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Rh(I) and Ir(I) Derivatives of a P(S),N-Substituted Indene Ligand: Synthetic, Structural, and Catalytic Alkene Hydrosilylation Studies

Dominik Wechsler,[†] Anne Myers,[†] Robert McDonald,[‡] Michael J. Ferguson,[‡] and Mark Stradiotto*[,†]

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3, and X-ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

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Treatment of 1-P^{i}Pr$_2$-indene or 1-P^{i}Pr$_2$-2-NMe$_2$-indene (**1a**) with elemental sulfur afforded 3-^{i}Pr$_2$P(S)-indene or 1-^{i}Pr$_2$P(S)-2-NMe$_2$-indene (**4a**) in 81% and 85% isolated yield, respectively. Addition of **4a** to [(COD)M(THF)$_2$]$^+$BF$_4^-$ afforded the corresponding [(COD)M(κ^2-*N*,*S*-**4a**)]$^+$BF$_4^-$ complexes (M = Rh, **5a**, 76%; M = Ir, **5b**, 59%; COD = η^4-1,5-cyclooctadiene), which were found to exhibit temperature-dependent NMR spectral features that were rationalized in terms of a dynamic process involving M-NMe$_2$ dissociation, rotation about the indenyl-NMe$_2$ bond, inversion at nitrogen, and re-coordination to M. Analysis of variable-temperature NMR data collected for **5a** and **5b** each yielded a value for $\Delta G^{\ddagger}$ of ca. 14 kcal/mol for this process. Exposure of **5a** or **5b** to NaN(SiMe$_3$)$_2$ generated the corresponding (COD)M(κ^2-*C*,*S*-1-^{i}Pr$_2$P(*S*)-2-NMe$_2$-(*C1*-indenyl)) complex (M = Rh, **6a**, 70%; M = Ir, **6b**, 86%) in which the metal is incorporated into an M–C–P–S ring via coordination to the indenyl ring in an η^1-fashion, as well as to sulfur. Alternatively, complex **6b** was prepared cleanly via lithiation of **4a** followed by treatment with 0.5 equiv of [(COD)IrCl]$_2$. The ability of **5a,b** and **6a,b** to mediate the addition of triethylsilane to styrene was also explored, and their performance was compared with that of Wilkinson's Catalyst ((PPh$_3$)$_3$RhCl) and Crabtree's catalyst ([(COD)Ir(PCy$_3$)(Py)]$^+$PF$_6^-$; Cy = cyclohexyl; Py = pyridine). Single-crystal X-ray diffraction data are provided for **4a**, 2-NMe$_2$-3-^{i}Pr$_2$P(S)-indene (**4b**), **6a**, and **6b**.

Introduction

Innovations in multidentate ancillary ligand design continue to enable significant breakthroughs in the field of metal-mediated reaction chemistry.[1] It has been demonstrated in a diversity of coordination complexes that even subtle modifications to the ancillary ligand architecture can alter the coordination behavior of the ligand, as well as influence the stability and reactivity properties of the associated metal fragment.[2] With the aim of identifying new classes of metal complexes that display interesting and synthetically useful patterns of reactivity with substrate E−H bonds (E = main group element), one aspect of our research program focuses on the study of complexes supported by donor-functionalized indene and indenide ancillary ligands.[3] In addition to evaluating how the geometric differences between isomeric neutral ligands such as κ^2-1-*P*^{i}Pr$_2$-2-*N*Me$_2$-indene (κ^2-**1a**) and κ^2-2-*N*Me$_2$-3-*P*^{i}Pr$_2$-indene (κ^2-**1b**) impact the reactivity behavior of coordinated metal fragments, we have also initiated studies comparing the structural and reactivity properties of complexes supported by **1b** and related neutral bidentate

* To whom correspondence should be addressed. E-mail: mark.stradiotto@dal.ca. Fax: 1-902-494-1310. Tel: 1-902-494-7190.
† Dalhousie University.
‡ University of Alberta.

