand is a participant, rather than a spectator, in the substrate activation process.[2] The most widely studied class of PGM complexes that exhibit such cooperative reactivity behavior are those pairing a Lewis acidic metal fragment with a directly coordinated

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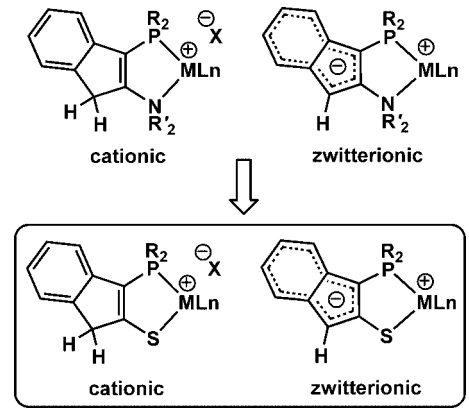
nucleophilic/basic, nondative X-type ligand (X = OR, NR_2, or other heteroatom-based fragment).[2−4] It has been demonstrated that the dual action of adjacent Lewis acidic (M) and Lewis basic (X) fragments in such M−X systems can enable the cooperative activation of a range of polar and nonpolar substrates.[3,4] Such PGM-amido species typify the mechanistically novel catalytic reactivity that can be accessed via M−X cooperativity; appropriately designed complexes of this type have been shown to mediate the catalytic hydrogenation and/or transfer hydrogenation of polar bonds via outer-sphere mechanisms involving the heterolytic splitting of H_2 (or the net extrusion of H_2 from a donor-solvent) across an M-NHR unit to give an (*H*)M-N*H*$_2$R intermediate, which in turn can deliver H_2 to the substrate in a cooperative fashion.[4] By comparison, alternative modes of net metal−ligand cooperative substrate activation involving a reactive PGM center and a *noncoordinating* anionic portion of a bound ancillary ligand (referred to herein as M∧X′ cooperativity) are rare. Nonetheless, the examples documented thus far in the literature exemplify the way in which M∧X′ cooperativity can provide access to unusual stoichiometric and catalytic substrate activation pathways, including the reversible 1,4-addition of ethylene and acetylene to (arene)Ru(β-diketiminate) complexes,[5,6] as well as the dehydrogenation of alcohols into esters[7a] and the dehydrogenative synthesis of amides from alcohols and amines[7b] mediated by (κ^3-P,N,N)Ru species.[8] In the quest to uncover novel modes of PGM-mediated substrate activation with potential applications in catalysis, the development of versatile new classes of ancillary ligands that can be modified easily so as to enable M−X and/or M∧X′ cooperativity represents an important challenge.

Chart 1



In this context, we have reported details of comparative reactivity studies featuring structurally analogous cationic and formally zwitterionic PGM complexes supported by 3-PR_2-2-NR'_2-indene and related monodeprotonated indenide ancillary ligands, respectively (Chart 1).[9−11] In the course of these investigations, we became intrigued by the unusual modes of substrate activation that might arise from net M∧X′ cooperativity involving a cationic PGM fragment and the 10π-electron indenide unit within the ancillary ligand backbone of such formally charge-separated zwitterions. While we have yet to obtain definitive experimental evidence of net M∧X′ cooperativity in our reactivity studies of these zwitterionic (κ^2-P,N)-PGM complexes, such behavior may underpin the remarkable catalytic activity exhibited by a zwitterionic (κ^2-P,N)Ru complex in the transfer hydrogenation of ketones.[9b]

Building on these results and motivated by the remarkable reactivity exhibited by $[Cp^*Ir(LX)]^+$ ($Cp^* = \eta^5$-C_5Me_5) intermediates in both stoichiometric[12] and catalytic[4b,13] substrate transformations, we identified coordinatively unsaturated Cp*Ir complexes supported by new chelating LX-type indene and indenide ancillary ligands as worthwhile targets of inquiry. Given that the reactivity properties of Ir-SR fragments within mononuclear complexes are less well-documented than those of Ir-OR and Ir-NR_2 linkages[3,4,14] and that isolable coordinatively unsaturated $[Cp'Ir(\kappa^2\text{-P,S})]^+X^-$ complexes had not been reported previously, we opted to develop synthetic routes to new cationic and zwitterionic species featuring bidentate ligands that pair neutral dialkylphosphino and anionic thiolate pendant donor groups (Chart 1). Whereas cationic complexes of this type featuring κ^2-PR_2,S-indene ligation may be well-suited to activate substrates via M−X cooperativity, we envisioned that the presence of a tethered anionic backbone within structurally related zwitterionic complexes featuring κ^2-PR_2,S-indenide ligation could provide access to alternative reaction manifolds arising from less-conventional M∧X′ cooperative reactivity. We

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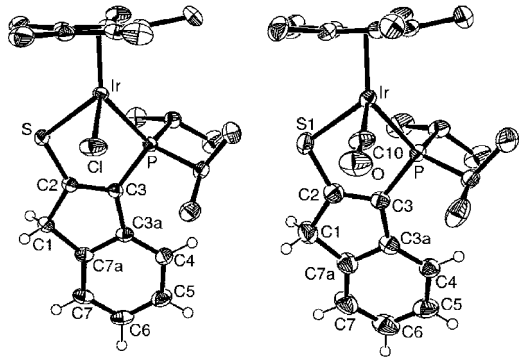
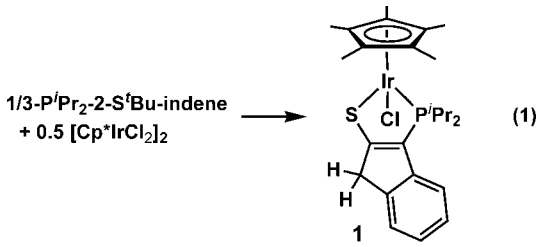


Figure 1. ORTEP diagrams for **1** (left) and $[\mathbf{2\cdot CO}]^+\mathbf{OTf}^-$ (right) shown with 50% ellipsoids; selected H-atoms and the triflate counteranion in $[\mathbf{2\cdot CO}]^+\mathbf{OTf}^-$ have been omitted for clarity.

report herein on the strikingly divergent substrate activation pathways (i.e., M−X versus M∧X′) that are traversed by such coordinatively unsaturated cationic and zwitterionic Cp*Ir(κ^2-P,S) complexes in reactions with acetonitrile and other L-donor ligands, as well as with organosilanes. We also report on our synthetic and reactivity investigations of related Rh complexes, including the application of cationic Cp*Rh(κ^2-P,S) species in the catalytic hydrosilylation of ketones.

Results and Discussion

The precursory compound Cp*Ir(Cl)(κ^2-3-P^{i}Pr$_2$-2-S-indene) **1** was prepared in 95% isolated yield from an isomeric mixture of 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene and 0.5 equiv of $[Cp^*IrCl_2]_2$ (eq 1). The structure of **1** was determined initially on the basis of NMR spectroscopic data, and subsequently was confirmed by use of single-crystal X-ray diffraction techniques. An ORTEP[15] diagram of **1** is provided in Figure 1, while X-ray experimental data and selected metrical parameters for each of the crystallographically characterized complexes reported herein are collected in Tables 1 and 2, respectively. The structural features in **1** are not unusual and can be compared with those found in a related Cp*Ir(κ^2-P,S)Cl complex.[16]



Synthesis and L-Donor Reactivity of the Coordinatively Unsaturated Cations $[\mathbf{2}]^+\mathbf{X}^-$. Treatment of an orange solution of **1** in CH_2Cl_2 with AgOTf or $LiB(C_6F_5)_4\cdot 2.5OEt_2$ in each case resulted in the quantitative conversion to a single phosphorus-containing product (^{31}P NMR) accompanied by an immediate color change to dark blue (Scheme 1). Our assignment of these products as the targeted coordinatively unsaturated, C_s-symmetric $[\mathbf{2}]^+\mathbf{X}^-$ complexes (X = OTf, 78%; X = $B(C_6F_5)_4$, 82%) is entirely consistent with ^{1}H and ^{13}C NMR spectra obtained for these species, in which resonances attributable to magnetically equivalent isopropyl fragments within the P^{i}Pr$_2$ group are observed. Combustion analysis data obtained for $[\mathbf{2}]^+\mathbf{X}^-$ precludes the presence of an additional coligand, as does the dark blue coloration of these complexes.[17] To the best of our knowledge, these represent the first examples of coordinatively unsaturated [Cp′Ir(κ^2-P,S)]$^+$X$^-$ complexes. As anticipated for such unsaturated species, exposure of a blue solution of $[\mathbf{2}]^+\mathbf{OTf}^-$ to an atmosphere of CO afforded cleanly an orange solution of the C_1-symmetric adduct $[\mathbf{2\cdot CO}]^+\mathbf{OTf}^-$ (ν_{CO} = 2053 cm^{-1}; for [Cp*Ir(CO)(TsDPEN)]$^+$X$^-$ a value of 2064 cm^{-1} is observed[11]), from which the product was isolated as an analytically pure, bright orange solid in 91% yield. Similarly, treatment of $[\mathbf{2}]^+\mathbf{B(C_6F_5)_4}^-$ with PMe_3 afforded the 18-electron complex $[\mathbf{2\cdot PMe_3}]^+\mathbf{B(C_6F_5)_4}^-$ in 94% isolated yield. The connectivity in these $[\mathbf{2\cdot L}]^+\mathbf{X}^-$ adducts is supported by NMR spectroscopic data, as well as X-ray diffraction data in the case of $[\mathbf{2\cdot CO}]^+\mathbf{OTf}^-$ (Figure 1). While efforts to prepare $[\mathbf{2\cdot CH_3CN}]^+\mathbf{X}^-$ by treatment of $[\mathbf{2}]^+\mathbf{X}^-$ with excess CH_3CN resulted in the partial bleaching of the dark blue solution along with the consumption of $[\mathbf{2}]^+\mathbf{X}^-$ (^{31}P NMR), an intractable mixture of phosphorus-containing products was generated.

Pursuit of the Coordinatively Unsaturated Zwitterion 3. Having successfully prepared the new coordinatively unsaturated cationic Ir complexes $[\mathbf{2}]^+\mathbf{X}^-$, we turned our focus to the synthesis of the structurally related zwitterion **3** (Scheme 2). Efforts to prepare **3** via HX extrusion from **1** or $[\mathbf{2}]^+\mathbf{X}^-$ employing $NaN(SiMe_3)_2$ afforded a green solid that exhibits broad ^{1}H and ^{31}P NMR features (223−333 K; δ ^{31}P ca. 44) and which has thus far resisted crystallization. Alternatively, treatment of **1** with K_2CO_3 in CH_3CN led to the consumption of **1** along with the formation of one major product ($\mathbf{3\cdot CH_3CN}$, >90% on the basis of ^{31}P NMR data). Upon workup, $\mathbf{3\cdot CH_3CN}$ was obtained as analytically pure, brown crystals in 41% isolated yield. Combustion analysis, NMR, and X-ray diffraction data (Figure 2) all support the identification of this product as the unusual tripodal κ^3-P,S,N Ir-iminato species $\mathbf{3\cdot CH_3CN}$, in which the CH_3CN can be described as bridging the Lewis acidic Cp*Ir and Lewis basic indenide fragments of zwitterionic **3** (i.e., net M∧X′ cooperative reactivity). In keeping with such a formulation, the normally linear acetonitrile moiety adopts a bent structure ($N-C27-C28$ = 121.6(2)°) in $\mathbf{3\cdot CH_3CN}$, with the sum of the angles at C27 (359.9°) being consistent with a trigonal planar geometry. Such crystallographically characterized Ir-iminato complexes are rare,[18] and there is scant precedent for net metal−ligand cooperative activation of nitriles involving a mononuclear Cp*Ir complex.[19] While the aforementioned green solid that is formed upon treatment of **1** or $[\mathbf{2}]^+\mathbf{X}^-$ with

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Table 1. Crystallographic Data for **1**, **[2·CO]⁺OTf⁻**, **3·CH₃CN**, **7**, and **11**

