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Exploring the Utility of Neutral Rhodium and Iridium κ^2-*P*,*O* and κ^2-P(*S*),*O* Complexes as Catalysts for Alkene Hydrogenation and Hydrosilylation

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Heating of $[(\mathrm{COD})\mathrm{M}(\kappa^2\text{-}3\text{-}P^i\mathrm{Pr}_2\text{-}2\text{-}N\mathrm{Me}_2\text{-indene})]^+\mathrm{X}^-$ (M = Rh or Ir; X = BF_4, PF_6; COD = η^4-1,5-cyclooctadiene) in a mixture of water and THF (48 h, 60 °C) afforded the neutral (COD)M(κ^2-*P*,*O*) complexes (M = Rh, **5a**, 80%; M = Ir, **5b**, 74%). Similarly, thermolysis of $[(\mathrm{COD})\mathrm{M}(\kappa^2\text{-}3\text{-}\mathrm{P}(S)^i\mathrm{Pr}_2\text{-}2\text{-}N\mathrm{Me}_2\text{-indene})]^+\mathrm{BF}_4^-$ (M = Rh or Ir) in a mixture of water and CH_2Cl_2 (14 h, 60 °C) produced the neutral (COD)M(κ^2-P(*S*),*O*) complexes (M = Rh, **13a**, 91%; M = Ir, **13b**, 90%). Subsequent preparation of 1-P^{i}Pr$_2$-2-indanone (**8**, 91%) enabled the non-hydrolytic synthesis of **5b** in 70% isolated yield via treatment with 0.5[(COD)IrCl]$_2$ in the presence of NEt_3. Lithiation of (*o*-P^{i}Pr$_2$)phenol followed by quenching with 0.5[(COD)IrCl]$_2$ afforded the neutral (COD)Ir(κ^2-*P*,*O*) complex **10** (91%). Single-crystal X-ray diffraction data are provided for **5b**, **10**, **13a**, and **13b**. Whereas **5a**, **13a**, and **13b** performed poorly as catalysts for the hydrogenation of alkenes, the known complex (COD)Ir(OPh)(PCy$_3$) **2** as well as **5b** and **10** proved to be excellent catalysts for hydrogenation of mono-, di-, and trisubstituted alkene substrates under mild conditions (22 °C, ∼1 atm H_2). Complexes **13a,b** were also shown to be competent catalysts for addition of triethylsilane to styrene.

Introduction

Cationic square-planar complexes of the heavier group 9 metals are among the most effective classes of homogeneous catalysts for addition of E−H bonds (E = main-group element) to unsaturated substrates.[1−3] Crabtree's catalyst ($[(\mathrm{COD})\mathrm{Ir}(\mathrm{PCy}_3)(\mathrm{Py})]^+\mathrm{PF}_6^-$, **1**; COD = η^4-1,5-cyclooctadiene, Cy = cyclohexyl, Py = pyridine) serves as a prototypical example of such species and remains among the most active catalysts for hydrogenation of substituted alkenes.[2] However, poor solubility in low-polarity media and thermal instability place limits on the conditions under which **1** and related cationic group 9 catalysts can be employed.[2] In building upon observations made by Crabtree and co-workers that a formally cationic Ir center and a mixed P,N ancillary ligand set were needed in order to achieve optimal catalytic performance in alkene hydrogenation,[2b] considerable effort has been directed toward development of heterobidentate relatives of **1**, including chiral variants.[4,5] While cationic chelate complexes of this type have proven to be less susceptible to thermal decomposition and/or bimolecular deactivation than **1**,[5] such salts are rarely soluble in aliphatic hydrocarbons and are commonly deactivated in polar, coordinating solvents. Although tuning of the accompanying counteranion can provide a means of improving the solubility profile of such group 9 salts, it has been demonstrated that such modifications can impact negatively the catalytic behavior of the cationic complex.[5,6] Given the potential for increased catalytic activity and/or altered substrate selectivity that might be achieved by carrying out Ir-mediated alkene hydrogenations in low-coordinating media, development of more lipophilic neutral Ir catalysts that are thermally stable, yet suitably reactive, represents a worthwhile pursuit. Surprisingly, the study of neutral Ir hydrogenation catalysts has received very little attention,[7] possibly due in part to early reports documenting the poor catalytic performance of complexes

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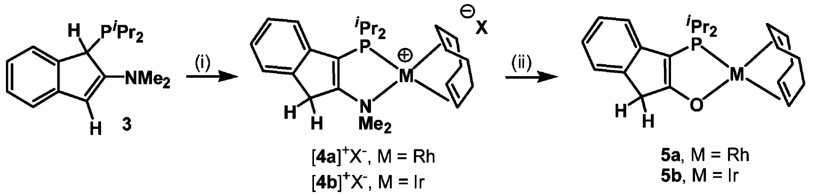
Scheme 1. Synthesis of κ^2-*P,O* Rh and Ir Complexes[a]



[a] Reagents: (i) 0.5 $[(COD)MCl]_2$, AgX (X = Bf_4, PF_6); (ii) excess H_2O in THF (1:5 volume ratio) (COD = η^4-1,5-cyclooctadiene).

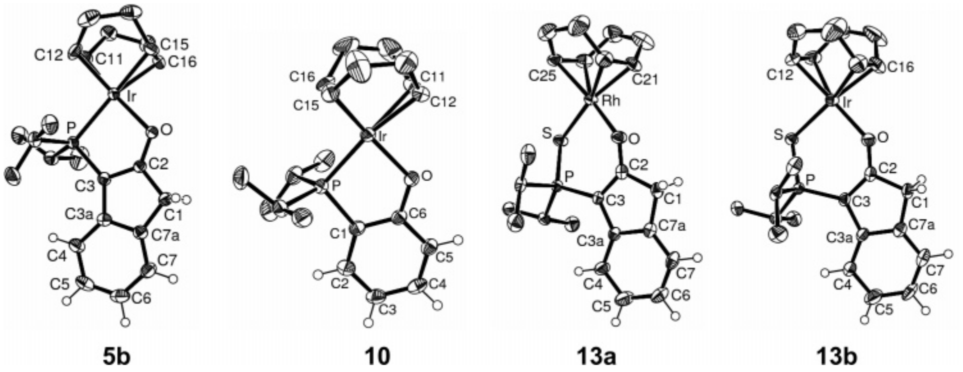


Figure 1. Crystallographically determined structures of **5b**, **10**, **13a**, and **13b** shown with 50% displacement ellipsoids and atomic numbering scheme indicated; only one of the two crystallographically independent molecules of **5b** is shown, and selected H atoms have been omitted for clarity.

including $(PPh_3)_3IrCl$,[8] relative to neutral Rh species such as Wilkinson's catalyst ($(PPh_3)_3RhCl$).[9]