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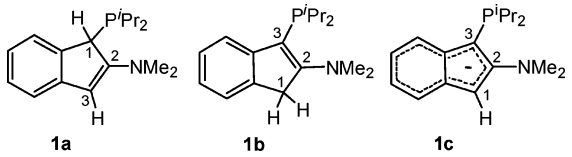
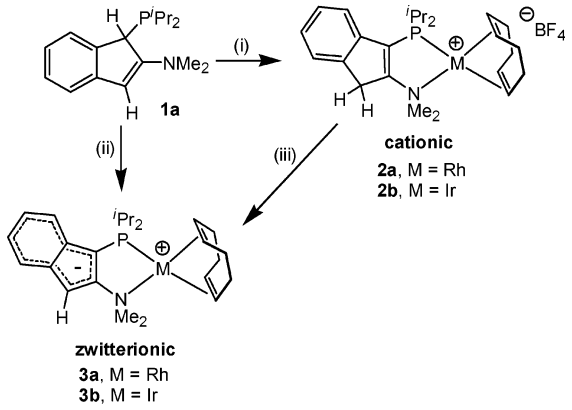
Chart 1



Scheme 1. Synthesis of Cationic (**2a**, **2b**) and Zwitterionic (**3a**, **3b**) κ^2-P,N Rh(I) and Ir(I) Complexes Derived from **1a**[a]

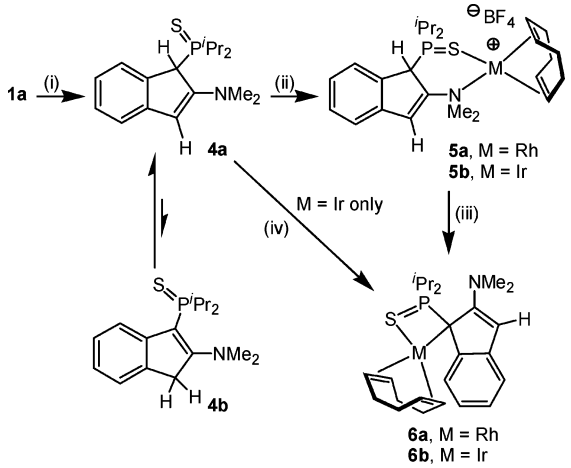


[a] Reagents: (i) 0.5 $[(COD)MCl]_2$, $AgBF_4$; (ii) *n*-BuLi or $NaN(SiMe_3)_2$, 0.5 $[(COD)MCl]_2$; (iii) $NaN(SiMe_3)_2$ (COD = η^4-1,5-cyclooctadiene).

ligands with those of analogous complexes featuring isosteric anionic ligands including κ^2-2-*N*Me_2-3-*P*^{i}Pr_2-indenide (κ^2-**1c**) (Chart 1).[3a,d,e,j]

We have described previously the synthesis and characterization of Rh and Ir cations of the type $[(COD)M(\kappa^2\text{-}\mathbf{1b})]^+X^-$ (M = Rh, **2a**; M = Ir, **2b**; COD = η^4-1,5-cyclooctadiene), as well as the structurally related and formally zwitterionic species, $(COD)M(\kappa^2\text{-}\mathbf{1c})$ (M = Rh, **3a**; M = Ir, **3b**; Scheme 1).[3e,j] Such zwitterions represent an unusual class of substituted indenyl-metal complexes that can be viewed as being comprised of a formally cationic $[(COD)M]^+$ fragment counterbalanced by an uncoordinated 10 π-electron indenide unit that is built into the backbone of the κ^2-P,N ligand and which functions as a sequestered anionic charge reservoir rather than as a locale for metal binding.[4−6] Preliminary reactivity investigations have revealed that **2a** and **3a** are active catalysts for the dehydrogenative silylation of styrene,[3j] while **2b** and **3b** have proven capable of mediating the hydrogenation of substituted alkenes under mild experimental conditions.[3e]

Scheme 2. Synthesis of Cationic κ^2-N,S (**5a**, **5b**) and Neutral κ^2-C,S (**6a**, **6b**) Rh(I) and Ir(I) Derivatives of **4a**[a]



[a] Reagents: (i) 0.125 S_8; (ii) 0.5 $[(COD)MCl]_2$, $AgBF_4$; (iii) $NaN(SiMe_3)_2$; (iv) *n*-BuLi or $NaN(SiMe_3)_2$, 0.5 $[(COD)IrCl]_2$, (COD = η^4-1,5-cyclooctadiene).