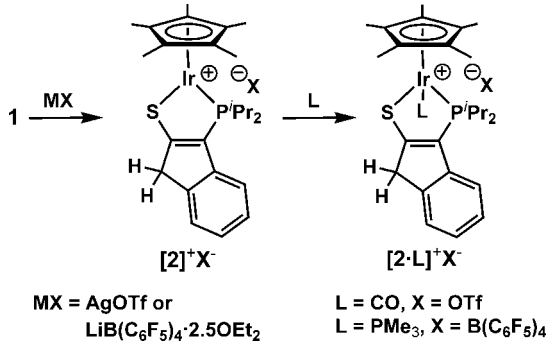
	1	[2·CO]⁺OTf⁻	3·CH₃CN	7	11
empirical formula	$C_{25}H_{35}ClIrPS$	$C_{27}H_{35}F_3IrO_4PS_2$	$C_{27}H_{37}NIrPS$	$C_{51}H_{41}BF_{20}IrPS$	$C_{37}H_{46}IrPSSi$
formula weight	626.21	767.84	630.81	1299.88	774.06
crystal dimensions	0.64 × 0.57 × 0.33	0.34 × 0.22 × 0.07	0.40 × 0.40 × 0.23	0.33 × 0.23 × 0.11	0.24 × 0.20 × 0.18
crystal system	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1$	$Pna2_1$
a (Å)	8.4287(9)	9.1759(8)	8.0173(5)	11.2171(9)	16.2760(12)
b (Å)	18.747(2)	10.9655(8)	19.3970(13)	12.4867(10)	9.3991(7)
c (Å)	15.3597(17)	15.4658(9)	16.3635(11)	18.0424(14)	22.3078(16)
α (deg)	90	80.643(2)	90	90	90
β (deg)	91.1555(15)	75.359(2)	95.6603(9)	103.9330(10)	90
γ (deg)	90	80.987(2)	90	90	90
V (Å^3)	2426.5(5)	1474.66(19)	2532.3(3)	2452.7(3)	3412.6(4)
Z	4	2	4	2	4
ρ_{calcd} (g cm^{-3})	1.714	1.729	1.655	1.760	1.507
μ (mm^{-1})	5.774	4.773	5.433	2.910	4.080
range of transmission	0.2516−0.1194	0.7165−0.2878	0.3680−0.2199	0.7402−0.4468	0.5271−0.4410
2θ limit (deg)	54.90	55.06	54.98	54.98	54.96
index ranges	$-10 \le h \le 10$ $-24 \le k \le 24$ $-19 \le l \le 19$	$-11 \le h \le 11$ $-13 \le k \le 14$ $-0 \le l \le 20$	$-10 \le h \le 10$ $-25 \le k \le 25$ $-21 \le l \le 21$	$-14 \le h \le 14$ $-16 \le k \le 16$ $-23 \le l \le 23$	$-21 \le h \le 21$ $-12 \le k \le 12$ $-28 \le l \le 28$
total data collected	21057	12226	21919	20942	28450
ind reflections	5539	12226	5811	11110	7816
R_{int}	0.0261	na	0.0188	0.0221	0.0331
obd reflections	5311	11389	5416	10394	7138
data/restraints/params	5539/0/267	12226/0/349	5811/0/286	11110/1/685	7816/1/379
goodness-of-fit	1.169	1.027	1.097	0.921	1.028
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0245	0.0378	0.0203	0.0244	0.0274
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0617	0.0945	0.0512	0.0548	0.0657

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **1**, **[2·CO]⁺OTf⁻**, **3·CH₃CN**, **7**, and **11**

	1[a]	[2·CO]⁺OTf⁻[b]	3·CH₃CN[c]	7[d]	11[e]
Ir−P	2.3220(8)	2.350(1)	2.2725(6)	2.2787(9)	2.267(1)
Ir−S	2.3566(9)	2.378(1)	2.3787(6)	2.2912(8)	2.345(1)
S−Cind	1.718(3)	1.734(5)	1.730(3)	1.759(4)	1.729(4)
^{i}Pr$_2$P−Cind	1.797(3)	1.792(4)	1.875(3)	1.817(4)	1.797(4)
C1−C2	1.516(4)	1.519(6)	1.531(3)	1.496(5)	1.503(6)
C2−C3	1.358(4)	1.351(6)	1.359(4)	1.350(5)	1.367(5)

[a] Ir−Cl 2.4021(9). [b] *Ir–C*O 1.887(5); Ir*C*−*O* 1.119(5). [c] Ir−N 2.053(2); N−C27 1.270(3); C1−C27 1.543(4); C27−C28 1.509(4); N−C27−C28 121.6(2); N−C27−C1 120.1(2); C1−C27−C28 118.2(2). [d] *S*−*C*H$_2$CH$_3$ 1.836(4). [e] Si−*C*ind 1.900(4).

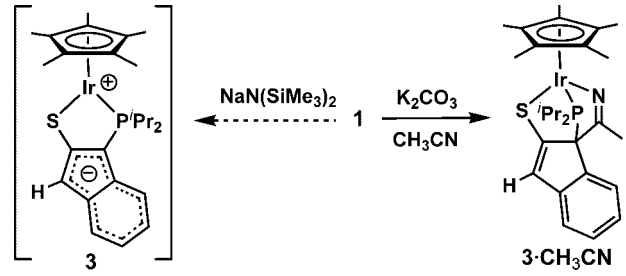
Scheme 1



$NaN(SiMe_3)_2$ behaves as a source of **3** in generating **3·CH₃CN** or **11** (*vide infra*) as the major product (^{31}P NMR) upon addition of CH_3CN or Ph_2SiH_2 (respectively), we are presently unable to unequivocally confirm the identity (or purity) of this green solid as being the desired zwitterionic species **3**.

Probing the Reactivity of 3·CH₃CN with CO and PMe₃. The rapid formation of **3·CD₃CN** and 1 equiv of free CH_3CN upon addition of CD_3CN (5 equiv, 15 min) to a solution of **3·CH₃CN** in C_6D_6 confirmed the lability of the coordinated acetonitrile

Scheme 2



ligand in **3·CH₃CN** (^{1}H NMR). In viewing **3·CH₃CN** as a potentially reactive source of the zwitterion **3**, we sought to explore further the L-donor substrate activation chemistry of **3·CH₃CN** to allow for comparisons to be made with the related

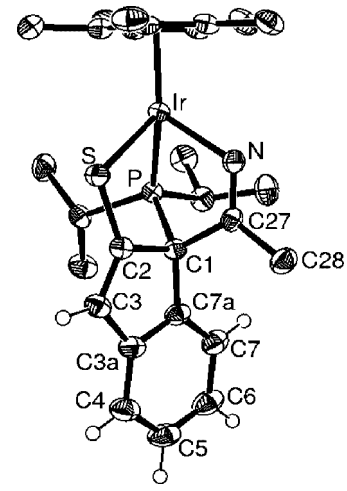
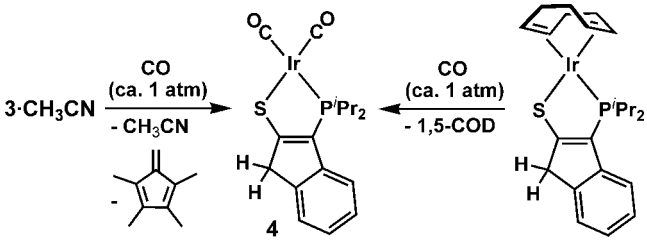


Figure 2. ORTEP diagram for **3·CH₃CN** shown with 50% ellipsoids; selected H-atoms have been omitted for clarity.

Scheme 3



cations $[2]^+X^-$. Unexpected reactivity was observed between $3\cdot CH_3CN$ and CO (Scheme 3). Unlike the clean formation of $[2\cdot CO]^+OTf^-$ that occurred upon treatment of $[2]^+OTf^-$ with CO (*vide supra*), exposure of $3\cdot CH_3CN$ to an atmosphere of CO did not afford the anticipated adduct $3\cdot CO$; rather, NMR analysis of the reaction mixture revealed the clean formation of (κ^2-3-P^{i}Pr$_2$-2-S-indene)Ir(CO)$_2$ **4** and 1,2,3,4-tetramethylfulvene (1:1).[20] To confirm this structural assignment, compound **4** was prepared independently from (κ^2-3-P^{i}Pr$_2$-2-S-indene)Ir(COD) and CO. The formation of **4** in the reaction of $3\cdot CH_3CN$ with CO can be viewed as arising from net deprotonation of (η^5-C$_5$*Me*$_5$)Ir[21] by the indenide unit in **3** (or possibly $3\cdot CO$), followed by substitution of the coordinated 1,2,3,4-tetramethylfulvene by CO ligands. In contrast to the quantitative conversion of $3\cdot CH_3CN$ into **4**, treatment of **1** or $[2\cdot CO]^+OTf^-$ with NaN(SiMe$_3$)$_2$ followed by the introduction of an atmosphere of CO gave rise to a mixture of phosphorus-containing products in which **4** represented less than 50% of the reaction mixture (on the basis of ^{31}P NMR data). Whereas addition of PMe$_3$ to $[2]^+B(C_6F_5)_4^-$ afforded the isolable adduct $[2\cdot PMe_3]^+B(C_6F_5)_4^-$ (*vide supra*), under similar conditions, $3\cdot CH_3CN$ gave rise to a first-formed bis(phosphine)Ir product[22a] (ca. 75%, possibly corresponding to $3\cdot PMe_3$) that was observed to decompose to a mixture of phosphorus-containing products upon standing in solution or upon workup. Notably, treatment of $[2\cdot PMe_3]^+B(C_6F_5)_4^-$ with NaN(SiMe$_3$)$_2$ affords an as-yet-unidentified bis(phosphine)Ir product (^{31}P NMR)[22b] that differs from the first-formed product generated upon addition of PMe$_3$ to $3\cdot CH_3CN$ and which we have yet to isolate in pure form.

Net M−X Cooperative H−Si Bond Activation by $[2]^+B(C_6F_5)_4^-$. Intrigued by the differing L-donor substrate activation pathways exhibited by $[2]^+X^-$ and **3**, we turned our attention to the study of H−E bond activation chemistry mediated by these structurally related complexes. The activation of H−Si containing substrates was selected as an entry point for these investigations, given the propensity of coordinatively unsaturated Cp*Ir complexes to mediate unusual transformations of organosilanes.[12a,b] Treatment of $[2]^+OTf^-$ with Ph_2SiH_2 resulted in the net loss of $Ph_2Si(OTf)H$ to give **5** in 44% isolated yield (Scheme 4). In contrast, the analogous reaction involving $[2]^+B(C_6F_5)_4^-$ proceeded via H−Si addition across Ir−S (i.e., net M−X cooperative reactivity) to give the cationic hydrido species **6a** (68% isolated yield), which features a newly established S−SiHPh$_2$ linkage. Although, under similar conditions employing PhSiH$_3$, the related addition product **6b** was obtained in 77% isolated yield, an intractable mixture of products was generated upon addition of Ph$_3$SiH to $[2]^+B(C_6F_5)_4^-$. While to the best of our knowledge net H−Si addition across an M−SR linkage to give an isolable mononuclear addition product has not been reported previously in the literature, the related activation of H$_2$ by dinuclear complexes featuring an M$_2$S$_2$ core (e.g., M = Rh,[23] Ir[24]) is known. No reaction was observed (^{1}H and ^{31}P NMR) upon exposure of $[2]^+X^-$ to H$_2$ (ca. 1 atm) at ambient temperature over the course of five days. Interestingly, while $[2]^+X^-$ proved unreactive toward diethyl ether, the H−Si addition product **6a** effected net C−O bond cleavage in this substrate with net loss of $Ph_2Si(OEt)H$ over the course of 24 h at ambient temperature (in the absence of spectroscopically observable intermediates), thereby affording the cationic Ir−S−Et complex **7** in 77% isolated yield (Scheme 5). An ORTEP[15] diagram for **7** is presented in Figure 3. The structural features of **7** can be compared with those of Cp*(H)Ir(PMe$_3$)(S^{t}Bu), the only closely

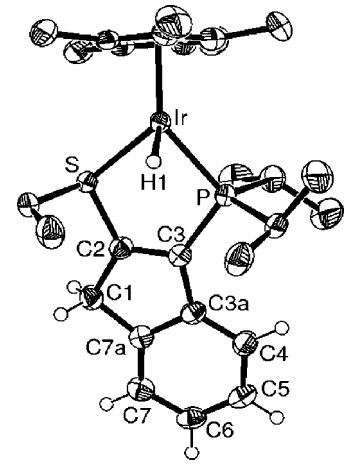
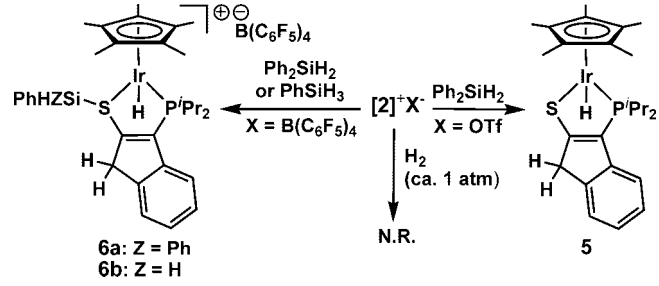
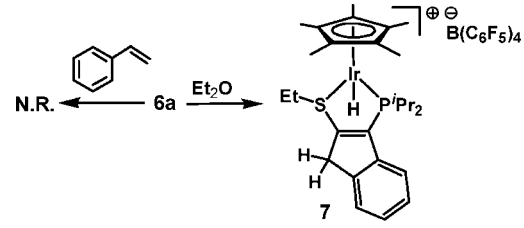


Figure 3. ORTEP diagram for **7** shown with 50% ellipsoids; selected H-atoms and the borate counteranion have been omitted for clarity.