In this context, we initiated a research program targeting new classes of neutral Rh and Ir complexes that exhibit the desirable reactivity properties of cationic catalysts such as **1** and function effectively in low-polarity solvents.[10] In consideration of the hard (N) and soft (P) donor ligands featured in **1** and given the beneficial reactivity properties imparted by P,O-ligands on alternative classes of metal catalysts,[11] we became interested in evaluating neutral Rh and Ir complexes supported by κ^2-*P*,*O* phosphinoenolates as catalysts for alkene hydrogenation and other E−H bond additions to unsaturated substrates. Related complexes featuring κ^2-P(*S*),*O* phosphine sulfide ligands also represented appealing targets from a practical perspective since phosphine sulfides typically exhibit increased oxygen stability relative to the parent phosphines while at the same time providing a relatively soft sulfur donor atom for binding to the heavier group 9 metals.[12] Although a few isolated reports examining (κ^2-*P*,*O*)Rh catalysts of this type have appeared,[13] the catalytic abilities of related neutral (κ^2-*P*,*O*)Ir complexes as well as (κ^2-P(*S*),*O*)M (M = Rh, Ir) species in E−H bond addition chemistry have yet to be documented systematically. Herein we report the synthesis and characterization of neutral Rh and Ir complexes featuring κ^2-*P*,*O* and κ^2-P(*S*),*O* ligands and the application of these new group 9 complexes, as well as the related complex (COD)Ir(OPh)(PCy_3) **2**,[14] as catalysts for the hydrogenation or hydrosilylation of alkenes. Despite the preponderance of experimental evidence suggesting that square-planar Ir complexes should be formally cationic in order to function effectively as catalysts for alkene hydrogenation, the thermally robust (COD)Ir(*P*,*O*) derivatives featured herein are capable of mediating the reduction of substituted alkenes under mild conditions (~1 atm H_2, 22 °C) in a range of solvents including aliphatic hydrocarbons and without the need for rigorous inert-atmosphere techniques. A portion of these results have been communicated previously.[15]

Results and Discussion

Synthesis and Characterization of Neutral κ^2-*P,O* Complexes. We reported that the P,N-substituted indene **3** can be employed in the preparation of Rh and Ir κ^2-*P*,*N* salts $[\mathbf{4a}]^+X^-$ and $[\mathbf{4b}]^+X^-$ (Scheme 1) as well as structurally related zwitterionic complexes.[10] In the course of examining the reactivity properties of these κ^2-*P*,*N* species, we became interested in assessing the stability of $[\mathbf{4a,b}]^+X^-$ in a mixture of water and THF (1:5 volume ratio). After 48 h at 60 °C each of these salts was transformed cleanly into the corresponding neutral κ^2-*P*,*O* complex **5a** or **5b**, which in turn was isolated in analytically pure form (80% and 74%, respectively) and characterized spectroscopically. One of the two crystallographically independent molecules of **5b** is presented as an ORTEP[16] diagram 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 **5b** compare well with those observed in alternative donor-substituted indene

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Table 1. Crystallographic Data for 5b, 10, 13a, and 13b

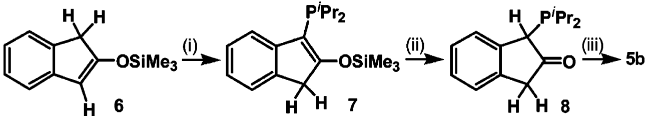
	5b	**10**	**13a**	**13b**
empirical formula	$C_{23}H_{32}OPIr$	$C_{20}H_{30}OPIr$	$C_{23}H_{32}OPSRh$	$C_{23}H_{32}OPSIr$
fw	547.66	509.61	490.43	579.72
cryst dimens	0.51 × 0.46 × 0.20	0.20 × 0.20 × 0.11	0.31 × 0.08 × 0.04	0.56 × 0.08 × 0.03
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	23.180(2)	9.5940(2)	11.5449(8)	11.238(1)
b (Å)	7.4095(8)	13.7660(3)	16.358(1)	16.826(2)
c (Å)	26.823(3)	15.0380(3)	12.4929(9)	12.621(1)
β (deg)	113.899(2)	103.801(1)	111.797(1)	112.260(1)
V (Å^3)	4211.8(8)	1928.73(7)	2190.6(3)	2208.7(3)
Z	8	4	4	4
ρ_{calcd} (g cm^{-3})	1.727	1.755	1.487	1.743
μ (mm^{-1})	6.425	7.008	0.958	6.222
2θ limit (deg)	52.90	60.02	52.80	52.78
	$-29 \leq h \leq 28$	$-13 \leq h \leq 13$	$-14 \leq h \leq 14$	$-14 \leq h \leq 14$
	$-8 \leq k \leq 9$	$-16 \leq k \leq 19$	$-20 \leq k \leq 20$	$-20 \leq k \leq 21$
	$-33 \leq l \leq 30$	$-21 \leq l \leq 20$	$-15 \leq l \leq 15$	$-15 \leq l \leq 15$
total data collected	23 833	9280	16 430	17 208
independent reflns	8649	5627	4490	4512
R_{int}	0.0473	0.0283	0.0759	0.0406
obs reflns	7504	4716	3296	3840
range of transmission	0.3598−0.1381	0.4868−0.3346	0.9627−0.7554	0.8353−0.1283
data/restraints/params	8649/0/469	5627/0/213	4490/0/244	4512/0/244
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0345	0.0339	0.0375	0.0243
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0744	0.0871	0.0796	0.0564
goodness-of-fit	1.060	1.052	0.992	1.038

Table 2. Selected Interatomic Distances (Å) for 5b, 10, 13a, and 13b

	5b^a	**5b**^{b}	**10**	**13a**	**13b**
M−P	2.320(1)	2.318(1)	2.289(1)		
M−S				2.3571(9)	2.335(1)
M−O	2.058(3)	2.059(3)	2.028(3)	2.057(2)	2.053(3)
M−$C_{alkene1}$^{c}	2.181(5)	2.172(5)	2.168(4)	2.112(3)	2.111(4)
M−$C_{alkene2}$^{c}	2.164(5)	2.184(5)	2.195(4)	2.119(4)	2.111(4)
M−$C_{alkene3}$^{d}	2.117(5)	2.105(5)	2.100(4)	2.103(3)	2.102(4)
M−$C_{alkene4}$^{d}	2.099(6)	2.122(5)	2.113(4)	2.104(4)	2.094(4)
$^iPr_2P-C$	1.779(5)	1.779(5)	1.807(4)	1.763(3)	1.766(4)
P−S				2.020(1)	2.027(1)
O−C	1.302(6)	1.311(6)	1.339(5)	1.277(4)	1.290(5)
C1−C2	1.514(7)	1.518(7)	1.396(6)	1.513(4)	1.509(5)
C2−C3	1.380(7)	1.369(7)	1.386(6)	1.397(5)	1.378(5)

[a,b] Within the first and second crystallographically independent molecules of **5b**, respectively. [c] The metal−cyclooctadiene distances trans to P or S. [d] The metal−cyclooctadiene distances trans to O.