Intrigued by the propensity of **1c** for κ^2-P,N binding, rather than η^5 coordination as is traditionally observed in indenyl-rhodium and -iridium complexes,[4−6] and motivated by the catalytic abilities exhibited by **2a,b** and **3a,b**, we sought to develop new bidentate Rh and Ir coordination complexes derived from alternative donor-substituted indenes, including those featuring phosphine sulfide donors. Such ligands represent 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.[7] In particular, we became interested in determining if the phosphine sulfide derivative of **1c** would support κ^2-P(S),N binding to $[(COD)M]^+$ fragments, reminiscent of the κ^2-P,N coordination of **1c** found in **3a,b**. Herein, we report the synthesis of the phosphine sulfide derivative of **1a** (i.e., **4a**), the use of this ligand in the preparation of neutral (κ^2-C,S) and cationic (κ^2-N,S) Rh and Ir coordination complexes, and the application of these complexes as catalysts for the addition of triethylsilane to styrene. A portion of these synthetic results have been communicated previously.[3h]

Results and Discussion

Synthesis and Characterization of 4a. Treatment of **1a** with elemental sulfur resulted in the clean conversion to **4a** (^{31}P NMR), which was isolated as an analytically pure yellow solid in 85% yield and spectroscopically characterized (Scheme 2). We have reported that in solution 1-P^iPr_2-indene slowly rearranges to 3-P^iPr_2-indene and that this transformation is accelerated upon treatment with alumina;[3i,8] under analogous conditions employing **1a** and alumina, an equi-

(4) The majority of indenyl-metal complexes exhibit approximate η^5 coordination to the C_5 ring: (a) Lobanova, I. A.; Zdanovich, V. I. *Russ. Chem. Rev.* **1988**, *57*, 967. (b) Birmingham, J. M. *Adv. Organomet. Chem.* **1964**, *2*, 365.

(5) For disussions of indenyl-metal complexes that deviate from simple η^5 coordination, see: (a) Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 10291. (b) Zargarian, D. *Coord. Chem. Rev.* **2002**, *233−234*, 157. (c) Stradiotto, M.; McGlinchey, M. J. *Coord. Chem. Rev.* **2001**, *219-221*, 311.

(6) For selected recent examples of η^5 indenyl-rhodium and -iridium complexes, see: (a) Santi, S.; Ceccon, A.; Carli, F.; Crociani, L.; Bisello, A.; Tiso, M.; Venzo, A. *Organometallics* **2002**, *21*, 2679. (b) Santi, S.; Ceccon, A.; Crociani, L.; Gambaro, A.; Ganis, P.; Tiso, M.; Venzo, A.; Bacchi, A. *Organometallics* **2002**, *21*, 565. (c) Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Blum, J.; Gelman, D.; Halterman, R. L. *Eur. J. Inorg. Chem.* **2002**, 211. (d) Rupert, K. C.; Liu, C. C.; Nguyen, T. T.; Whitener, M. A.; Sowa, J. R., Jr. *Organometallics* **2002**, *21*, 144. (e) Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Halterman, R. L. *Organometallics* **2001**, *20*, 5360. (f) Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Halterman, R. L. *Organometallics* **2001**, *20*, 2215. (g) Westcott, S. A.; Kakkar, A. K.; Taylor, N. J.; Roe, D. C.; Marder, T. B. *Can. J. Chem.* **1999**, *77*, 205.

(7) (a) Bayón, J. C.; Claver, C.; Masdeu-Bultó, A. M. *Coord. Chem. Rev.* **1999**, *193−195*, 73. (b) Lobana, T. S. *Prog. Inorg. Chem.* **1989**, *37*, 495.

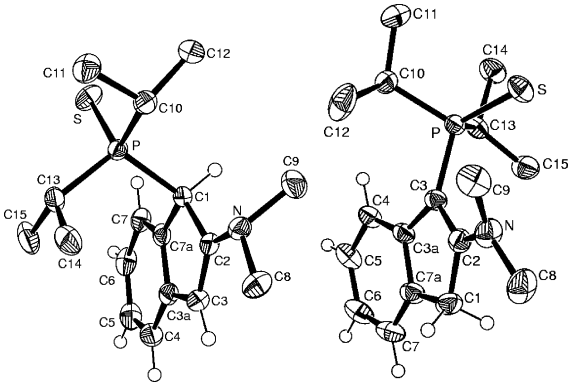
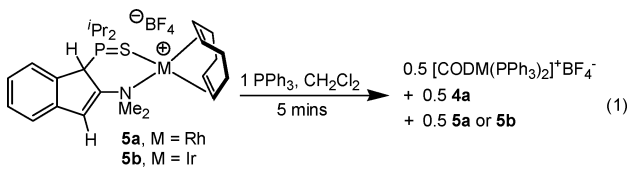