Scheme 4

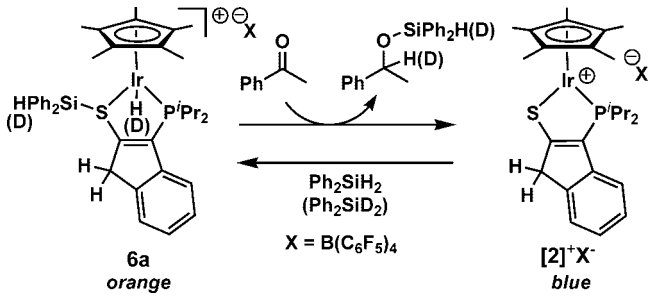


Scheme 5



(20) The 1,2,3,4-tetramethylfulvene byproduct was identified by comparison to published spectral data: Hashimoto, H.; Tobita, H.; Ogino, H. *Organometallics* **1993**, *12*, 2182.
(21) Glueck, D. S.; Bergman, R. G. *Organometallics* **1990**, *9*, 2862.
(22) (a)^{31}P{^{1}H} NMR ($CDCl_3$): δ 25.0 (d, $^2J_{PP}$ = 27.9 Hz),−37.7 (d, $^2J_{PP}$ = 27.9 Hz). (b)^{31}P{^{1}H} NMR (CH_2Cl_2): δ 34.1 (d, $^2J_{PP}$ = 28.8 Hz),−40.8 (d, $^2J_{PP}$ = 28.0 Hz).
(23) Ienco, A.; Calhorda, M. J.; Reinhold, J.; Reineri, F.; Bianchini, C.; Peruzzini, M.; Vizza, F.; Mealli, C. *J. Am. Chem. Soc.* **2004**, *126*, 11954, and references cited therein.
(24) Linck, R. C.; Pafford, R. J.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 8856, and references cited therein.

Scheme 6



related Cp*Ir complex for which crystallographic data have been reported.[14] We are presently unable to comment definitively regarding the mechanistic details of the conversion of **6a** into **7**; while such reactivity may arise from S_N2 attack of diethyl ether on silicon in **6a**, alternative reaction pathways involving silylium ion that could be transiently generated upon loss of $[Ph_2SiH]^+BAr_4^-$ from **6a** cannot be discounted.[25] Notably, the mixture of $Ph_2Si(OTf)H$ and **5** that is apparently formed upon treatment of $\mathbf{[2]^+OTf^-}$ with Ph_2SiH_2 (Scheme 4) was not observed to react with diethyl ether under similar conditions (^1H and ^{31}P NMR).

Stoichiometric Silane Transfer from 6a to Acetophenone. Toste and co-workers[26] have reported that $(PPh_3)_2Re(O)_2I$ catalyzes the hydrosilylation of carbonyl compounds by way of a previously unprecedented mechanism involving net H−Si addition across a Re═O linkage. Given the conceptual relationship between this elementary reaction step and the stoichiometric H−Si addition of Ph_2SiH_2 to $\mathbf{[2]^+B(C_6F_5)_4^-}$ giving **6a**, and in light of the apparent ability of **6a** to effect the silylation of diethyl ether (*vide supra*), we sought to assess the ability of **6a** to transfer the bound fragments of the activated silane to unsaturated substrates. While no reaction was observed visually or by use of NMR methods upon exposure of **6a** to excess styrene (10 equiv; Scheme 5), treatment of an initially orange solution of **6a** (ca. 0.05 mmol) in CH_2Cl_2 (2 mL) with excess acetophenone (0.26 mmol) resulted in a color change of the solution to dark blue over the course of several minutes at ambient temperature, in keeping with the formation of $\mathbf{[2]^+B(C_6F_5)_4^-}$ (Scheme 6). This qualitative assessment was substantiated on the basis of ^{31}P NMR data obtained after a total reaction time of 0.25 h, which confirmed the consumption of **6a** with concomitant formation of $\mathbf{[2]^+B(C_6F_5)_4^-}$ as the major product (>85% on the basis of ^{31}P NMR). Subsequent addition of Ph_2SiH_2 to this reaction mixture led to the complete transformation of $\mathbf{[2]^+B(C_6F_5)_4^-}$ back into **6a** (^{31}P NMR). In an effort to monitor the fate of the H−Si fragment in these reactions, $\mathbf{[2]^+B(C_6F_5)_4^-}$ was treated with Ph_2SiD_2, affording **6a**-d_2, in which deuterium incorporation was observed only at the Si-*H* and Ir-*H* positions. In keeping with a process involving net transfer of Ir-*D* and S-*SiDPh*$_2$ fragments, the addition of acetophenone to **6a**-d_2 produced exclusively PhMeC(D)-$(OSiPh_2D)$ on the basis of NMR data. While these experiments unequivocally confirm the ability of **6a** to transfer Ph_2SiH_2 to acetophenone in a stoichiometric fashion, we have also observed that an *in situ* generated mixture of $Ph_2Si(OTf)H$ and **5** (Scheme 4) is also transformed cleanly into $PhMeC(H)(OSiPh_2H)$ and $\mathbf{[2]^+OTf^-}$ upon treatment with acetophenone (^1H and ^{31}P NMR). On the basis of these observations, and in the absence of further mechanistic data, we are presently unable to comment definitively regarding the role of the sulfur atom participation in acetophenone hydrosilylation reactions involving **6a** and/or mixtures of $Ph_2Si(OTf)H$ and **5**.

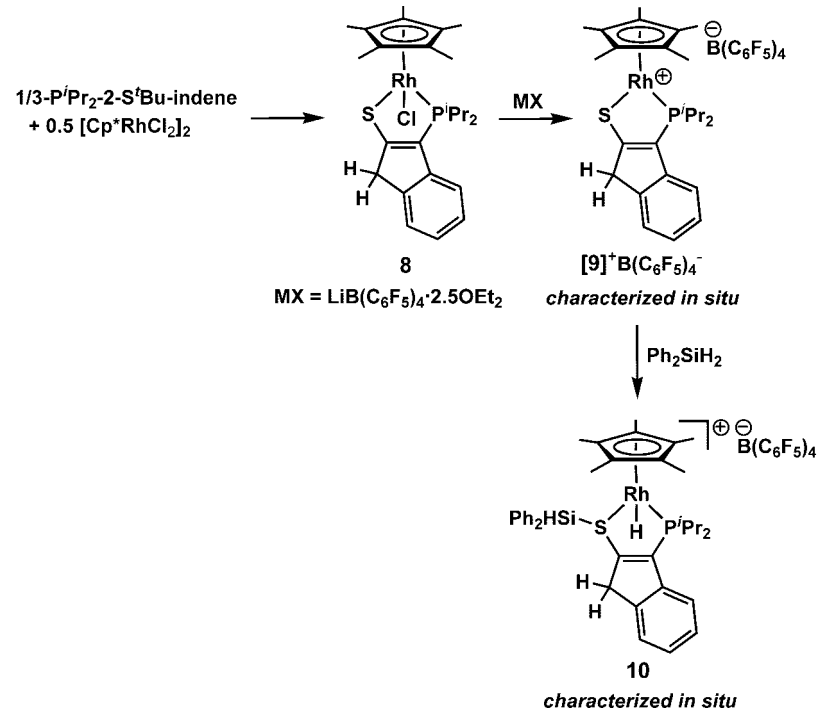
Formation of Rh Complexes and Ketone Hydrosilylation Catalysis. Having established that Ph_2SiH_2 adds cleanly to the Ir−S linkage in $\mathbf{[2]^+B(C_6F_5)_4^-}$ and that the resulting adduct **6a** can transfer the activated silane to acetophenone, the ability of $\mathbf{[2]^+B(C_6F_5)_4^-}$ to catalyze the hydrosilylation of acetophenone with Ph_2SiH_2 was examined. However, only modest conversions (<20%, on the basis of GC-FID data) were achieved under a variety of conditions employing 2.0 mol% $\mathbf{[2]^+B(C_6F_5)_4^-}$ (prepared *in situ* from 2.0 mol% **1** and 2.0 mol% $LiB(C_6F_5)_4\cdot 2.5Et_2O$). In the pursuit of an analogous system that might offer improved catalytic activity, we turned our attention to the preparation of Cp*Rh derivatives of 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene (Scheme 7). Treatment of 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene with 0.5 equiv of $[Cp^*RhCl_2]_2$ afforded $Cp^*Rh(Cl)(\kappa^2$-3-P^{i}Pr$_2$-2-S-indene) (**8**) as an analytically pure, light brown solid in 94% isolated yield. In keeping with the stoichiometric reactions observed in the Ir system, combination of **8** and $LiB(C_6F_5)_4\cdot 2.5Et_2O$ resulted in the consumption of **8** along with the formation of a dark green solution of the desired coordinatively unsaturated cation $\mathbf{[9]^+B(C_6F_5)_4^-}$ (ca. 75% on the basis of ^{31}P NMR data), which in turn was transformed into an orange solution of **10** (ca. 80% on the basis of ^{31}P NMR data) upon addition of Ph_2SiH_2 to the reaction mixture. However, we have thus far not been able to isolate $\mathbf{[9]^+B(C_6F_5)_4^-}$ or **10** in analytically pure form, and efforts to explore the ability of **10** to transfer silane to acetophenone in a stoichiometric fashion (as was observed for the Ir analogue **6a**; Scheme 6) have been thwarted by the apparent instability of **10**. Furthermore, attempts to prepare Rh analogues of **3** or $\mathbf{3\cdot CH_3CN}$ by using similar protocols resulted in complex reaction mixtures from which no pure materials could be isolated.

In a preliminary catalytic survey of the ambient temperature hydrosilylation of acetophenone employing 2.0 mol% $\mathbf{[9]^+B(C_6F_5)_4^-}$ (prepared *in situ* from a mixture of 2.0 mol% **8** and 2.0 mol% $LiB(C_6F_5)_4\cdot 2.5Et_2O$), efficient conversion (^1H NMR) to the corresponding silyl ether was achieved by using either Ph_2SiH_2 (85%) or $PhSiH_3$ (98%); by comparison, negligible conversion (<5%) was noted for analogous reactions employing Ph_3SiH. The inability of $\mathbf{[9]^+B(C_6F_5)_4^-}$ to catalyze the reduction of acetophenone employing Ph_3SiH may correlate with the complex stoichiometric reactivity observed between the Ir analogue $\mathbf{[2]^+B(C_6F_5)_4^-}$ and this tertiary silane (*vide supra*). Consistent with the stoichiometric reactivity observed for **6a**-d_2 (*vide supra*), the catalytic reduction of acetophenone mediated by $\mathbf{[9]^+B(C_6F_5)_4^-}$ and employing Ph_2SiD_2 produced exclusively $PhMeC(D)(OSiPh_2D)$. Encouraged by these preliminary results, the ability of *in situ* prepared $\mathbf{[9]^+B(C_6F_5)_4^-}$ to catalyze the hydrosilylation of various ketone substrates using $PhSiH_3$ was examined (THF, 5 h, ambient temperature; Table 3); for convenience, the progress of each hydrosilylation reaction was monitored through analysis of the product mixture obtained following hydrolytic workup (eq 2). In keeping with the preliminary catalytic survey, the reduction of acetophenone proceeded with near quantitative conversion (98%, entry 1) on the basis of GC-FID data, thereby enabling the isolation of $PhMeC(H)(OH)$ in 89% yield. Furthermore, *in situ* prepared

(25) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090, and references cited therein.

(26) (a) Nolin, K. A.; Krumper, J. R.; Pluth, M. D.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 14684. (b) Kennedy-Smith, J. J.; Nolin, K. A.; Gunterman, H. P.; Toste, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 4056.

Scheme 7



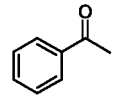
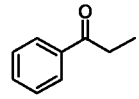
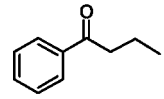
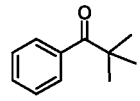
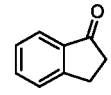
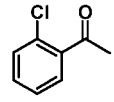
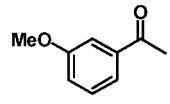
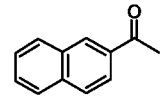
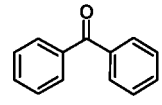
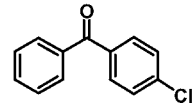
[9]$^+$B(C$_6$F$_5$)$_4^-$ proved effective in reducing a range of other aryl alkyl ketones (entries 2−5), functionalized acetophenones (entries 6−8), and diaryl ketones (entries 9 and 10).