Scheme 2. Rational Synthesis of 5b[a]



[a] Reagents: (i) *n*-BuLi, then ClP^iPr_2; (ii) $HCl_{(aq)}$, then $NH_4OH_{(aq)}$; (iii) NEt_3, 0.5 $[(COD)IrCl]_2$ (COD = η^4-1,5-cyclooctadiene).

complexes and related Ir κ^2-*P*,*O* species.[10,17,18] The C2−C3 distances in the two crystallographically independent molecules of **5b** (1.380(7) and 1.369(7) Å) each are in keeping with a C═C double bond, and the O−C2 linkages (1.302(6) and 1.311(6) Å) are elongated relative to the O═C bond typically found in ketones (~ 1.23 Å).[19] While these structural data suggest that **5b** can be described as a phosphinoenolate complex, the contracted $^iPr_2P-C_{ind}$ distances in **5b** (both 1.779(5) Å) indicate that alternative β-ketophosphine-type resonance contributors, including those featuring a $^iPr_2P{=}C3$ linkage and a formal anionic charge on phosphorus, may also figure prominently in **5b**.[20] In addition, the Ir−alkene distances trans to P are elongated relative to the Ir−alkene distances trans to O, in keeping with the greater trans influence anticipated for a phosphine fragment relative to an alkoxy donor on Ir. Although the direct insertion of Rh and Ir into N−C bonds is precedented,[21] we propose that the N−C_{ind} cleavage process leading to formation of **5a** and **5b** proceeds by an enamine hydrolysis reaction involving a coordinated 3-P^iPr_2-2-NMe_2-indene ligand in $[\mathbf{4a}]^+X^-$ and $[\mathbf{4b}]^+X^-$ in which the bound $[(COD)M]^+$ fragment functions as a Lewis acid activator.[22] Interestingly, the uncoordinated enamine **3** is not hydrolyzed under similar experimental conditions. In contrast to the cationic Ir complexes **1**[2] and $[\mathbf{4b}]^+X^-$,[10] the neutral Ir species **5b** is soluble in high-polarity (THF, CH_2Cl_2, CH_3CN) and low-polarity (hexanes, benzene) solvents. Moreover, no decomposition was detected spectroscopically (^{31}P NMR) for either **2** or **5b** upon heating in toluene for a minimum of 1 week at 100 °C.[23]

Given the desirable catalytic properties exhibited by **5b** (vide infra), we sought to develop an alternative, non-hydrolytic synthetic route to this Ir complex (Scheme 2). Treatment of 2-indanone with $ClSiMe_3$ in the presence of NEt_3 afforded the known silyl ether **6**.[24] Subsequent lithiation of **6** followed by quenching with ClP^iPr_2 provided the intermediate **7**, which was converted to the β-ketophosphine **8** in 91% isolated yield upon exposure to aqueous HCl followed by workup with aqueous NH_4OH. Treatment of **8** with 0.5$[(COD)IrCl]_2$ in the presence of NEt_3 afforded **5b** in 70% isolated yield.

An alternative neutral (COD)Ir(κ^2-*P*,*O*) complex **10** was prepared in 90% isolated yield via lithiation of the known ortho-

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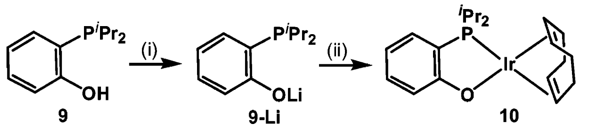
Scheme 3. Preparation of 10^a



^{a} Reagents: (i) n-BuLi; (ii) 0.5 [(COD)IrCl]$_2$ (COD = η^4-1,5-cyclooctadiene).

Table 3. Ir-Catalyzed Styrene Hydrogenation Results^a

entry	catalyst (mol %)	solvent	t (h)^b	%^{b}
3-1	**5b** (1.0)	CH_2Cl_2	4	68
3-2	**5b** (1.0)	THF	4	>99
3-3	**5b** (1.0)	benzene	4	>99
3-4	**5b** (0.5)	hexanes^c	0.25	>99
3-5	**5b** (0.05)	hexanes	4	>99
3-6	**10** (0.5)	hexanes	0.5	>99
3-7	**10** (0.05)	hexanes	4	41
3-8	**2** (0.5)	CH_2Cl_2^{d}	4	>99

^{a} Conditions: 22 °C; ~1 atm H_2. ^{b} Percent conversion at time (t) of styrene to ethylbenzene, determined on the basis of GC-MS and GC-FID data rounded to the nearest percent. For reactions employing 5.0 mol % **5a** as a catalyst, <10% styrene conversion was achieved after 4 h in either CH_2Cl_2, THF, or hexanes. ^{c} No reduction in catalyst performance was observed when the reagents, catalyst, and solvent were handled in the open air, and no efforts were made to purify the hexanes prior to use. ^{d} Solvent chosen due to the poor solubility of **2** in THF or hexanes.

Table 4. Ir-Catalyzed Hydrogenation of Cyclohexene (C) and 1-Methylcyclohexene (M)^a

entry	catalyst (mol %)	substrate	solvent	t (h)^b	%^{b}
4-1	**5b** (1.0)	C	hexanes	20	87
4-2	**5b** (5.0)	C	hexanes	4	97^c
4-3	**10** (1.0)	C	hexanes	20	>99
4-4	**10** (5.0)	C	hexanes	4	98^c
4-5	**2** (1.0)	C	CH_2Cl_2^{d}	4	>99
4-6	**5b** (5.0)	M	hexanes	20	41
4-7	**10** (5.0)	M	hexanes	20	81^e
4-8	**2** (5.0)	M	CH_2Cl_2^{d}	20	39

^{a} Conditions: 22 °C; ~1 atm H_2. ^{b} Percent conversion at time (t) of the alkene to the corresponding saturated hydrocarbon, determined on the basis of GC-MS and GC-FID data rounded to the nearest percent. ^{c} Greater than 99% conversion is achieved after 20 h. ^{d} Solvent chosen due to the poor solubility of **2** in THF or hexanes. ^{e} 91% conversion is achieved after 36 h.

substituted phenol **9**,[25] followed by quenching of the intermediate **9-Li** with 0.5[(COD)IrCl]$_2$ (Scheme 3). The connectivity in **10** was established by use of NMR spectroscopic and X-ray crystallographic techniques (Figure 1). While in general the structural features observed in **10** mirror those of **5b**, the former exhibits an elongated O−C linkage (1.339(5) Å) and somewhat shorter Ir−P (2.289(1) Å) and Ir−O (2.028(3) Å) distances relative to the latter. In keeping with the thermal stability exhibited by **2** and **5b**, complex **10** proved stable upon heating in toluene for a minimum of 1 week at 100 °C (^{31}P NMR).

Alkene Hydrogenation Studies. The hydrogenation of styrene (22 °C, ~1 atm H_2) was selected as an initial test reaction with which to evaluate the catalytic abilities of complexes **2**, **5a**, **5b**, and **10** (Table 3). In contrast to the poor catalytic performance exhibited by **5a** (<10% conversion, 4 h, 5.0 mol % **5a**), each of the neutral Ir complexes under similar conditions was found to be a competent catalyst for this transformation at relatively low catalyst loadings (≤1.0 mol %). In evaluating the influence of solvent on the catalytic performance of **5b** (1.0 mol %), incomplete styrene conversion was observed for reactions conducted in CH_2Cl_2 (68%, 4 h; entry 3-1), while clean reductions were achieved after 4 h in both THF (entry 3-2) and benzene (entry 3-3). In contrast to **1**, for which chlorocarbons such as CH_2Cl_2 are the solvents of choice for alkene hydrogenations,[2b] optimal catalytic performance for **5b** was achieved by use of hexanes as the reaction medium with quantitative conversions achieved after only 0.25 h by use of 0.5 mol % **5b** (entry 3-4) or after 4 h by use of 0.05 mol % **5b** (entry 3-5). Notably, the catalytic performance of **5b** in hexanes rivals that of the benchmark complex **1** in CH_2Cl_2,[2,10] and no significant reduction in catalytic performance was noted when employing 0.5 mol % **5b** (entry 3-4) on the benchtop without the rigorous exclusion of oxygen and using hexanes that had not been dried. Complex **10** also proved to be an effective styrene hydrogenation catalyst in hexanes at the 0.5 mol % loading level (>99%, 0.5 h; entry 3-6). However, unlike **5b**, incomplete styrene conversion (41%) was achieved after 4 h using 0.05 mol % **10** as a catalyst (entry 3-7). The nonchelating species **2** exhibited poor solubility in hexanes despite the structural similarities that exist between this complex and the hydrocarbon-soluble bidentate complexes **5b** and **10**. While the low solubility of **2** in hexanes precluded an investigation of the catalytic abilities of this complex in aliphatic hydrocarbons, complex **2** was observed to out-perform **5b** as a catalyst in CH_2Cl_2, providing ethylbenzene quantitatively after 4 h by use of 0.5 mol % **2** (entry 3-8).