Figure 1. ORTEP diagrams for **4a** (left) and **4b** (right), shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms have been omitted for clarity.

librium mixture of **1a** and **1b** (~3:1; ^{1}H and ^{31}P NMR) is obtained.[3i] In contrast, the vinylic isomer **4b** was not detected by use of NMR spectroscopic methods upon extended exposure of solutions of **4a** to alumina or triethylamine or with prolonged heating (80 °C). It is unclear whether steric or electronic factors predominate in altering the equilibrium distribution of isomers in the **1a,b** versus **4a,b** systems. The possible involvement of the phosphine sulfide unit in preventing the rearrangement of **4a** to **4b** was ruled out through the oxidation of 1-P^{i}Pr$_2$-indene with elemental sulfur; this reaction yielded directly a mixture of 1- and 3-^{i}Pr$_2$P(S)-indene (~5:95; ^{1}H and ^{31}P NMR) after only 1 h, an observation which is apparently inconsistent with the formation of 3-^{i}Pr$_2$P(S)-indene via sulfur oxidation of 3-P^{i}Pr$_2$-indene formed in situ from 1-P^{i}Pr$_2$-indene. Pure 3-^{i}Pr$_2$P(S)-indene was isolated as a light yellow analytically pure solid in 81% yield. In an effort to complement the solution characterization of **4a**, the structure of this compound was confirmed by use of X-ray diffraction techniques. Moreover, in the course of recrystallizing **4a**, a crystal whose morphology was different from that of **4a** was isolated and subsequently identified as **4b** following single-crystal X-ray diffraction analysis. The crystal structures of **4a** and **4b** are provided in Figure 1 and can be compared with other crystallographically characterized 1- and 3-indenylphosphine sulfides.[9] Salient X-ray experimental data and metrical parameters for all of the crystallographically characterized complexes reported herein are collected in Tables 1 and 2, respectively. While the P−S distances in **4a** and **4b** are equivalent, the P−C$_{ind}$ distance in **4a** (1.873(2) Å) is longer than the related distance in **4b** (1.803(1) Å), in keeping with the P−C$_{ind}$(sp^3) > P−C$_{ind}$(sp^2) trend in bond lengths found in 1,3-(^{i}Pr$_2$P(S))$_2$-indene[9b] and related compounds. As well, the contracted N−C2 distance in **4b** (1.351(2) Å) in comparison to that found in **4a** (1.392(2) Å) and the diminished pyramidalization at nitrogen in **4b** ($\Sigma_{\text{angles at N}} \approx$ 357°) versus **4a** ($\Sigma_{\text{angles at N}} \approx$ 342°) are both indicative of more extensive conjugation of the nitrogen lone pair with the adjacent indene framework in **4b**, relative to **4a**.