Net M∧X′ Cooperative H−Si Bond Activation Employing 3·CH$_3$CN. Having documented the addition of H−Si fragments to M−S linkages in **[2]$^+$B(C$_6$F$_5$)$_4^-$** and **[9]$^+$B(C$_6$F$_5$)$_4^-$**, we sought to explore if the indenide fragment in the structurally related Ir zwitterion **3** might provide access to alternative net M∧X′ cooperative reaction pathways in σ-bond activation chemistry. Whereas no reaction was observed upon exposure of **[2]$^+$X$^-$** to H_2 (ca. 1 atm) at ambient temperature, reactions conducted under similar conditions employing **3·CH$_3$CN** (as a source of **3**) produced a complex mixture of phosphorus-containing products (^{31}P NMR). Conversely, treatment of **3·CH$_3$CN** with Ph_2SiH_2 resulted in the liberation of CH_3CN (^{1}H NMR) along with the quantitative formation of **11** (64% isolated yield; Scheme 8). Notably, the formation of **11** corresponds to heterolytic H−Si bond activation, involving net addition of H^- and Ph_2HSi^+ fragments to Ir and indenide (respectively) in the unobserved zwitterion **3**. Compound **11** is formed as a mixture of two diastereomers (**11a**,**b**, ca. 3:1) that arise from the stereogenic nature of C1 and Ir, and a similar **11a**,**b** mixture can be prepared via addition of NaN(SiMe$_3$)$_2$ to a solution of **1** and Ph_2SiH_2 (79% isolated yield). Both diastereomers of **11** are detected early on in each synthesis in the absence of other phosphorus-containing products (^{31}P NMR), and their relative proportions in the final reaction mixture do not change substantially, even upon heating. While the connectivity in **11a**,**b** was determined initially on the basis of NMR data, single crystals obtained from the reaction mixture that were subjected to X-ray diffraction analysis correspond to the diastereomer of **11** whereby the Ir−H and C1−SiHPh$_2$ groups adopt an *anti*-relationship with regard to the plane defined by the indene backbone of **11** (Figure 4). Reactions employing Ph_2SiD_2 afforded **11**-d_2, in which exclusive deuterium incorporation at the Si-*H* and Ir-*H* positions of both diastereomers was noted, thereby precluding more complex mechanistic pathways that would lead to scrambling of the isotopic label (e.g., C−H/Si-D exchange). Upon treatment of the cationic H−Si addition product **6a** with NaN(SiMe$_3$)$_2$, **11a**,**b** is generated as the major phosphorus-containing species (ca. 75%, ^{31}P NMR). This result supports the possible intermediacy of **6a′** (the conjugate base of **6a**; Scheme 8) as an unobserved first-formed addition product in the reaction of Ph_2SiH_2 with putative **3**, which in turn could rearrange to **11a**,**b** via net transfer of Ph_2HSi^+ from sulfur to the indenide backbone. On the basis of these and other observations, we are currently conducting mechanistic experiments directed toward ascertaining if the H−Si bond cleavage process leading to **11a**,**b** involves the net addition of silane across a single molecule of **3**. Unlike the case of **6a**, no reaction was observed between **11a**,**b** and acetophenone, suggesting that the newly formed Si−C$_{indenide}$ linkage in such complexes must be rendered more labile (via ancillary ligand modification) in order to allow for the incorporation of such net M∧X′ cooperative H−Si activation steps into productive catalytic cycles.

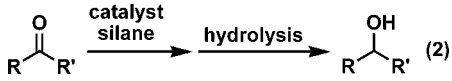
Summary and Conclusions

In summary, we have described our efforts to prepare and characterize a previously unreported class of coordinatively unsaturated cationic (**[2]$^+$X$^-$**) and formally zwitterionic (**3**) Cp*Ir(κ^2-P,S) complexes that feature structurally analogous monoanionic κ^2-P^{i}Pr$_2$,S-indene and dianionic κ^2-P^{i}Pr$_2$,S-indenide ancillary ligands, respectively. The versatility of donor-functionalized indene ancillary ligands in allowing for the selection of divergent metal−ligand cooperativity pathways (simply by ancillary ligand deprotonation) in the activation of small molecule substrates was demonstrated in comparative reactivity studies involving **[2]$^+$X$^-$** and putative **3**. In this regard, the cationic complex **[2]$^+$B(C$_6$F$_5$)$_4^-$** was observed to activate organosilanes via the first well-documented H−Si addition across an M−SR linkage (i.e., net M−X cooperative reactivity); the resulting adduct proved capable of effecting the stoichiometric silylation of diethyl ether via C−O bond cleavage and

Table 3. Rh-Catalyzed Hydrosilylation of Ketones[a]

Entry	Substrate	Conversion (%)[b]
1		98(89[c])
2		98
3		98
4		96
5		83
6		99
7		98
8		95
9		93
10		95

[a] Reaction conditions: 0.2 mmol of ketone, 0.3 mmol of $PhSiH_3$, 2.0 mol % **8**, and 2.0 mol % $LiB(C_6F_5)_4 \cdot 2.5Et_2O$ in 2 mL of THF at ambient temperature for 5 h. [b] Conversion to the secondary alcohol determined on the basis of GC-FID data. [c] Isolated yield of 89% (>95% purity on the basis of ^1H NMR data) when the reaction was conducted on a 0.8 mmol ketone scale.



of selectively transferring the bound fragments of the activated silane to acetophenone. Related cationic Cp*Rh complexes exhibited similar stoichiometric H−Si bond activation chemistry and in turn proved capable of mediating the catalytic hydrosilylation of various ketone substrates. The possible involvement of H−Si addition to M−SR as an elementary step in this catalysis is intriguing, in that such a transformation is without precedent in metal-mediated hydrosilylation chemistry. Conversely, the unusual stoichiometric reactivity of putative **3** with CH_3CN or Ph_2SiH_2 can be viewed as resulting from the dual action of the Lewis acidic Cp*Ir fragment and the Lewis basic 10π-electron indenide unit within this formally charge-separated

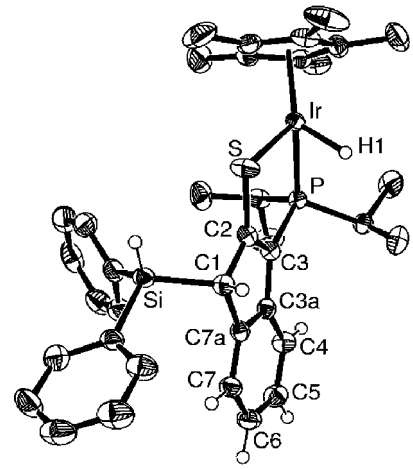
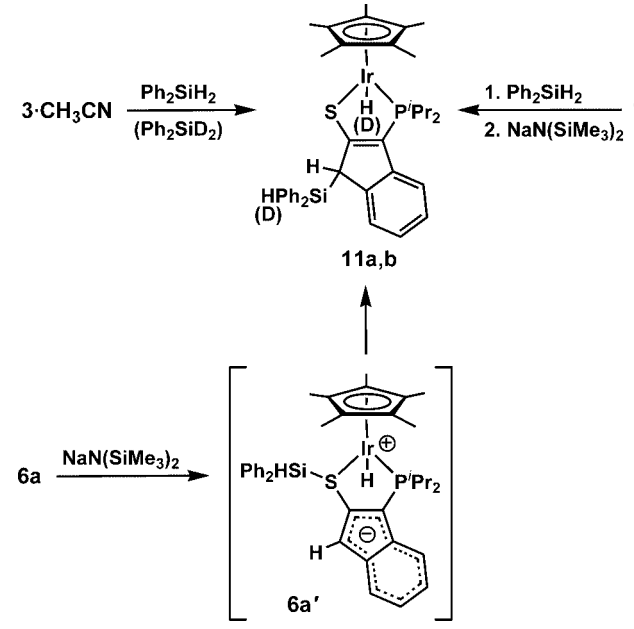


Figure 4. ORTEP diagram for one diastereomer of **11** shown with 50% ellipsoids; selected H-atoms have been omitted for clarity.

Scheme 8



zwitterion (i.e., net M∧X′ cooperative reactivity). Building on these and other encouraging observations, we are currently examining in greater detail the utility of donor-functionalized indene and indenide ancillary ligands in the development of selective new stoichiometric and catalytic substrate activation chemistry that is enabled by novel metal−ligand cooperative behavior.

Experimental Section

General Considerations. All manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Celite (Aldrich) was oven-dried for 5 days and then evacuated for 24 h prior to use. The nondeuterated solvents dichloromethane, diethyl ether, tetrahydrofuran, benzene, toluene, and pentane were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system purchased from mBraun Inc. Dichloromethane, tetrahydrofuran, and diethyl ether were purified over two alumina-packed columns, while benzene, toluene,

and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. Purification of CH_3CN was achieved by refluxing over CaH_2 for 4 days under dinitrogen, followed by distillation. $CDCl_3$ (Aldrich) was degassed by using three repeated freeze−pump−thaw cycles, dried over CaH_2 for 7 days, distilled *in vacuo*, and stored over 4 Å molecular sieves for 24 h prior to use. Benzene-d_6, tetrahydrofuran-d_8, and methylene chloride-d_2 (Cambridge Isotopes) were degassed by using three repeated freeze−pump−thaw cycles and then dried over 4 Å molecular sieves for 24 h prior to use. All solvents used within the glovebox were stored over activated 4 Å molecular sieves. The ligand precursor 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene was prepared by using literature procedures[27] and was dried *in vacuo* for 24 h prior to use. $NaN(SiMe_3)_2$ (Aldrich), anhydrous K_2CO_3 (Aldrich), $[(COD)IrCl]_2$ (Strem), $[Cp^*IrCl_2]_2$ (Strem), $[Cp^*RhCl_2]_2$ (Strem), and $LiB(C_6F_5)_4\cdot 2.5Et_2O$ (Boulder Scientific) were dried *in vacuo* for 24 h prior to use (COD = η^4-1,5-cyclooctadiene; Cp* = η^5-C_5Me_5). Ph_3SiH, Ph_2SiH_2, and $PhSiH_3$ (Gelest, shipped under argon) were dried over 4 Å molecular sieves for 24 h prior to use; Ph_2SiD_2 was prepared via reduction of Ph_2SiCl_2 with $LiAlD_4$ and was dried over 4 Å molecular sieves for 24 h prior to use. All ketones were obtained from commercial sources in high purity; solid ketones were dried *in vacuo* for a minimum of 12 h prior to use, while liquid ketones were degassed by use of three repeated freeze−pump−thaw cycles. All other reagents were used as received. ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, 99.4, and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of $SiMe_4$ (for ^{1}H, ^{13}C, and ^{29}Si) or 85% H_3PO_4 in D_2O (for ^{31}P). ^{1}H and ^{13}C NMR chemical shift assignments are made on the basis of data obtained from ^{13}C-DEPT, ^{1}H−^{1}H COSY, ^{1}H−^{13}C HSQC, and ^{1}H−^{13}C HMBC NMR experiments, and ^{13}C resonances associated with $B(C_6F_5)_4^-$ and $SO_3CF_3^-$ (OTf^-) were not assigned. ^{29}Si NMR chemical shift assignments are given on the basis of data obtained from ^{1}H−^{29}Si HMQC NMR experiments. UV−vis data were obtained using a Varian Cary 100 Bio spectrometer within a 10 mm cell. IR data were collected on a Bruker VECTOR 22 FT-IR instrument using neat CH_2Cl_2 solutions of the target compound that were evaporated on NaCl plates. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada.

Synthesis of (κ^2-3-P^{i}Pr$_2$-2-S-indene)Ir(COD). A solution of 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene (0.12 g, 0.38 mmol) in CH_2Cl_2 (1 mL) was added dropwise to a magnetically stirred mixture of $[(COD)IrCl]_2$ (0.13 g, 0.19 mmol) and CH_2Cl_2 (2 mL), causing an immediate darkening of the solution to dark red. The reaction mixture was magnetically stirred at ambient temperature for 0.25 h, followed by treatment with $Na(SiMe_3)_2$ (0.070 g, 0.38 mmol) and continued magnetic stirring for 20 h. Subsequent removal of the solvent and other volatiles *in vacuo* afforded a dark red solid that was extracted into benzene followed by filtration through Celite and removal of the solvent and volatiles *in vacuo*. The residual solid was then washed with pentane (3 × 2 mL) and dried *in vacuo*, affording (κ^2-3-P^{i}Pr$_2$-2-S-indene)Ir(COD) as an analytically pure, red solid (0.13 g, 0.23 mmol, 61%). Anal. Calcd for $C_{23}H_{32}IrPS$: C, 49.00; H, 5.72; N, 0.00. Found: C, 49.11; H, 5.62; N, <0.3. ^{1}H NMR ($CDCl_3$): δ 7.27 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C4−H or C7−H), 7.22 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4−H or C7−H), 7.17 (t, $^3J_{HH}$ = 8.0 Hz, 1H, C5−H or C6−H), 7.03 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 4.81 (m, 2H, COD), 3.93 (m, 2H, COD), 3.67 (s, 2H, C1(H)$_2$), 3.01 (m, 2H, P(C*H*Me$_a$Me$_b$)), 2.31 (m, 2H, COD), 2.14 (m, 2H, COD), 1.97 (m, 2H, COD), 1.82 (m, 2H, COD), 1.34 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.5 Hz, 6H, P(CH*Me$_a$*Me$_b$)), 1.27 (d of d, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe$_a$*Me$_b$*)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 182.5 (quaternary), 149.5 (quaternary), 143.7 (quaternary), 129.9 (quaternary), 126.0 (C5 or C6), 124.5 (C4 or C7), 122.2 (C5 or C6), 118.4 (C4 or C7), 83.8 (d, $^2J_{PC}$ = 12.5 Hz, CH (COD)), 59.7 (CH (COD)), 42.2 (d, $^3J_{PC}$ = 13.1 Hz, C1), 33.8 (CH$_2$ (COD)), 29.5 (CH$_2$ (COD)), 25.8 (d, $^1J_{PC}$ = 28.8 Hz, P(*C*HMe$_a$Me$_b$)), 19.6 (P(CH*Me$_a$*Me$_b$)), 18.3 (d, $^2J_{PC}$ = 3.0 Hz, P(CHMe$_a$*Me$_b$*)). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 45.9.