Cationic square-planar Ir complexes including **1** are noteworthy for their ability to reduce polysubstituted alkenes lacking adjacent polar functionalities.[2,4,5] In this regard, we became interested in assessing the catalytic utility of the neutral Ir complexes **2**, **5b**, and **10** for the hydrogenation of cyclohexene and 1-methylcyclohexene under mild experimental conditions (22 °C, ~1 atm H_2; Table 4). Building on the results of our styrene hydrogenation reactivity survey, hexanes was selected as the solvent of choice when using either **5b** or **10** as a catalyst, while reactions employing **2** as a catalyst were conducted in CH_2Cl_2. Use of 1.0 mol % **5b** as a catalyst enabled the reduction of cyclohexene to a significant extent (87%; entry 4-1) after 20 h, while under similar conditions employing 1.0 mol % **10**, quantitative conversion to cyclohexane was achieved (entry 4-3). Upon increasing the catalyst loading to 5.0 mol % **5b** or **10**, nearly quantitative reductions were realized after 4 h (entries 4-2 and 4-4, respectively). Complex **2** proved more effective than either **5b** or **10**, providing quantitative cyclohexene reductions in 4 h at the 1.0 mol % catalyst loading level (entry 4-5). Other differences in the catalytic abilities of **2**, **5b**, and **10** emerged when employing 5.0 mol % catalyst for the reduction of 1-methylcyclohexene over 20 h; whereas 81% conversion to 1-methylcyclohexane was achieved by use of **10** (entry 4-7; 91% after 36 h), lower conversions were obtained either using **5b** (41%; entry 4-6) or **2** (39%; entry 4-8). While **10** was observed to out-perform the prototypical neutral group 9 catalyst $(PPh_3)_3RhCl$ in the reduction of 1-methylcyclohexene,[26] it is important to recognize that the activity exhibited by **10** is vastly inferior to that of **1**; under similar experimental conditions employing 0.5 mol % **1** in CH_2Cl_2, the near quantitative reduction (97%) of this trisubstituted alkene was achieved after only 4 h.[27]

Synthesis and Characterization of Neutral κ^2-P(S),O Complexes. We have described previously the conversion of **3**

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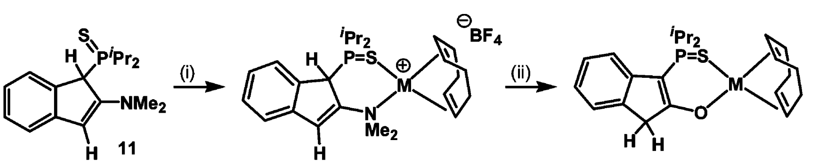
[25] Heinicke, J.; Köhler, M.; Peulecke, N.; He, M.; Kindermann, M. K.; Keim, W.; Fink, G. *Chem. Eur. J.* **2003**, *9*, 6093.

[26] Under similar conditions employing 5.0 mol% $(PPh_3)_3RhCl$ (22 °C, ~1 atm H_2, THF, 20 h), 59 % conversion to 1-methylcyclohexane was achieved. In attempting to employ hexanes in place of THF as the reaction medium, <5 % conversion was achieved as a result of the poor solubility of $(PPh_3)_3RhCl$ in aliphatic hydrocarbons.

[27] Cipot, J.; McDonald, R.; Stradiotto, M. *Chem. Commun.* **2005**, 4932.

Scheme 4. Synthesis of κ^2-P(*S*),*O* Rh and Ir Complexes[a]



[**12a**]$^+$BF$_4^-$, M = Rh
[**12b**]$^+$BF$_4^-$, M = Ir

13a, M = Rh
13b, M = Ir

[a] Reagents: (i) 0.5 [(COD)MCl]$_2$, AgBF$_4$; (ii) excess H$_2$O in dichloromethane (1:8 volume ratio) (COD = η^4-1,5-cyclooctadiene).

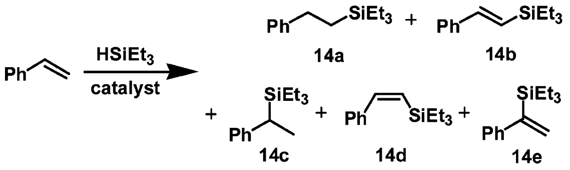
Table 5. Addition of Triethylsilane to Styrene[a]

entry	catalyst	solvent	%[b]	**14a**[c]	**14b**[c]	**14c**[c]	other[c]
5-1	**13a**	DCE	>99	14	84	2	<1
5-2	**13a**	benzene	94	12	79	3	<1
5-3	**13b**	DCE	95	29	53	5	8
5-4	**13b**	benzene	6	2	4	<1	<1

[a] Conditions: 60 °C, 5.0 mol % catalyst; styrene-to-silane ratio of 5:1; DCE = 1,2-dichloroethane. [b] Percent conversion based on the consumption of triethylsilane at 24 h. [c] Product distribution determined on the basis of GC-MS and GC-FID data, rounded to the nearest percent; other silicon-containing products including **14d** and **14e**.

into **11** and use of this phosphine sulfide as a ligand in the preparation of the cationic complexes [**12a,b**]$^+$BF$_4^-$ (Scheme 4).[28] In keeping with the clean hydrolysis of [**4a,b**]$^+$X$^-$ leading to **5a,b** (vide supra), in solution the κ^2-P(*S*),*N* complexes [**12a,b**]$^+$BF$_4^-$ were transformed cleanly into the corresponding κ^2-P(*S*),*O* species **13a,b** upon heating in the presence of water. Complexes **13a,b** were isolated in analytically pure form (91% and 90%, respectively) and in turn characterized by use of NMR spectroscopic and X-ray crystallographic techniques (Figure 1). The overall structural features found in **13a,b** can be compared with those observed in **5a,b** as well as in some other indenylphosphine sulfide complexes of Rh and Ir.[18,28] While the ^{i}Pr$_2$(S)P−C_{ind} distances in both **13a** (1.763(3) Å) and **13b** (1.766(4) Å) are contracted relative to **11** (1.873(2) Å),[28] the corresponding P−S linkages in **13a** (2.020(1) Å) and **13b** (2.027(1) Å) are elongated relative to **11** (1.9665(6) Å).[28,29] These metrical data, when considered along with the relatively short O−*C*2 distances observed in **13a,b** (1.277(4) and 1.290(5) Å, respectively), indicate that a resonance structure featuring ^{i}Pr$_2$(S)P=C3 and *O*=*C*2 linkages and a formal anionic charge on sulfur contributes significantly in these κ^2-P(*S*),*O* complexes. In addition, the equidistant M−COD linkages point to a similar trans influence for the O and S donors in **13a,b**. Notably, complexes **13a,b** proved stable to heating in toluene for a minimum of 1 week at 100 °C.