Synthesis of 1. To a magnetically stirred mixture of $[Cp^*IrCl_2]_2$ (0.25 g, 0.32 mmol) and CH_2Cl_2 (5 mL) was added a solution of 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene (0.20 g, 0.64 mmol) in CH_2Cl_2 (1 mL). After 20 h of magnetic stirring at ambient temperature, ^{31}P NMR analysis of the reaction mixture confirmed the consumption of the starting material and the presence of a single new phosphorus-containing product (**1**). The solvent and other volatiles were removed *in vacuo*, affording an orange solid that was washed with pentane (2 × 2 mL). Removal of the solvent from the residual solid afforded **1** as an analytically pure, orange solid (0.38 g, 0.62 mmol, 97%). Anal. Calcd for $C_{25}H_{35}ClIrPS$: C, 47.95; H, 5.63; N, 0.00. Found: C, 47.91; H, 5.49; N, <0.3. ^{1}H NMR ($CDCl_3$): δ 7.18 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4 or C7), 7.14 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C4 or C7), 7.12 (t, $^3J_{HH}$ = 7.0 Hz, 1H, C5 or C6), 6.97 (d of t, $^3J_{HH}$ = 7.0 Hz, J = 1.0 Hz, C5 or C6), 3.67−3.51 (m, 2H, C1(H)$_2$), 3.46 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.18 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.82 (d, J = 2.0 Hz, 15H, C_5Me_5), 1.51 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 1.38 (d of d, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.36 (d of d, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 1.00 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 179.4 (d, $^2J_{PC}$ = 22.8 Hz, C2), 148.6 (d, J_{PC} = 7.5 Hz, C3a or C7a), 145.1 (d, J_{PC} = 4.2 Hz, C7a or C3a), 128.0 (d, $^1J_{PC}$ = 60.1 Hz, C3), 126.2 (C5 or C6), 124.2 (C6 or C5), 121.7 (C4 or C7), 117.6 (C7 or C4), 92.5 (d, $^2J_{PC}$ = 2.8 Hz, *C*$_5$Me$_5$), 41.9 (d, $^3J_{PC}$ = 10.6 Hz, C1), 30.7 (d, $^1J_{PC}$ = 28.8 Hz, P(*C*HMe$_c$Me$_d$)), 25.6 (d, $^1J_{PC}$ = 35.6 Hz, P(*C*HMe$_a$Me$_b$)), 20.3 (d, $^2J_{PC}$ = 1.4 Hz, P(CH*Me$_a$*Me$_b$)), 20.1 (d, $^2J_{PC}$ = 6.4 Hz, P(CH*Me$_c$*Me$_d$)), 19.8 (d, $^2J_{PC}$ = 5.7 Hz, P(CHMe$_a$*Me$_b$*)), 18.1 (d, $^2J_{PC}$ = 1.6 Hz, P(CHMe$_c$*Me$_d$*)), 9.1 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 32.9. Crystals suitable for X-ray crystallographic analysis were grown by vapor diffusion of pentane into a concentrated solution of **1** in benzene at ambient temperature.

Synthesis of [2]$^+$OTf$^-$. To a magnetically stirred solution of **1** (0.029 g, 0.047 mmol) in CH_2Cl_2 (2 mL) was added solid AgOTf (0.012 g, 0.047 mmol), which effected an immediate color change from orange to dark blue, accompanied by the formation of precipitate. The blue solution was magnetically stirred for 0.5 h; ^{31}P NMR analysis of the reaction mixture showed complete consumption of **1** and the presence of a single new phosphorus-containing product ([**2**]$^+$**OTf**$^-$). The precipitate was then removed by filtration through Celite. Removal of the solvent and other volatiles afforded a dark blue solid that was triturated with pentane (2 × 2 mL) followed by removal of the pentane layer by use of a Pasteur pipet. Residual pentane and other volatiles were removed *in vacuo*, affording [**2**]$^+$**OTf**$^-$ as an analytically pure, dark blue solid (0.028 g, 0.037 mmol, 78%). Anal. Calcd for $C_{26}H_{35}F_3IrO_3PS_2$: C, 42.20; H, 4.77; N, 0.00. Found: C, 42.12; H, 4.69; N, <0.3. ^{1}H NMR (CD_2Cl_2): δ 7.44 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4−H or C7−H), 7.39 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4−H or C7−H), 7.33 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 7.28 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 3.92 (s, 2H, C1(H)$_2$), 3.12 (br m, 2H, P(C*H*Me$_a$Me$_b$)), 1.95 (s, 15H, C_5Me_5), 1.29 (d of d, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CH*Me$_a$*Me$_b$)), 1.22 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe$_a$*Me$_b$*)). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 177.8 (quaternary), 150.2 (quaternary), 140.3 (quaternary), 126.5 (quaternary), 126.8 (C5 or C6), 125.3 (C5 or C6), 124.8 (C4 or C7), 119.2 (C4 or C7), 96.7 (*C*$_5$Me$_5$), 40.9 (d, J_{PC} = 11.4 Hz, C1), 23.8 (br m, P(*C*HMe$_a$Me$_b$)), 18.2 (P(CHMe$_a$*Me$_b$*)), 17.8 (d, $^2J_{PC}$ = 2.8 Hz, P(CH*Me$_a$*Me$_b$)), 10.4 (C$_5$*Me$_5$*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 64.9 (br s).

Synthesis of [2]$^+$B(C$_6$F$_5$)$_4^-$. A protocol similar to that described for the synthesis of [**2**]$^+$**OTf**$^-$ was employed, using **1** (0.039 g, 0.062 mmol) and solid $LiB(C_6F_5)_4\cdot 2.5Et_2O$ (0.054 g, 0.062 mmol; in place of AgOTf), thereby affording [**2**]$^+$**B(C$_6$F$_5$)$_4^-$** as an analytically pure, dark blue solid (0.065 g, 0.051 mmol, 82%). Anal. Calc for $C_{49}H_{35}BF_{20}IrPS$: C, 46.32; H, 2.78; N, 0.00. Found: C,

(27) Hesp, K. D.; McDonald, R.; Ferguson, M. J.; Schatte, G.; Stradiotto, M. *Chem. Commun.* **2008**, DOI: 10.1039/B6.

46.19; H, 3.00; N, <0.3. ^{1}H NMR (CD_2Cl_2): δ 7.47 (m, 1H, C4 or C7), 7.41 (m, 1H, C4 or C7), 7.36−7.30 (m, 2H, C5 and C6), 3.96 (d, J = 2.5 Hz, 2H, C1(H)$_2$), 3.11 (m, 2H, P(C*H*Me$_a$Me$_b$)), 1.94 (d, $^4J_{PH}$ = 1.5 Hz, 15H, C_5Me_5), 1.30 (d of d, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CH*Me$_a$*Me$_b$)), 1.20 (d of d, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe$_a$*Me$_b$*)). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 177.8 (d, $^2J_{PC}$ = 25.2 Hz, C2), 150.2 (d, J_{PC} = 10.1 Hz, C3a or C7a), 140.1 (d, J_{PC} = 37.7 Hz, C3a or C7a), 134.7 (d, $^1J_{PC}$ = 62.9 Hz, C3), 127.2 (C5 or C6), 125.8 (C4 or C7), 125.7 (C5 or C6), 120.5 (C4 or C7), 96.9 (C_5Me_5), 41.1 (d, $^3J_{PC}$ = 11.4 Hz, C1), 23.9 (d, $^1J_{PC}$ = 31.1 Hz, P(*C*HMe$_a$Me$_b$)), 18.3 (P(CHMe$_a$*Me$_b$*)), 18.0 (d, $^2J_{PC}$ = 1.8 Hz, P(CH*Me$_a$*Me$_b$)), 10.7 (C_5Me_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 65.2. UV−vis (THF): λ_{max} 569 (ε = 1.49 × 10^3), 673 (ε = 1.40 × 10^3).

Synthesis of [2·CO]$^+$OTf$^-$. Compound **[2]$^+$OTf$^-$** was prepared *in situ* by treatment of a solution of **1** (0.068 g, 0.11 mmol) in CH_2Cl_2 (2 mL) with solid AgOTf (0.028 g, 0.11 mmol), causing an immediate color change to dark blue accompanied by the formation of a precipitate. The reaction mixture was stirred at ambient temperature for 0.5 h followed by filtration through Celite to remove the precipitate. The resulting dark blue CH_2Cl_2 solution containing **[2]$^+$OTf$^-$** was transferred to a resealable flask and was degassed by use of three consecutive freeze−pump−thaw cycles, followed by backfilling with CO (ca. 1 atm), which effected an immediate color change to bright orange. After 1 h of periodic shaking of the reaction flask, the solvent and other volatiles were removed *in vacuo*, affording an oily orange solid that was triturated with pentane (3 mL). Subsequent drying *in vacuo* afforded **[2·CO]$^+$OTf$^-$** as an analytically pure, bright orange powder (0.081 g, 0.10 mmol, 91%). Anal. Calcd for $C_{27}H_{35}F_3IrO_4PS_2$: C, 42.23; H, 4.59; N, 0.00. Found: C, 42.12; H, 4.28; N, <0.3. ^{1}H NMR (CD_2Cl_2): δ 7.26 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4−H or C7−H), 7.22 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 7.13 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4−H or C7−H), 7.10 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 3.61 (m, 2H, C1(H)$_2$), 3.31 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.28 (m, 1H, P(C*H*Me$_c$Me$_d$)), 2.15 (d, $^4J_{PH}$ = 1.5 Hz, 15H, C_5Me_5), 1.37 (d of d, $^3J_{PH}$ = 19.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.24 (d of d, $^3J_{PH}$ = 19.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 1.15 (d of d, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 0.95 (d of d, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 178.0 (d, $^2J_{PC}$ = 18.5 Hz, CO), 166.6 (d, $^2J_{PC}$ = 13.6 Hz, C2), 147.8 (d, J_{PC} = 8.3 Hz, C3a or C7a), 142.7 (d, J_{PC} = 6.0 Hz, C3a or C7a), 130.0 (d, $^1J_{PC}$ = 62.3 Hz, C3), 127.2 (C5 or C6), 125.0 (C4 or C7), 124.2 (C4 or C7), 118.3 (C5 or C6), 104.5 (C_5Me_5), 41.6 (d, $^3J_{PC}$ = 10.9 Hz, C1), 29.6 (d, $^1J_{PC}$ = 27.8 Hz, P(*C*HMe$_c$Me$_d$)), 25.4 (d, $^1J_{PC}$ = 37.7 Hz, P(*C*HMe$_a$Me$_b$)), 19.1 (d, $^2J_{PC}$ = 6.5 Hz, P(CH*Me$_c$*Me$_d$)), 18.6 (P(CHMe$_a$*Me$_b$*)), 18.5 (P(CH*Me$_a$*Me$_b$)), 17.3 (P(CHMe$_c$*Me$_d$*)), 9.7 (C_5Me_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 42.6. FT-IR (NaCl; cm^{-1}) ν(CO): 2053. Crystals suitable for X-ray crystallographic analysis were grown by vapor diffusion of diethyl ether into a concentrated CH_2Cl_2 solution of **[2·CO]$^+$OTf$^-$** at ambient temperature.

Synthesis of [2·PMe$_3$]$^+$B(C$_6$F$_5$)$_4^-$. Compound **[2]$^+$B(C$_6$F$_5$)$_4^-$** was prepared *in situ* by treatment of a solution of **1** (0.10 g, 0.17 mmol) in CH_2Cl_2 (2 mL) with solid LiB(C$_6$F$_5$)$_4$·2.5Et$_2$O (0.14 g, 0.17 mmol), causing an immediate color change to dark blue accompanied by the formation of a precipitate. The reaction mixture was stirred at ambient temperature for 0.5 h followed by filtration through Celite to remove the precipitate. To the dark blue supernatant solution containing **[2]$^+$B(C$_6$F$_5$)$_4^-$** was added a 1.0 M solution of PMe_3 in toluene (198 μL, 0.20 mmol), which effected an immediate color change to bright orange. After 1 h of magnetic stirring, the solvent and other volatiles were removed *in vacuo*, affording an oily orange solid that was triturated with pentane (3 mL). Subsequent drying *in vacuo* afforded **[2·PMe$_3$]$^+$B(C$_6$F$_5$)$_4^-$** as an analytically pure, bright orange powder (0.22 g, 0.16 mmol, 94%). Anal. Calcd for $C_{52}H_{44}BF_{20}IrP_2S$: C, 46.40; H, 3.30; N, 0.00. Found: C, 46.79; H, 3.43; N, <0.3. ^{1}H NMR ($CDCl_3$): δ 7.29−7.19 (m, 2H, Ar−H), 7.17 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4−H or C7−H), 7.13 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 3.62 (m, 1H, C1(*H$_a$*)(H$_b$)), 3.52 (m, 1H, C1(H$_a$)(*H$_b$*)), 3.24 (m, 1H, P(C*H*-Me$_a$Me$_b$)), 2.34 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.92 (m, 15H, C_5Me_5), 1.65 (br m, 9H, PMe_3), 1.35 (d of d, $^3J_{PH}$ = 13.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.27 (d of d, $^3J_{PH}$ = 13.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 1.23 (d of d, $^3J_{PH}$ = 11.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 0.91 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 176.6 (d, $^2J_{PC}$ = 21.3 Hz, C2), 147.8 (d, J_{PC} = 7.8 Hz, C3a or C7a), 142.5 (d, J_{PC} = 5.4 Hz, C3a or C7a), 129.7 (C3), 127.1 (Ar−C), 124.9 (Ar−C), 123.8 (C5 or C6), 118.6 (C4 or C7), 99.6 (C_5Me_5), 40.8 (d, $^3J_{PC}$ = 10.4 Hz, C1), 30.7 (d, $^1J_{PC}$ = 28.4 Hz, P(*C*HMe$_c$Me$_d$)), 25.8 (d, $^1J_{PC}$ = 34.5 Hz, P(*C*HMe$_a$Me$_b$)), 20.2 (d, $^2J_{PC}$ = 6.8 Hz, P(CH*Me$_c$*Me$_d$)), 20.1 (P(CHMe$_a$*Me$_b$*)), 19.5 (d, $^2J_{PC}$ = 3.4 Hz, P(CH*Me$_a$*Me$_b$)), 18.0 (P(CHMe$_c$*Me$_d$*)), 17.2 (d, $^1J_{PC}$ = 40.6 Hz, PMe_3), 9.8 (C_5Me_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 33.6 (d, $^2J_{PP}$ = 28.3 Hz, ^{i}Pr$_2$PInd), −41.5 (d, $^2J_{PP}$ = 28.3 Hz, PMe_3).

Synthesis of 3·CH$_3$CN. To a magnetically stirred suspension of **1** (0.17 g, 0.27 mmol) in CH_3CN (2 mL) was added solid anhydrous K_2CO_3 (0.077 g, 0.55 mmol) followed by stirring at ambient temperature for 48 h; the suspension darkened from orange to brown during the reaction time. The reaction mixture was filtered through Celite followed by removal of solvent and other volatiles *in vacuo*, affording a mixture of **3·CH$_3$CN** and another phosphorus-containing product (ca. 92:8 on the basis of ^{31}P NMR data). Analytically pure **3·CH$_3$CN** was subsequently isolated by crystallization from a concentrated CH_3CN solution of the aforementioned mixture stored at −35 °C (0.069 g, 0.11 mmol, 41%). From these brown crystals was selected a sample that proved suitable for X-ray diffraction analysis. Anal. Calcd for $C_{27}H_{37}IrNPS$: C, 51.39; H, 5.92; N, 2.22. Found: C, 51.37; H, 5.94; N, 2.39. ^{1}H NMR (C_6D_6): δ 7.22−7.16 (m, 2H, C5 or C6 and C4 or C7), 7.05 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4 or C7), 6.95 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5 or C6), 6.81 (s, 1H, C3−H), 2.40 (m, 1H, P(*C*HMe$_a$Me$_b$)), 2.21 (m, 1H, P(*C*H-Me$_c$Me$_d$)), 1.83 (s, 3H, *N*═C−CH$_3$), 1.77 (d, $^4J_{PH}$ = 2.0 Hz, 15H, C_5Me_5), 1.11 (d of d, $^3J_{PH}$ = 14.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 0.91 (d of d, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 0.71 (d of d, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 0.49 (d of d, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHMe$_c$*Me$_d$*)). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.0 (d, $^2J_{PC}$ = 7.4 Hz, *N*═*C*−CH$_3$), 158.8 (d, $^2J_{PC}$ = 9.2 Hz, C2), 151.7 (d, J_{PC} = 4.3 Hz, C3a or C7a), 140.6 (d, J_{PC} = 4.9 Hz, C3a or C7a), 126.6 (C5 or C6), 122.4 (d, J_{PC} = 1.9 Hz, C4 or C7), 119.7 (d, J_{PC} = 1.5 Hz, C5 or C6), 117.9 (C4 or C7), 115.6 (d, $^3J_{PC}$ = 3.5 Hz, C3), 92.2 (d, J = 3.1 Hz, C_5Me_5), 24.1 (*N*═C−*C*H$_3$), 22.1 (d, $^1J_{PC}$ = 26.3 Hz, P(*C*HMe$_c$Me$_d$)), 21.2 (d, $^2J_{PC}$ = 3.3 Hz, P(CH*Me$_c$*Me$_d$)), 21.1 (d, $^1J_{PC}$ = 10.3 Hz, P(*C*HMe$_a$Me$_b$)), 19.6 (d, $^2J_{PC}$ = 1.3 Hz, P(CH*Me$_a$*Me$_b$)), 17.6 (d, $^2J_{PC}$ = 3.0 Hz, P(CHMe$_a$*Me$_b$*)), 15.9 (d, $^2J_{PC}$ = 4.5 Hz, P(CHMe$_c$*Me$_d$*)), 8.8 (C_5Me_5). ^{31}P{^{1}H} NMR (C_6D_6): δ 91.6.

Synthesis of 4. A solution of (κ²-3-P^{i}Pr$_2$-2-S-indene)Ir(COD) (0.11 g, 0.20 mmol) in CH_2Cl_2 (4 mL) was degassed by use of three freeze−pump−thaw cycles and was subsequently exposed to an atmosphere of CO, which caused a gradual color change from dark red to orange. After 0.75 h, ^{31}P NMR data collected on an aliquot of the reaction mixture confirmed the quantitative formation of **4**. Removal of the solvent caused a darkening of the solution to dark brown, ultimately affording a brown solid that was extracted into pentane (3 × 2 mL) and filtered through Celite. Removal of the solvent and other volatiles afforded **4** as an analytically pure, orange solid (0.041 g, 0.079 mmol, 39%). Anal. Calcd for $C_{17}H_{20}IrO_2PS$: C, 39.91; H, 3.94; N, 0.00. Found: C, 40.03; H, 4.25; N, <0.3. ^{1}H NMR (C_6D_6): δ 7.10 (t, $^3J_{HH}$ = 8.0 Hz, 1H, C5−H or C6−H), 6.96−6.86 (m, 3H, Ar−H), 3.40 (d, $^4J_{PC}$ = 2.0 Hz, 2H, C1(H)$_2$), 2.40 (m, 2H, P(C*H*Me$_a$Me$_b$)), 1.15 (d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CH*Me$_a$*Me$_b$)), 0.89 (d of d, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe$_a$*Me$_b$*)). ^{13}C{^{1}H} NMR (C_6D_6): δ 181.6 (d, $^2J_{PC}$ = 88.8 Hz, CO trans to P), 180.4 (d, $^2J_{PC}$ = 30.7 Hz, C2), 178.5 (d, $^2J_{PC}$ = 10.8 Hz, CO cis to P), 149.1 (d, J_{PC} =

6.8 Hz, C3a or C7a), 141.8 (d, J_{PC} = 5.5 Hz, C3a or C7a), 126.4 (C3), 126.6 (Ar−C), 124.3 (Ar−C), 122.5 (Ar−C), 117.0 (Ar−C), 42.2 (d, $^3J_{PC}$ = 14.1 Hz, C1), 26.1 (d, $^1J_{PC}$ = 33.0 Hz, P(*C*HMe$_a$Me$_b$)), 19.2 (d, $^2J_{PC}$ = 2.6 Hz, P(CH*Me$_a$*Me$_b$)), 18.1 (P(CHMe$_a$*Me$_b$*)). ^{31}P{^{1}H} NMR (C_6D_6): δ 62.2. FT-IR (NaCl; cm^{-1}) ν(CO): 2059, 1983.

Reaction of 3·CH$_3$CN with CO To Give 4. A benzene-d_6 solution (2 mL) of **3·CH$_3$CN** (0.019 g, 0.030 mmol) was transferred to a J. Young NMR tube, degassed by use of three freeze−pump−thaw cycles, and subsequently exposed to an atmosphere of CO, which caused an immediate color change from brown to orange. ^{31}P NMR analysis of the reaction mixture after 0.75 h confirmed the quantitative consumption of **3·CH$_3$CN** along with the clean formation of **4**. ^{1}H and ^{13}C NMR analysis of the reaction mixture also confirmed the formation of **4**, along with a stoichiometric equivalent amount of 1,2,3,4-tetramethylfulvene.[20]

Synthesis of 5. Compound **[2]$^+$OTf$^-$** was prepared *in situ* by treatment of a solution of **1** (0.098 g, 0.16 mmol) in CH_2Cl_2 (2 mL) with solid AgOTf (0.040 g, 0.16 mmol), followed by magnetic stirring at ambient temperature, during which time the solution turned dark blue with the concomitant formation of a precipitate. After 0.5 h of stirring, the precipitate was removed by filtration through Celite. To the dark blue supernatant solution was added Ph_2SiH_2 (29 μL, 0.16 mmol), which caused an immediate color change to orange. After 1 h of magnetic stirring, the solvent and other volatiles were removed *in vacuo* followed by washing with pentane (2 mL). Subsequent drying *in vacuo* afforded an orange solid that was extracted into pentane (2 × 2 mL). Concentration of the pentane solution and storage at −35 °C afforded **5** as analytically pure, orange crystals (0.041 g, 0.068 mmol, 44%). Anal. Calcd for $C_{25}H_{36}IrPS$: C, 50.74; H, 6.13; N, 0.00. Found: C, 50.53; H, 5.94; N, <0.3. ^{1}H NMR (C_6D_6): δ 7.19−7.12 (m, 2H, Ar−H), 6.94−6.87 (m, 2H, Ar−H), 3.50 (d, $^2J_{HH}$ = 22.0 Hz, 1H, C1(H_a)(H$_b$)), 3.42 (d, $^2J_{HH}$ = 22.0 Hz, 1H, C1(H$_a$)(H_b)), 2.63 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.00 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.82 (s, 15H, C_5Me_5), 1.21 (d of d, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.03 (d of d, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)), 0.95 (d of d, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 0.87 (d of d, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), −15.74 (d, $^2J_{PH}$ = 37.5 Hz, 1H, Ir−H). ^{13}C{^{1}H} NMR (C_6D_6): δ 182.4 (d, $^2J_{PC}$ = 24.5 Hz, C2), 147.9 (d, J_{PC} = 7.0 Hz, C3a or C7a), 144.9 (d, J_{PC} = 4.4 Hz, C3a or C7a), 128.6 (d, $^1J_{PC}$ = 62.1 Hz, C3), 125.9 (Ar−C), 123.7 (Ar−C), 120.6 (Ar−C), 116.2 (Ar−C), 91.4 (C_5Me_5), 40.4 (d, $^3J_{PC}$ = 10.6 Hz, C1), 28.7 (d, $^1J_{PC}$ = 25.4 Hz, P(*C*HMe$_c$Me$_d$)), 22.6 (d, $^1J_{PC}$ = 42.8 Hz, P(*C*HMe$_a$Me$_b$)), 18.4 (P(CH*Me$_a$*Me$_b$)), 18.2 (d, $^2J_{PC}$ = 5.7 Hz, P(CH*Me$_c$*Me$_d$)), 17.9 (d, $^2J_{PC}$ = 4.7 Hz, P(CHMe$_a$*Me$_b$*)), 17.3 (d, $^2J_{PC}$ = 3.6 Hz, P(CHMe$_c$-*Me$_d$*)), 9.4 (C_5Me_5). ^{31}P{^{1}H} NMR (C_6D_6): δ 43.8.

Synthesis of 6a. A magnetically stirred solution of **[2]$^+$B(C$_6$F$_5$)$_4^-$** (0.12 g, 0.098 mmol) in CH_2Cl_2 (2 mL) was treated with Ph_2SiH_2 (18 μL, 0.098 mmol), which caused an immediate color change from dark blue to orange; ^{31}P NMR analysis of the reaction mixture revealed the quantitative formation of **6a**. After 0.5 h of magnetic stirring, the CH_2Cl_2 was removed *in vacuo* followed by the addition of benzene (2 mL), which caused the separation of a red oil that was isolated by removal of the benzene supernatant by use of a Pasteur pipet. The red oil was washed with benzene (3 × 2 mL) followed by drying *in vacuo* to afford **6a** as an analytically pure, orange solid (0.097 g, 0.067 mmol, 68%). Anal. Calcd for $C_{61}H_{47}BF_{20}IrPSSi$: C, 50.36; H, 3.26; N, 0.00. Found: C, 50.11; H, 3.45; N, <0.3. ^{1}H NMR (CD_2Cl_2): δ 7.67−7.15 (m, 14H, Ar−H), 5.52 (s, 1H, Si−H), 3.28 (d, $^2J_{HH}$ = 23.5 Hz, 1H, C1(H_a)(H$_b$)), 3.12 (d, $^2J_{HH}$ = 24.0 Hz, 1H, C1(H$_a$)(H_b)), 2.75 (m, 1H, P(C*H*-Me$_a$Me$_b$)), 2.22 (m, 1H, P(C*H*Me$_c$Me$_d$)), 2.00 (s, 15H, C_5Me_5), 1.35 (d of d, $^3J_{PH}$ = 14.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 0.94 (d of d, $^3J_{PH}$ = 19.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 0.77 (d of d, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHMe$_c$*Me$_d$*)), 0.076 (d of d, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CHMe$_a$*Me$_b$*)), −15.12 (d, $^2J_{PH}$ = 50.0 Hz, 1H, Ir−H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 152.4 (quaternary), 148.9 (quaternary), 148.4 (quaternary), 148.0 (quaternary), 139.3 (quaternary), 135.9 (Ar−C), 135.4 (quaternary), 132.4 (Ar−C), 128.9 (Ar−C), 128.1 (Ar−C), 127.0 (Ar−C), 126.3 (Ar−C), 125.4 (Ar−C), 121.4 (Ar−C), 96.0 (C_5Me_5), 39.9 (d, $^3J_{PC}$ = 8.9 Hz, C1), 27.1 (d, $^1J_{PC}$ = 28.3 Hz, P(*C*HMe$_c$Me$_d$)), 23.4 (d, $^1J_{PC}$ = 40.0 Hz, P(*C*HMe$_a$Me$_b$)), 18.1 (d, $^2J_{PC}$ = 6.3 Hz, P(CH-*Me$_c$*Me$_d$)), 17.6 (d, $^2J_{PC}$ = 3.8 Hz, P(CH*Me$_a$*Me$_b$)), 17.4 (P(CH-Me$_a$*Me$_b$*) and P(CHMe$_c$*Me$_d$*)), 9.9 (C_5Me_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 49.3. ^{29}Si NMR (CD_2Cl_2): δ 3.6.