Alkene Hydrosilylation Mediated by 13a and 13b. In stark contrast to the desirable catalytic properties exhibited by **2**, **5b**, and **10** in the hydrogenation of alkenes, for reactions employing 5.0 mol % **13a** or **13b** as a catalyst, less than 10% styrene conversion was achieved after 4 h in CH$_2$Cl$_2$, THF, or hexanes. In a preliminary effort to assess the catalytic utility of **13a,b** in alternative E−H addition reactions, addition of triethylsilane to styrene was examined (60 °C, 5.0 mol % **13a** or **13b**, 24 h; Table 5); the predominant products typically formed in this transformation (**14a**−**e**) are depicted in eq 1.[30] The Rh complex



(1)

13a proved to be an effective catalyst for this transformation, affording quantitative substrate conversion and good selectivity (84% **14b**; entry 5-1) for reactions conducted in 1,2-dichloroethane. The activity and selectivity of **13a** was diminished only modestly in changing the solvent to benzene (entry 5-2). By comparison, the Ir complex **13b** proved inferior to **13a** both in terms of activity and selectivity, especially for reactions conducted in benzene (entries 5-3 and 5-4).

Summary and Conclusions

In contrast to the many neutral Rh complexes (e.g., Wilkinson's catalyst) that have proven capable of mediating the hydrogenation of alkene substrates, analogous neutral Ir catalysts are still very rare. In this context the results presented herein establish neutral (COD)Ir(*P*,*O*) complexes, including **2**, **5b**, and **10**, as a highly active class of catalysts for the hydrogenation of substituted alkenes under mild conditions (22 °C, ~1 atm H$_2$). In the case of styrene hydrogenation, the catalytic performance of **5b** was found to be competitive with Crabtree's prototypical cationic Ir catalyst (**1**), and no significant reduction in catalytic performance was noted for reactions mediated by **5b** when employing benchtop experimental protocols. In contrast, the neutral (COD)Rh(κ^2-*P*,*O*) species **5a** as well as the (COD)M(κ^2-P(*S*),*O*) complexes (M = Rh, **13a**; M = Ir, **13b**) functioned poorly as catalysts for styrene hydrogenation under similar conditions. Complexes **2**, **5b**, and **10** also proved to be effective catalysts for reduction of cyclohexene and 1-methylcyclohexene, in some cases out-performing Wilkinson's catalyst under similar conditions. Whereas the noteworthy catalytic activity exhibited by **2**, **5b**, and **10** in the reduction of polysubstituted alkenes was found to be less than that of **1**, it is evident that the solubility and stability profiles of these neutral (COD)Ir(*P*,*O*) complexes can offer some practical advantages over traditionally employed cationic Ir complexes. While **1** is temperature sensitive and functions almost exclusively in chlorocarbons, the neutral complexes **2**, **5b**, and **10** are thermally robust and in the case of **5b** and **10** exhibit optimal catalytic performance in aliphatic hydrocarbons while remaining active

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(28) Wechsler, D.; Myers, A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Inorg. Chem.* **2006**, *45*, 4562.

(29) Similar structural characteristics have been observed in other complexes featuring anionic phosphine sulfide ligands. For selected examples, see: (a) Browning, J.; Dixon, K. R.; Meanwell, N. J.; Wang, F. *J. Organomet. Chem.* **1993**, *460*, 117. (b) Browning, J.; Bushnell, G. W.; Dixon, K. R.; Hilts, R. W. *J. Organomet. Chem.* **1993**, *452*, 205. (c) Browning, J.; Bushnell, G. W.; Dixon, K. R.; Hilts, R. W. *J. Organomet. Chem.* **1992**, *434*, 241.

(30) For selected reviews on metal-catalyzed hydrosilylation, see: (a) Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374. (b) Ojima, I.; Li, Z.; Zhu, J. In *Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, p 1687. (c) Marciniec, B.; Guliński, J. *J. Organomet. Chem.* **1993**, *446*, 15. (d) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, p 763.

in other polar and nonpolar media. Encouraged by the experimental results detailed herein, our current research efforts are directed toward development of increasingly active neutral Ir catalyst complexes for use in hydrogenation reactions as well as other conceptually related catalytic transformations involving addition of E−H bonds to unsaturated substrates with an emphasis on identification of active catalysts that are complementary to more traditional cationic group 9 catalysts. Our progress in these areas will be the subject of future reports.

Experimental Section

General Considerations. Except where noted, 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 non-deuterated solvents tetrahydrofuran, diethyl ether, dichloromethane, benzene, hexanes, 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. Tetrahydrofuran, diethyl ether, and dichloromethane were purified over two alumina-packed columns, while benzene, hexanes, and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. $CDCl_3$ (Aldrich) was degassed 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. Purification of NEt_3 was achieved by stirring over KOH for 7 days, followed by distillation; the distilled NEt_3 was then refluxed over CaH_2 for 3 days under dinitrogen, followed by distillation. The solvents used within the glovebox were stored over activated 4 Å molecular sieves. Hydrogen (99.999%, UHP Grade) was obtained from Air Liquide and used as received. Compounds **2**,[14] $[\mathbf{4a,b}]^+X^-$,[10] **6**,[24] and $[\mathbf{12a,b}]^+BF_4^-$,[28] were prepared using literature methods and dried in vacuo for 24 h prior to use. Compound **9** was prepared using a modification to the synthesis described by Heinicke et al.,[25] whereby *N,N,N′,N′*-tetramethylethylenediamine was not used in the lithiation of phenyl methoxymethyl ether and 2-(diisopropylphosphino)phenyl methoxymethyl ether was converted into **9** using a deprotection protocol similar to that described by Long et al.[31] Compound **9-Li** was prepared via addition of *n*-BuLi to a pentane solution of **9**; the precipitated **9-Li** was washed with pentane, dried in vacuo for 24 h, and used without further purification. All other liquid solvents or reagents (Aldrich) were degassed using three repeated freeze−pump−thaw cycles and then dried over 4 Å molecular sieves for 24 h prior to use (with the exception of 1.6 M *n*-BuLi in hexanes, which was used as received), while solid reagents were dried in vacuo for 24 h prior to use. All ^{1}H, ^{13}C, and ^{31}P NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 125.8, and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of $SiMe_4$ (for ^{1}H and ^{13}C) 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, ^{1}H−^{13}C HMBC, and/or 1D ^{1}H NOE NMR experiments. GC-FID analyses were performed on a Perkin-Elmer Autosystem Gas Chromatograph, while GC-MS analyses were performed on a Varian Saturn-2000 system. All GC analyses were carried out using a 30 m × 0.53 mm J&W DB5 column, with helium as the carrier gas. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia (Canada). The atomic numbering scheme employed herein is that featured in Figure 1.