Synthesis of 6b. A protocol analogous to that described for the synthesis of **6a** was employed, using $PhSiH_3$ (12 μL, 0.098 mmol) in place of Ph_2SiH_2, with similar qualitative observations. Compound **6b** was isolated as an analytically pure, orange solid (0.10 g, 0.075 mmol, 77%). Anal. Calcd for $C_{55}H_{43}BF_{20}IrPSSi$: C, 47.94; H, 3.15; N, 0.00. Found: C, 47.81; H, 3.18; N, <0.3. ^{1}H NMR (CD_2Cl_2): δ 7.66−7.57 (m, 3H, Ar−H), 7.56−7.46 (m, 3H, Ar−H), 7.42−7.32 (m, 3H, Ar−H), 5.40 (m, 1H, Si(H_a)(H$_b$)), 4.99 (m, 1H, Si(H$_a$)(H_b)), 3.51 (s, 2H, C1(H)$_2$), 2.93 (m, 1H, P(C*H*Me$_a$Me$_b$)), 2.34 (m, 1H, P(C*H*Me$_c$Me$_d$)), 2.07 (m, 15H, C_5Me_5), 1.47 (d of d, $^3J_{PH}$ = 13.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.09 (d of d, $^3J_{PH}$ = 19.5 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 0.86 (d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)), 0.57 (d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), −15.02 (d, $^2J_{PH}$ = 34.0 Hz, Ir−H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 153.4 (quaternary), 149.4 (quaternary), 149.0 (quaternary), 139.4 (quaternary), 135.7 (Ar−C), 132.8 (Ar−C), 129.1 (Ar−C), 127.3 (Ar−C), 126.7 (Ar−C), 125.7 (Ar−C), 121.8 (Ar−C), 96.4 (C_5Me_5), 39.3 (d, $^3J_{PC}$ = 9.1 Hz, C1), 27.1 (d, $^1J_{PC}$ = 28.4 Hz, P(*C*HMe$_c$Me$_d$)), 23.8 (d, $^1J_{PC}$ = 39.9 Hz, P(*C*HMe$_a$Me$_b$)), 18.3 (d, $^2J_{PC}$ = 6.2 Hz, P(CH*Me$_c$*Me$_d$)), 18.2 (P(CHMe$_a$*Me$_b$*)), 17.9 (d, $^2J_{PC}$ = 4.5 Hz, P(CH*Me$_a$*Me$_b$)), 17.8 (P(CHMe$_c$*Me$_d$*)), 10.1 (C_5Me_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 49.5. ^{29}Si NMR (CD_2Cl_2): δ 94.1.

Synthesis of 7. Compound **6a** (prepared *in situ* employing the protocols described above using **1** (0.098 g, 0.16 mmol), LiB(C$_6$F$_5$)$_4$·2.5Et$_2$O (0.14 g, 0.16 mmol), and Ph_2SiH_2 (29 μL, 0.16 mmol)) was dissolved in diethyl ether (2 mL), and the resulting solution was stored at ambient temperature for 24 h, during which time **7** precipitated from the solution as an analytically pure, orange crystalline solid (0.12 g, 0.092 mmol, 58% based on **1**). Anal. Calcd for $C_{51}H_{41}BF_{20}IrPS$: C, 47.10; H, 3.18; N, 0.00. Found: C, 47.08; H, 3.24; N, <0.3. ^{1}H NMR (CD_2Cl_2): δ 7.60 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 7.50 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 7.46−7.36 (m, 2H, C4−H and C7−H), 3.65 (m, 2H, C1(H)$_2$), 3.09−2.93 (m, 2H, P(C*H*Me$_a$Me$_b$) and S(C*H$_a$*H$_b$)CH$_3$), 2.59 (m, 1H, S(CH$_a$*H$_b$*)CH$_3$), 2.35 (m, 1H, P(C*H*Me$_c$Me$_b$)), 2.11 (s, 15H, C_5Me_5), 1.49 (d of d, $^3J_{PH}$ = 14.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.16 (d of d, $^3J_{PH}$ = 19.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 1.02 (t, $^3J_{HH}$ = 7.5 Hz, 3H, SCH$_2$C*H*$_3$), 0.90 (d of d, $^3J_{PH}$ = 14.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)), 0.86 (d of d, $^3J_{PH}$ = 13.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), −15.36 (d, $^2J_{PH}$ = 32.5 Hz, 1H, Ir−H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 157.9 (d, $^2J_{PC}$ = 18.9 Hz, C2), 149.5 (d, J_{PC} = 6.0 Hz, C3a or C7a), 138.9 (C3a or C7a), 127.6 (C5 or C6), 127.2 (C5 or C6), 126.0 (C4 or C7), 125.8 (C3), 122.3 (C4 or C7), 96.8 (C_5Me_5), 37.7 (d, $^3J_{PC}$ = 6.2 Hz, C1), 37.6 (S*C*H$_2$CH$_3$), 26.9 (d, $^1J_{PC}$ = 29.4 Hz, P(*C*HMe$_c$-Me$_d$)), 24.2 (d, $^1J_{PC}$ = 39.2 Hz, P(*C*HMe$_a$Me$_b$)), 18.6 (P(CH-Me$_a$*Me$_b$*)), 18.3 (d, $^2J_{PC}$ = 6.2 Hz, P(CH*Me$_c$*Me$_d$)), 18.0 (d, $^2J_{PC}$ = 4.4 Hz, P(CH*Me$_a$*Me$_b$)), 17.9 (P(CHMe$_c$*Me$_d$*)), 11.6 (SCH$_2$*C*H$_3$), 10.1 (C_5Me_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 48.6. Crystals suitable for X-ray crystallographic analysis were grown from a concentrated diethyl ether solution of **7** at ambient temperature.

Synthesis of 8. A solution of 1/3-P^{i}Pr$_2$-2-S^{t}Bu-indene (0.10 g, 0.32 mmol) in CH_2Cl_2 (2 mL) was added dropwise to a suspension of [Cp*RhCl$_2$]$_2$ (0.097 g, 0.16 mmol) in CH_2Cl_2 (2 mL), resulting in an immediate darkening of the solution. The reaction mixture was magnetically stirred at ambient temperature for 16 h prior to removal of the solvent and other volatiles *in vacuo*. The residual solid was washed with pentane (3 × 2 mL) and dried *in vacuo* to afford **8** as an analytically pure, light brown solid (0.16 g, 0.30

mmol, 94%). Anal. Calcd for $C_{25}H_{35}ClRhPS$: C, 55.92; H, 6.57; N, 0.00. Found: C, 55.88; H, 6.52; N, <0.3. ^{1}H NMR ($CDCl_3$): δ 7.19 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4−H or C7−H), 7.13 (t, $^3J_{HH}$ = 8.0 Hz, 1H, C5−H or C6−H), 7.06 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4−H or C7−H), 6.96 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 3.63 (m, 1H, C1(H_a)(H_b)), 3.54 (m, 1H, C1(H_a)(H_b)), 3.19 (m, 1H, P(C*H*-Me_aMe_b)), 2.30 (m, 1H, P(C*H*Me_cMe_d)), 1.77 (d, J_{PC} = 3.0 Hz, 15H, C_5Me_5), 1.51 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_a$Me$_b$)), 1.45−1.37 (m, 6H, P(CHMe$_a$*Me*$_b$) and P(CH*Me*$_c$-Me$_d$)), 1.10 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me*$_d$)). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 179.5 (d, $^2J_{PC}$ = 24.3 Hz, C2), 147.7 (d, J_{PC} = 6.9 Hz, C3a or C7a), 145.8 (C3a or C7a), 126.2 (C5 or C6), 123.5 (C4 or C7), 121.9 (C5 or C6), 117.6 (C4 or C7), 98.8 (d of d, $^1J_{RhC}$ = 5.9 Hz, $^2J_{PC}$ = 3.0 Hz, C_5Me_5), 43.1 (d of d, $^3J_{PC}$ = 11.8 Hz, $^3J_{RhC}$ = 1.4 Hz, C1), 29.4 (d of d, $^1J_{PC}$ = 19.6 Hz, $^2J_{RhC}$ = 1.4 Hz, P(*C*HMe$_c$Me$_d$)), 26.4 (d, $^1J_{PC}$ = 28.9 Hz, P(*C*HMe$_a$Me$_b$)), 20.5 (P(CH*Me*$_a$Me$_b$)), 20.2 (d, $^2J_{PC}$ = 7.5 Hz, P(CHMe$_a$*Me*$_b$)), 19.7 (d, $^2J_{PC}$ = 6.8 Hz, P(CH*Me*$_c$Me$_d$)), 18.7 (d, $^2J_{PC}$ = 2.1 Hz, P(CHMe$_c$*Me*$_d$)), 9.6 (C_5Me_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 65.7 (d, $^1J_{RhP}$ = 141.7 Hz).

Formation of [9]$^+$B(C$_6$F$_5$)$_4^-$. To a magnetically stirred solution of **8** (0.023 g, 0.042 mmol) in CD_2Cl_2 (2 mL) was added solid $LiB(C_6F_5)_4 \cdot 2.5Et_2O$ (0.037 g, 0.042 mmol), which caused an immediate color change of the reaction mixture to dark green. After 0.25 h, ^{31}P NMR analysis of the reaction mixture revealed the complete consumption of **8** and the presence of a major phosphorus-containing product (ca. 75% of mixture, ^{31}P NMR) that we assign as **[9]$^+$B(C$_6$F$_5$)$_4^-$**. Although we have thus far not been able to isolate **[9]$^+$B(C$_6$F$_5$)$_4^-$** in analytically pure form due to the apparent instability of this complex in solution and upon workup, ^{1}H and ^{13}C NMR characterization data obtained *in situ* are consistent with the C_s-symmetric nature of the target complex. Alternative reactions conducted in THF-d_8 afforded red reaction mixtures in which the transformation of **8** into **[9]$^+$B(C$_6$F$_5$)$_4^-$** in a similar fashion was observed by use of NMR methods. ^{1}H NMR (CD_2Cl_2): δ 7.47 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4−H or C7−H), 7.36−7.29 (m, 2H, Ar−H), 7.25 (d of t, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, C5−H or C6−H), 3.89 (d, $^4J_{PH}$ = 2.0 Hz, 2H, C1(H)$_2$), 2.96 (m, 2H, P(C*H*Me$_a$Me$_b$)$_2$), 1.86 (d, $^4J_{PH}$ = 2.0 Hz, 15H, C_5Me_5), 1.32 (d of d, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.0 Hz, P(CH*Me*$_a$Me$_b$)$_2$), 1.22 (d of d, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.0 Hz, P(CHMe$_a$*Me*$_b$)$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 175.0 (C2), 149.5 (C3a or C7a), 141.4 (C3a or C7a), 131.7 (C3), 127.2 (Ar−C), 125.3 (C5 or C6), 125.1 (C4 or C7), 120.4 (Ar−C), 102.6 (d, $^1J_{RhC}$ = 5.2 Hz, C_5Me_5), 42.3 (d, $^3J_{PC}$ = 12.8 Hz, C1), 24.9 (d, $^1J_{PC}$ = 24.0 Hz, P(*C*HMe$_a$Me$_b$)$_2$), 18.6 (P(CHMe$_a$*Me*$_b$)$_2$), 18.4 (d, $^2J_{PC}$ = 4.0 Hz, P(CH*Me*$_a$Me$_b$)$_2$), 10.9 (C_5Me_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 69.3 (d, $^1J_{RhP}$ = 172.0 Hz).

Formation of 10. Treatment of a magnetically stirred THF-d_8 solution of **[9]$^+$B(C$_6$F$_5$)$_4^-$** (0.042 mmol scale; prepared *in situ* as outlined above) with Ph_2SiH_2 (7.8 μL, 0.042 mmol) caused an immediate color change to dark orange. After 0.25 h, ^{31}P NMR analysis of the reaction mixture revealed the complete consumption of **[9]$^+$B(C$_6$F$_5$)$_4^-$** and the presence of a major phosphorus-containing product (ca. 80% of mixture, ^{31}P NMR) that we assign as **10**. Although we have thus far not been able to isolate **10** in analytically pure form due to the apparent instability of this complex in solution and upon workup, NMR characterization data obtained *in situ* are consistent with the identity of **10** as being the Rh analogue of the isolable Ir complex **6a**. ^{1}H NMR (THF-d_8): δ 7.78−7.73 (m, Ar−H), 7.60−7.55 (m, 2H, Ar−H), 7.54−7.49 (m, Ar−H), 7.16−7.10 (m, 2H, C4−H and C7−H), 7.08 (t, $^3J_{HH}$ = 7.0 Hz, 1H, C5−H or C6−H), 6.87 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 5.79 (s, 1H, S−*H*), 3.42 (m, 1H, C1(H_a)(H_b)), 3.33 (m, 1H, C1(H_a)(H_b)), 2.99 (m, 1H, P(C*H*Me$_2$)), 2.43 (m, 1H, P(C*H*Me$_2$)), 1.99 (m, 15H, C_5Me_5), 1.41 (d of d, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.0 Hz, P(CHMe*Me*)), 1.20 (d of d, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 7.5 Hz, P(CHMe*Me*)), 1.17 (d of d, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.0 Hz, P(CHMe*Me*)), 1.02 (d of d, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.0 Hz, P(CHMe*Me*)), −12.81 (d of d, $^1J_{RhP}$ = 45.0 Hz, $^2J_{PH}$ = 20.0 Hz, 1H, Rh−H). ^{13}C NMR data on the basis of ^{1}H−^{13}C HMBC/HSQC experiments (THF-d_8): δ 135.0 (Ar−C), 134.7 (Ar−C), 131.7 (Ar−C), 129.1 (Ar−C), 129.0 (Ar−C), 128.8 (Ar−C), 126.5 (C5 or C6), 123.9 (C4 or C7), 121.6 (C5 or C6), 117.5 (C4 or C7), 42.8 (C1), 29.1 (P(*C*HMe$_2$)), 23.9 (P(*C*HMe$_2$)), 19.3 (P(CHMe*Me*)), 19.2 (P(CHMe*Me*)), 18.8 (P(CHMe*Me*)), 18.6 (P(CHMe*Me*)), 10.5 (C_5Me_5). ^{31}P{^{1}H} NMR (THF-d_8): δ 77.4 (d, $^1J_{RhP}$ = 143.7 Hz).

Synthesis of 11. Method A: To a magnetically stirred solution of **3·CH$_3$CN** (0.066 g, 0.10 mmol) in THF (2 mL) was added Ph_2SiH_2 (19 μL, 0.10 mmol), which effected an immediate color change from dark red to orange. The reaction mixture was magnetically stirred at ambient temperature for 2 h, at which time ^{31}P NMR data collected on an aliquot of the reaction mixture indicated the complete consumption of **3·CH$_3$CN** and the appearance of two new phosphorus-containing products (**11a,b**). The solvent was removed *in vacuo*, affording an orange residue that was extracted into pentane (3 mL). Removal of the pentane afforded **11** as a mixture of diastereomers (**11a**,**b**) in a 3:1 ratio (0.049 g, 0.064 mmol, 64%). **Method B**: A mixture of **1** (0.053 g, 0.085 mmol) and Ph_2SiH_2 (16 μL, 0.085 mmol) in THF (2 mL) was cooled to −35 °C followed by the dropwise addition of a solution of $NaN(SiMe_3)_2$ (0.016 g, 0.085 mmol) in THF (1 mL), which caused a rapid color change from orange to dark brown followed by an immediate return to orange. The reaction mixture was magnetically stirred and allowed to warm to ambient temperature followed by magnetic stirring for 3 h, at which time ^{31}P NMR data collected on an aliquot of the reaction mixture indicated complete consumption of **1** and the formation of **11a**,**b**. The solvent was removed *in vacuo*, affording an orange residue that was extracted into pentane (3 mL). Removal of the pentane afforded **11** as a mixture of diastereomers (**11a**,**b**; similar to that observed by use of Method A) in a 4:1 ratio (0.052 g, 0.067 mmol, 79%). Anal. Calcd for $C_{37}H_{46}IrPSSi$: C, 57.41; H, 5.99; N, 0.00. Found: C, 57.09; H, 6.20; N, <0.3. **Diastereomer 11a**: ^{1}H NMR (C_6D_6): δ 7.55 (m, 2H, Ar−H), 7.38 (m, 2H, Ar−H), 7.21−6.99 (m, 8H, Ar−H), 6.88 (m, 1H, Ar−H), 6.82 (m, 1H, Ar−H), 5.66 (d, $^3J_{HH}$ = 1.0 Hz, 1H, Si−H), 4.18 (m, 1H, C1−H), 2.60 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.86−1.79 (m, 16H, C_5Me_5 and P(C*H*Me$_c$Me$_d$)), 1.06 (d of d, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_c$Me$_d$)), 0.91 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CH*Me*$_a$Me$_b$)), 0.84 (d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CHMe$_a$*Me*$_b$)), 0.37 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me*$_d$)), −15.81 (d, $^2J_{PH}$ = 37.0 Hz, 1H, Ir−H). ^{13}C{^{1}H} NMR (C_6D_6): δ 182.8 (d, $^2J_{PC}$ = 25.5 Hz, C2), 148.5 (d, $^2J_{PC}$ = 7.5 Hz, C3a or C7a), 144.5 (d, $^2J_{PC}$ = 4.9 Hz, C3a or C7a), 135.7 (Ar−C), 135.2 (Ar−C), 132.9 ($SiPh_2$-quaternary), 130.8 ($SiPh_2$-quaternary), 129.0 (Ar−C), 128.7 (Ar−C), 127.1 (Ar−C), 127.0 (d, $^1J_{PC}$ = 23.3 Hz, C3), 126.9 (Ar−C), 124.8 (Ar−C), 123.8 (Ar−C), 119.7 (Ar−C), 116.2 (Ar−C), 91.4 (d, $^2J_{PC}$ = 3.0 Hz, C_5Me_5), 44.2 (d, $^3J_{PC}$ = 9.8 Hz, C1), 27.8 (d, $^1J_{PC}$ = 26.3 Hz, P(*C*HMe$_c$Me$_d$)), 22.4 (d, $^1J_{PC}$ = 42.8 Hz, P(*C*HMe$_a$Me$_b$)), 18.3 (P(CH*Me*$_a$Me$_b$)), 17.9 (d, $^2J_{PC}$ = 5.9 Hz, P(CH*Me*$_c$Me$_d$)), 17.8 (d, $^2J_{PC}$ = 4.8 Hz, P(CHMe$_a$*Me*$_b$)), 16.6 (d, $^2J_{PC}$ = 4.3 Hz, P(CHMe$_c$*Me*$_d$)), 9.3 (C_5Me_5). ^{31}P{^{1}H} NMR (C_6D_6): δ 42.3. ^{29}Si NMR (C_6D_6): δ 89.1. **Diastereomer 11b**: ^{1}H NMR (C_6D_6): δ 7.59−7.57 (m, 2H, Ar−H), 7.37−7.35 (m, 2H, Ar−H), 7.13−6.99 (m, 9H, Ar−H), 6.84−6.81 (m, 1H, Ar−H), 5.72 (d, $^3J_{HH}$ = 1.0 Hz, 1H, Si−H), 4.21 (m, 1H, C1−H), 2.48 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.99 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.79 (s, 15H, C_5Me_5), 1.19 (d of d, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_c$Me$_d$)), 0.99 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me*$_d$)), 0.86 (d of d, $^3J_{PH}$ = 13.0 Hz, $^3J_{HH}$ = 6.5 Hz, 3H, P(CH*Me*$_a$Me$_b$)), 0.41 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me*$_b$)), −16.04 (d, $^2J_{PH}$ = 37.5 Hz, 1H, Ir−H). ^{13}C{^{1}H} NMR (C_6D_6): δ 181.4 (d, $^2J_{PC}$ = 25.2 Hz, C2), 148.3 (d, J_{PC} = 7.5 Hz, C3a or C7a), 144.0 (d, J_{PC} = 4.7 Hz, C3a or C7a), 135.6 (Ar−C), 135.2 (Ar−C), 132.5 (SiPh-quaternary), 130.3 (SiPh-quaternary), 128.8 (Ar−C), 128.7 (Ar−C), 127.3 (d, $^1J_{PC}$ = 25.9 Hz, C3), 127.0 (Ar−C), 126.6 (Ar−C), 124.6 (Ar−C), 123.5 (Ar−C), 119.8 (Ar−C), 116.4 (Ar−C), 91.4 (d, $^2J_{PC}$ = 3.0 Hz, C_5Me_5), 43.9 (d, $^3J_{PC}$ = 9.7 Hz,

C1), 28.8 (d, $^1J_{PC}$ = 25.4 Hz, P(*C*HMe$_c$Me$_d$)), 22.8 (d, $^1J_{PC}$ = 42.8 Hz, P(*C*HMe$_a$Me$_b$)), 18.4 (d, $^2J_{PC}$ = 5.7 Hz, P(CH*Me$_c$*Me$_d$)), 18.0 (d, $^2J_{PC}$ = 4.8 Hz, P(CH*Me$_a$*Me$_b$)), 17.9 (P(CHMe$_a$*Me$_b$*)), 17.2 (d, $^2J_{PC}$ = 3.8 Hz, P(CHMe$_c$*Me$_d$*)), 9.4 (C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 43.2. ^{29}Si NMR δ 89.1. A crystal of one of the diastereomers of **11** suitable for X-ray crystallographic analysis was grown by evaporation of a concentrated diethyl ether solution of **11a**,**b** at ambient temperature.

General Protocol for Ketone Hydrosilylation Experiments. Representative protocols for reactions involving acetophenone and $PhSiH_3$ are presented. Within a glovebox, a glass vial was charged with a stir-bar, **8** (2.1 mg, 0.004 mmol), $LiB(C_6F_5)_4 \cdot 2.5Et_2O$ (3.5 mg, 0.004 mmol), THF (2 mL), and acetophenone (23.4 μL, 0.2 mmol). The resulting solution was stirred for 10 min followed by the addition of $PhSiH_3$ (37.0 μL, 0.3 mmol). The resulting mixture was magnetically stirred for 5 h at ambient temperature, at which time the contents of the vial were cooled to 0 °C followed by the addition of acetone (5 mL) and 1 M HCl(aq) (ca. 5 mL). The mixture was stirred for 2 h at 0 °C followed by 0.5 h at ambient temperature. An aqueous solution of saturated sodium bicarbonate was added (ca. 5 mL), and the reaction mixture was stirred until no more gas evolution was observed (ca. 0.25 h). The reaction mixture was extracted with Et_2O (2 × 5 mL). The combined organic layers were dried over Na_2SO_4, filtered through a plug of silica, and concentrated *in vacuo*. This solution was transferred to a GC vial and sealed. Products were identified by comparison to the ^{1}H NMR of authentic samples, while quantitative data (average of at least two independent experiments) were obtained from GC-FID analysis using a Supelco BETA-DEX 120 column.

Crystallographic Solution and Refinement Details. For each of the crystallographically characterized compounds reported herein, single-crystal X-ray diffraction data were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, and data reduction were supplied by Bruker. Gaussian integration (for **1** and **11**), TWINABS (for **[2·CO]$^+$OTf$^-$**), or SADABS (for **3·CH$_3$CN** and **7**) was employed as the absorption correction method, and the structure was solved by use of a Patterson search/structure expansion (for **1** and **3·CH$_3$CN**) or direct methods (for **[2·CO]$^+$OTf$^-$**, **7**, and **11**). The crystal of **[2·CO]$^+$OTf$^-$** used for data collection was found to display nonmerohedral twinning, and both components of the twin were indexed by use of the program CELL_NOW (Bruker AXS Inc., Madison, WI, 2004). The second twin component can be related to the first component by 180° rotation about the [−0.390 −0.180 1] axis in real space and about the [−0.002 0 1] axis in reciprocal space. Integrated intensities for the reflections from the two components were written into a SHELXL-93 HKLF 5 reflection file by use of the data integration program SAINT (version 7.06A), employing all reflection data (exactly overlapped, partially overlapped, and nonoverlapped). Each structure was refined by use of full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-H atoms, and all H-atoms were added at calculated positions (with the exception of Si−*H* and Ir−*H*, which were located in the difference map) and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. For each of **7** and **11**, the near-zero final refined value of the Flack[28] absolute structure parameter (−0.005(3) for **7**; 0.002(5) for **11**) supported that the correct absolute structure had been chosen. Additional crystallographic information is provided in the accompanying crystallographic information file (CIF).

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Note Added in Proof. While this manuscript was under review, a related study of Cp*Ir(PS) complexes was reported: Ohki, Y.; Sakamoto, M.; Tatsumi, K. *J. Am. Chem. Soc.* **2008**, *130*, 11610.

Supporting Information Available: X-ray crystallographic information files (CIF) for **1**, **[2·CO]$^+$OTf$^-$**, **3·CH$_3$CN**, **7**, and **11**, as well as *in situ* NMR spectra for the reactions involving the formation of **[9]$^+$B(C$_6$F$_5$)$_4^-$** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) The Flack absolute structure parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration: (a) Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, *A55*, 908. (b) Flack, H. D.; Bernardinelli, G. *J. Appl. Crystallogr.* **2000**, *33*, 1143.