Preparation of 5a. Complex $[\mathbf{4a}]^+BF_4^-$ (0.065 g, 0.12 mmol) was dissolved in THF (5 mL). The resulting orange solution was transferred to a resealable reaction flask that was sealed under nitrogen with a PTFE valve. The reaction flask was transferred to the Schlenk line, and distilled water (1 mL; previously sparged 30 min with nitrogen) was added to the mixture via syringe. The headspace of the reaction flask was partially evacuated, and the vessel was sealed and placed into a 60 °C oil bath. After 48 h of heating, the flask was removed from the oil bath and cooled to room temperature, at which time all solvent and other volatile materials were removed in vacuo. The flask was transferred to the glovebox, and the solid yellow residue was extracted with pentane (3 × 5 mL). The pentane fractions were combined and filtered through a Celite column to remove any insoluble material. Removal of the pentane solvent and other volatile materials in vacuo yielded **5a** as an analytically pure, yellow solid (0.045 g, 0.098 mmol, 80%). Anal. Calcd for $C_{23}H_{32}PORh$: C, 60.27; H, 7.04; N, 0.00. Found: C, 59.98; H, 6.98; N, <0.1. ^{1}H NMR (C_6D_6): δ 7.20 (m, 1H, Ar−H), 7.01 (m, 1H, Ar−H), 6.95−6.90 (m, 2H, Ar−Hs), 5.37−5.36 (m, 2H, COD), 3.76−3.73 (m, 2H, COD), 3.39 (s, 2H, C1(H)$_2$), 2.25−2.15 (m, 4H, P(C*H*Me$_2$)$_2$ and COD), 2.14−2.05 (m, 2H, COD), 1.82−1.75 (m, 2H, COD), 1.67−1.59 (m, 2H, COD), 1.21−1.15 (m, 12H, P(CH*Me*$_a$Me$_b$)$_2$ and P(CHMe$_a$*Me*$_b$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 202.7 (d, $^2J_{PC}$ = 24.2 Hz, *C*2), 145.8 (s, C7a), 140.1 (d, $^2J_{PC}$ = 7.8 Hz, C3a), 126.4, 124.3, 120.1, 116.5 (C4, C5, C6, and C7), 101.1 (COD), 94.3 (d, $^1J_{PC}$ = 44.6 Hz, C3), 66.5 (d, J_{PC} = 13.1 Hz, COD), 38.4 (d, $^3J_{PC}$ = 12.1 Hz, C1), 33.5 (COD), 28.1 (COD), 23.9 (d, $^1J_{PC}$ = 24.4 Hz, P(*C*HMe$_2$)$_2$), 19.2 (P(CH*Me*$_a$-Me$_b$)$_2$), 18.6 (P(CHMe$_a$*Me*$_b$)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 38.1 (d, $^1J_{PRh}$ = 153.0 Hz).

Preparation of 5b (Method A). A procedure analogous to that described for the synthesis of **5a** was employed using $[\mathbf{4b}]^+PF_6^-$ (0.067 g, 0.093 mmol) in place of $[\mathbf{4a}]^+BF_4^-$ and a larger amount of pentane (3 × 10 mL) for the extraction step. Complex **5b** was isolated as an analytically pure, yellow solid (0.038 g, 0.067 mmol, 74%). Anal. Calcd for $C_{23}H_{32}POIr$: C, 50.44; H, 5.89; N, 0.00. Found: C, 50.22; H, 6.11; N, <0.1. ^{1}H NMR (C_6D_6): δ 7.19 (m, 1H, Ar−H), 7.00−6.97 (m, 2H, Ar−Hs), 6.93 (m, 1H, Ar−H), 5.09−5.04 (m, 2H, COD), 3.75−3.52 (m, 2H, COD), 3.42 (s, 2H, C1(H)$_2$), 2.36 (m, 2H, P(C*H*Me$_2$)$_2$), 2.20−2.11 (m, 2H, COD), 2.05−1.95 (m, 2H, COD), 1.70−1.64 (m, 2H, COD), 1.51−1.47 (m, 2H, COD), 1.16−1.11 (m, 12H, P(CH*Me*$_a$Me$_b$)$_2$ and P(CH-Me$_a$*Me*$_b$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 205.4 (d, $^2J_{PC}$ = 22.0 Hz, *C*2), 144.9 (s, C7a), 141.2 (d, $^2J_{PC}$ = 8.2 Hz, C3a), 127.2 (C4 or C7), 125.6 (C5 or C6), 121.3 (C7 or C4), 117.7 (C6 or C5), 97.9 (d, $^1J_{PC}$ = 51.7 Hz, C3), 89.6 (d, J_{PC} = 12.3 Hz, COD), 50.8 (COD), 38.5 (d, $^3J_{PC}$ = 10.2 Hz, C1), 35.2 (COD), 29.4 (COD), 25.0 (d, $^1J_{PC}$ = 30.3 Hz, P(*C*HMe$_2$)$_2$), 19.9 (P(CH*Me*$_a$Me$_b$)$_2$), 18.9 (P(CH-Me$_a$*Me*$_b$)$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 31.7. Crystals of **5b** suitable for single-crystal X-ray diffraction analysis were obtained from a concentrated pentane solution of **5b** stored at −35 °C.

Preparation of 5b (Method B). To a glass vial containing a magnetically stirred solution of **8** (0.065 g, 0.26 mmol) in THF (3 mL) was added NEt_3 (36.6 μL, 0.26 mmol), followed by addition of a solution of $[(COD)IrCl]_2$ (0.087 g, 0.13 mmol) in THF (2 mL). Addition was accompanied by a color change of the solution from light brown to bright orange. The vial was then sealed with a PTFE-lined cap, and the solution was stirred magnetically for 2 h, at which point ^{31}P NMR data collected on an aliquot of the crude reaction indicated quantitative formation of **5b**. After removing all volatiles in vacuo the product was extracted from the residue by treatment with pentane (3 × 2 mL). Filtration of the combined pentane solutions through Celite followed by removal of the solvent in vacuo afforded **5b** as an analytically pure orange solid (0.101 g, 0.18 mmol, 70%).

Preparation of 7. A solution of **6** (0.807 g, 3.96 mmol) in diethyl ether (5 mL) was cooled to −35 °C, and magnetic stirring was

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(31) Long, R. J.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2006**, *45*, 511.

initiated. To this cooled solution was added *n*-BuLi (2.7 mL of a 1.6 M solution in hexanes, 4.32 mmol). The resulting solution was allowed to warm to ambient temperature over the course of 2 h under the influence of magnetic stirring. The vial was cooled to −35 °C followed by addition of ^{i}Pr$_2$PCl (0.63 mL, 3.96 mmol), which effected the precipitation of a white solid. The resulting solution was allowed to warm to ambient temperature over the course of 18 h under the influence of magnetic stirring. The reaction mixture was then filtered through Celite to remove the white precipitate. The diethyl ether was removed in vacuo, affording a dark brown oil (1.19 g) that was characterized spectroscopically as **7** (>95% pure) and used without further purification in the preparation of **8**. ^{1}H NMR (C$_6$D$_6$): δ 7.79 (m, 1H, C4-H or C7-H), 7.28 (m, 1H, C5-H or C6-H), 7.18 (m, 1H, C7-H or C4-H), 7.09 (m, 1H, C6-H or C5-H), 3.14 (s, 2H, CH$_2$), 2.54 (m, 2H, P(C*H*Me$_a$Me$_b$)$_2$), 1.23 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CH*Me$_a$*Me$_b$)$_2$), 1.16 (d of d, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe$_a$*Me$_b$*)$_2$), 0.13 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 166.5 (d, $^2J_{PC}$ = 2.3 Hz, C2), 148.8 (d, J = 17.0 Hz, C3a or C7a), 136.0 (d, J = 4.3 Hz, C7a or C3a), 126.7 (C5 or C6), 122.8 (d, J = 0.9 Hz, C6 or C5), 122.7 (d, J = 0.6 Hz, C4 or C7), 120.5 (d, J = 8.7 Hz, C7 or C4), 112.2 (d, $^1J_{PC}$ = 23.5 Hz, C3), 39.8 (d, $^3J_{PC}$ = 1.4 Hz, C1), 22.8 (d, $^1J_{PC}$ = 9.9 Hz, P(*C*HMe$_a$Me$_b$)), 21.2 (d, $^2J_{PC}$ = 22.0 Hz, P(CH*Me$_a$*Me$_b$)), 20.2 (d, $^2J_{PC}$ = 9.3 Hz, P(CHMe$_a$*Me$_b$*)), 0.33 (SiMe$_3$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −10.5.

Preparation of 8. To a Schlenk flask containing a magnetically stirred solution of **7** (0.176 g, 0.55 mmol) in THF (5 mL) was added 5 M aqueous HCl (5 mL). The resulting solution was placed in a temperature-controlled 60 °C oil bath for 18 h followed by removal of all volatiles in vacuo. The light yellow residue was suspended in diethyl ether (5 mL), treated with 7.5 M aqueous NH$_4$OH solution (5 mL), and stirred at ambient temperature for 1 h. All volatiles were then removed in vacuo to afford a dark brown residue. The residue was treated with diethyl ether (3 × 3 mL), the resultant mixture was filtered through Celite, and the filtrate was collected. Removal of the solvent afforded **8** as an analytically pure, dark brown oil (0.124 g, 0.50 mmol, 91%). Anal. Calcd for C$_{15}$H$_{21}$OP: C, 72.56; H, 8.52; N, 0.00. Found: C, 72.61; H, 8.44; N, <0.1. ^{1}H NMR (C$_6$D$_6$): δ 7.39 (d, $^3J_{HH}$ = 7.0 Hz, 1H, Ar−H), 7.08 (t, $^3J_{HH}$ = 7.5 Hz, 1H, Ar−H), 7.00 (t, $^3J_{HH}$ = 7.0 Hz, 1H, Ar−H), 6.90 (d, $^3J_{HH}$ = 7.5 Hz, 1H, Ar−H), 3.56 (s, 1H, C−H), 3.27−3.13 (m, 2H, CH$_2$ (AB pattern)), 2.34 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.70 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.24 (d of d, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_a$*Me$_b$)), 1.02 (d of d, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me$_b$*)), 0.84 (d of d, $^3J_{PH}$ = 11.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 0.74 (d of d, $^3J_{PH}$ = 14.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me$_d$*)). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 212.8 (d, $^2J_{PC}$ = 3.8 Hz, C═O), 142.4 (d, J = 10.6 Hz, quat.-C), 137.0 (d, J = 3.1 Hz, quat.-C), 127.6 (Ar−CH), 126.9 (Ar−CH), 125.7 (d, J = 8.6 Hz, Ar−CH), 124.6 (Ar−CH), 48.6 (d, $^2J_{PC}$ = 33.0 Hz, C−H), 44.4 (CH$_2$), 22.2 (d, $^1J_{PC}$ = 24.2 Hz, P(*C*HMe$_c$Me$_d$)), 22.0 (d, $^1J_{PC}$ = 3.6 Hz, P(*C*HMe$_a$Me$_b$)), 21.6 (d, $^2J_{PC}$ = 18.0 Hz, P(CHMe$_c$*Me$_d$*)), 20.7 (d, $^2J_{PC}$ = 13.0 Hz, P(CHMe$_a$*Me$_b$*)), 20.5 (d, $^2J_{PC}$ = 2.3 Hz, P(CH*Me$_a$*Me$_b$)), 19.8 (d, $^2J_{PC}$ = 10.1 Hz, P(CH*Me$_c$*Me$_d$)). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 33.5.

Preparation of 10. To a glass vial containing a magnetically stirred solution of **9-Li** (0.041 g, 0.19 mmol) in THF (2 mL) was added a solution of [(COD)IrCl]$_2$ (0.063 g, 0.094 mmol) in THF (2 mL). The vial was then sealed with a PTFE-lined cap, and the solution was stirred magnetically for 1 h, at which point ^{31}P NMR data collected on an aliquot of the reaction mixture indicated quantitative formation of **10**. The volatiles were removed in vacuo, and the residue was extracted into pentane (3 × 2 mL), followed by filtration through Celite. The filtrate was collected, and removal of the solvent afforded **10** as an analytically pure, orange solid (0.087 g, 0.17 mmol, 90%). Anal. Calcd for C$_{20}$H$_{30}$IrOP: C, 47.11; H, 5.94; N, 0.00. Found: C, 47.21; H, 6.11; N, <0.1. ^{1}H NMR (CDCl$_3$): δ 7.18 (m, 1H, Ar−H), 7.12 (m, 1H, Ar−H), 6.84 (m, 1H, Ar−H), 6.54 (m, 1H, Ar−H), 4.96 (m, 2H, COD), 3.54 (m, 2H, COD), 2.56 (m, 2H, P(C*H*Me$_a$Me$_b$)$_2$), 2.27 (m, 2H, COD), 2.17 (m, 2H, COD), 1.88 (m, 2H, COD), 1.76 (m, 2H, COD), 1.22 (d of d, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.5 Hz, 6H, P(CH*Me$_a$*Me$_b$)$_2$), 1.15 (d of d, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 6.5 Hz, 6H, P(CHMe$_a$*Me$_b$*)$_2$). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 180.7 (d, $^2J_{PC}$ = 17.1 Hz, C−O), 133.4 (d, J = 2.0 Hz, Ar−CH), 131.2 (Ar−CH), 118.8 (d, J = 8.7 Hz, Ar−CH), 116.1 (d, J = 6.3 Hz, Ar−CH), 115.8 (d, $^1J_{PC}$ = 46.5 Hz, Ar-*C*P^{i}Pr$_2$), 92.0 (d, J = 12.3 Hz, COD), 49.0 (d, J = 1.3 Hz, COD), 34.4 (d, J = 2.6 Hz, COD), 28.6 (d, J = 2.1 Hz, COD), 24.9 (d, $^1J_{PC}$ = 28.8 Hz, P(*C*HMe$_a$Me$_b$)$_2$), 18.2 (d, $^2J_{PC}$ = 4.2 Hz, P(CH*Me$_a$*-Me$_b$)$_2$), 17.8 (P(CHMe$_a$*Me$_b$*)$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 40.1. Crystals of **10** suitable for single-crystal X-ray diffraction analysis were grown from pentane at −35 °C.

Preparation of 13a. A procedure analogous to that described for the synthesis of **5a** was employed using [**12a**]$^+$BF$_4$$^-$ (0.22 g, 0.37 mmol) in dichloromethane (8 mL) over 14 h in place of [**4a**]$^+$BF$_4$$^-$in THF over 48 h and a larger amount of pentane (3 × 10 mL) for the extraction step. Complex **13a** was isolated as an analytically pure, yellow solid (0.16 g, 0.33 mmol, 91%). Anal. Calcd for C$_{23}$H$_{32}$PSORh: C, 56.33; H, 6.58; N, 0.00. Found: C, 56.64; H, 6.58; N, <0.1. ^{1}H NMR (C$_6$D$_6$): δ 7.15 (t, $^3J_{HH}$ = 7.7 Hz, 1H, C6-H), 7.00 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C7-H), 6.92 (t, $^3J_{HH}$ = 7.3 Hz, 1H, C5-H), 6.83 (d, $^3J_{HH}$ = 7.7 Hz, 1H, C4-H), 4.64 (m, 2H, COD), 4.10 (m, 2H, COD), 3.37 (s, 2H, C1-H), 2.32−2.24 (m, 6H, COD and P(C*H*Me$_2$)$_2$), 1.71−1.63 (m, 4H, COD), 1.30 (d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 6.9 Hz, 6H, P(CH*Me*Me)$_2$), 1.04 (d of d, $^3J_{PH}$ = 18.1 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe*Me*)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 191.7 (d, J = 5.0 Hz, C2), 147.4 (d, J = 12.1 Hz, C7a), 134.4 (d, J = 13.3 Hz, C3a), 126.6 (C6), 123.5 (C7), 120.7 (C5), 116.3 (C4), 86.6 (d, J = 12.2 Hz, COD), 81.3 (d, J = 42.3 Hz, C3), 71.0 (d, J = 13.7 Hz, COD), 43.9 (d, J = 9.8 Hz, C1), 32.2 (COD), 30.0 (COD), 27.8 (d, J = 50.7 Hz, P(*C*HMe$_2$)$_2$), 16.9 (P(CHMe*Me*)$_2$), 16.4 (P(CHMe*Me*)$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 50.8. Crystals of **13a** suitable for single-crystal X-ray diffraction analysis were grown from pentane at −35 °C.

Preparation of 13b. A procedure analogous to that described for the synthesis of **13a** was employed using [**12b**]$^+$BF$_4$$^-$ (0.18 g, 0.26 mmol) in place of [**12a**]$^+$BF$_4$$^-$. Complex **13b** was isolated as an analytically pure, bright yellow solid (0.14 g, 0.24 mmol, 90%). Anal. Calcd for C$_{23}$H$_{32}$PSOIr: C, 47.65; H, 5.56; N, 0.00. Found: C, 47.92; H, 5.67; N, <0.1. ^{1}H NMR (C$_6$D$_6$): δ 7.12 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C6-H), 6.98 (d, $^3J_{HH}$ = 7.2 Hz, 1H, C7-H), 6.92 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C5-H), 6.78 (d, $^3J_{HH}$ = 7.7 Hz, 1H, C4-H), 4.33 (m, 2H, COD), 3.98 (m, 2H, COD), 3.37 (s, 2H, C1-H), 2.29−2.22 (m, 6H, COD and P(C*H*Me$_2$)$_2$), 1.64−1.61 (m, 2H, COD), 1.52−1.47 (m, 2H, COD), 1.15 (d of d, $^3J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 6.9 Hz, 6H, P(CH*Me*Me)$_2$), 0.97 (d of d, $^3J_{PH}$ = 18.2 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe*Me*)$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 190.4 (*C*2), 146.7 (d, J = 11.4 Hz, C7a), 134.1 (d, J = 13.1 Hz, C3a), 126.5 (C6), 123.4 (C7), 121.1 (C5), 116.5 (C4), 81.9 (d, J = 82.4 Hz, C3), 70.1 (COD), 53.6 (COD), 43.6 (d, J = 9.7 Hz, C1), 32.8 (COD), 30.4 (COD), 27.7 (d, J = 49.5 Hz, P(*C*HMe$_2$)$_2$), 16.6 (P(CH*Me*Me)$_2$), 15.9 (P(CHMe*Me*)$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 46.6. Crystals of **13b** suitable for single-crystal X-ray diffraction analysis were grown from pentane at −35 °C.

General Protocol for Hydrogenation Experiments. The protocol used for hydrogenation reactions employing 0.5 mol % catalyst loading in hexanes under inert-atmosphere conditions is provided as a representative procedure. A solution of catalyst compound in hexanes (0.014 mmol in 7 mL to give a 0.002 M solution) was allowed to equilibrate for 5 min, at which point the alkene (2.8 mmol) was added by use of an Eppendorf pipet. The vial was then sealed and shaken vigorously. Subsequently, 1 mL aliquots of the mixture were placed in glass reactor cells, which were each equipped with a magnetic stir bar and sealed under nitrogen with a PTFE valve. The cells were transferred immediately to a Schlenk line and degassed by use of three freeze−pump−thaw cycles employing liquid nitrogen. Magnetic stirring of the solutions was initiated, and the evacuated cells were backfilled with hydrogen gas (∼1 atm, UHP grade). At the desired sampling time, the reactor cell was opened to air and 2 mL of hexanes (or pentane in the case of the hydrogenation of cyclohexene or 1-methylcyclohexene) was added via Pasteur pipet. The resultant mixtures were then filtered through a short Al_2O_3 column (2 cm) from which clear, colorless solutions eluted. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC-MS, and quantitative data were obtained from GC-FID analysis; tabulated data represent the average of at least two runs.

General Protocol for Hydrosilylation Experiments. A solution of catalyst compound in the desired solvent (0.0225 mmol in 4.5 mL to give a 0.005 M solution) was allowed to equilibrate for 5 min, at which point the alkene (2.25 mmol) was added by use of an Eppendorf pipet. The vial was then sealed and shaken vigorously. Subsequently, Et_3SiH (0.45 mmol) was added by use of an Eppendorf pipet to the reaction mixture, and the vial was then sealed and shaken as before. Aliquots (1 mL) of the mixture were placed in glass reactor cells, which were each equipped with a magnetic stir bar and sealed under nitrogen with a PTFE valve. The cells were transferred immediately to a Schlenk line and submersed in a temperature-controlled oil bath, and magnetic stirring of the solutions was initiated. At the desired sampling time, the reactor cell was opened to air and ∼1 mL of pentane was added via Pasteur pipet. The resultant mixtures were then filtered through a short Al_2O_3 column (2 cm) from which clear, colorless solutions eluted. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC-MS, while quantitative data were obtained from GC-FID analysis; tabulated data represent the average of at least two runs.

Crystallographic Solution and Refinement Details for 5b, 13a, and 13b. Crystallographic 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 samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, data reduction, and absorption correction (including SAINT and SADABS) were supplied by Bruker. The structures were solved either by use of direct methods (for **13a**) or a Patterson search/structure expansion (for **5b** and **13b**) and refined by use of the SHELXL97-2 program[32] employing 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 and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. In the course of the solution and refinement process involving **5b** a model featuring two crystallographically independent molecules in the asymmetric unit was employed successfully. Additional experimental details related to the crystallographic characterization of **5b**, **13a**, and **13b** are provided in the accompanying crystallographic information file (Supporting Information).

Crystallographic Solution and Refinement Details for 10. Crystallographic data were obtained at 173(±2) K on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using a 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. Cell parameters were initially retrieved using the COLLECT software (Nonius) and refined with the HKL DENZO and SCALEPACK software.[33] Data reduction and absorption correction (multiscan) were also performed with the HKL DENZO and SCALEPACK software. The structure was solved using the direct methods package in SIR-97[34] and refined by use of the SHELXL97-2 program[32] employing 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-hydrogen atoms, and all H atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Additional experimental details related to the crystallographic characterization of **10** are provided in the accompanying crystallographic information file (Supporting Information).

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Supporting Information Available: Single-crystal X-ray diffraction data in CIF format for **5b**, **10**, **13a**, and **13b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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