Cationic κ^2-N,S Complexes of 4a. Treatment of **4a** with [(COD)M(THF)$_2$]$^+$BF$_4^-$ (M = Rh or Ir, prepared in situ) afforded **5a** and **5b** as analytically pure orange-red solids in 76% and 59% yield, respectively. In contrast to the facile isomerization of **1a** to **1b** that occurs upon coordination to [(COD)M]$^+$ fragments,[3e,j] both ^{1}H and ^{13}C NMR data confirm that the allylic structure of **4a** is retained in **5a** and **5b**, in keeping with the observed stability of **4a** over **4b** in solution (vide supra). Whereas the C_1 symmetry of **5a** and **5b** should result in the observation of two unique NMe ^{1}H NMR resonances for each complex, at 298 K only a single broad NMe$_2$ signal is detected; however, in both cases, two distinct NMe resonances are observed at 223 K. These temperature-dependent spectroscopic data are consistent with a dynamic process involving M−N dissociation, rotation about the C2−NMe$_2$ bond, inversion at N, and re-coordination to M, as depicted in Scheme 3. Analysis of variable-temperature ^{1}H NMR data for both **5a** and **5b** yielded a value for $\Delta G^{\ddagger}_{T_c}$ of ca. 14 kcal/mol for these processes (T_c = 279 K for **5a**; 284 K for **5b**).[10] The ^{31}P{^{1}H} NMR spectra of **5a** are also temperature-dependent; at 298 K, the spectrum in $CDCl_3$ is comprised of a broad resonance centered at 103 ppm, while at 223 K, a sharp doublet ($^2J_{RhP}$ = 5 Hz) is observed at 107 ppm, along with a low-intensity resonance at 73 ppm corresponding to **4a**. We attribute the temperature-dependent ^{31}P{^{1}H} NMR spectra of **5a** as arising due to dynamic exchange of free **4a** with bound **4a** (in **5a**). Indeed, the extent of broadening of the ^{31}P{^{1}H} NMR resonance associated with **5a** at 298 K increases considerably upon addition of **4a** to a solution of **5a**. In contrast, $CDCl_3$ solutions of **5b** exhibit a single sharp ^{31}P{^{1}H} NMR resonance at 115 ppm over this temperature range, and the sharpness of this signal is unaffected upon addition of **4a**. Notably, the shift to high frequency of the phosphorus NMR resonance on going from **4a** to either **5a** or **5b**, along with the magnitude of the observed Rh−P coupling constant in **5a** at 223 K, provide evidence for the existence of an M−S linkage in **5a,b**.

The rearrangement pathway outlined in Scheme 3 implies that the κ^2-N,S ligand in **5a** and **5b** can be described as hemilabile,[11] with the S-donor serving as an anchor to the Group 9 metal. In an effort to obtain further experimental support for such a proposal, **5a** and **5b** were separately treated



with 1 equiv of PPh$_3$ (eq 1). However, instead of obtaining the anticipated [(COD)M(κ^1-N,*S*-**4a**)(PPh$_3$)]$^+$BF$_4^-$ product,

(8) This process is directly analogous to the isomerization of 1-PPh$_2$-indene to 3-PPh$_2$-indene: Fallis, K. A.; Anderson, G. K.; Rath, N. P. *Organometallics* **1992**, *11*, 885.

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(10) The Gutowsky−Holm approximation was employed in the calculation of $\Delta G^{\ddagger}_{T_c}$: Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

(11) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233.

Table 1. Crystallographic Data for **4a**, **4b**, **6a**, and **6b**

	4a	4b	6a	6b
empirical formula	$C_{17}H_{26}NPS$	$C_{17}H_{26}NPS$	$C_{25}H_{37}NPSRh$	$C_{25}H_{37}NPSIr$
fw	307.42	307.42	517.50	606.79
cryst dimensions	0.51 × 0.14 × 0.12	0.70 × 0.52 × 0.41	0.64 × 0.20 × 0.08	0.42 × 0.18 × 0.15
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	17.316(2)	10.5482(4)	10.1379(7)	10.1288(5)
b (Å)	10.834(1)	11.2705(5)	12.4282(8)	12.3895(7)
c (Å)	17.787(2)	14.3990(6)	18.848(1)	18.927(1)
β (deg)	90	98.752(1)	93.763(1)	93.2465(8)
V (Å^3)	3337.0(6)	1691.9(1)	2369.6(3)	2371.4(2)
Z	8	4	4	4
ρ_{calcd} (g cm^{-3})	1.224	1.207	1.451	1.700
μ (mm^{-1})	0.281	0.277	0.888	5.798
2*θ* limit (deg)	52.84	52.74	52.74	52.78
	$-21 \le h \le 21$	$-13 \le h \le 13$	$-12 \le h \le 11$	$-12 \le h \le 12$
	$-13 \le k \le 13$	$-14 \le k \le 14$	$-15 \le k \le 15$	$-15 \le k \le 14$
	$-21 \le l \le 22$	$-18 \le l \le 17$	$-23 \le l \le 23$	$-23 \le l \le 23$
total data collected	22 338	10 798	15 830	13 444
independent reflns	3424	3442	4830	4856
R_{int}	0.0440	0.0162	0.0314	0.0248
observed reflns	2883	3227	4087	3914
absorption correction	multiscan (SADABS)	multiscan (SADABS)	multiscan (SADABS)	multiscan (SADABS)
range of transmission	0.9670−0.8698	0.8948−0.8295	0.9323−0.6002	0.4767−0.1945
data/restraints/params	3424/0/187	3442/0/183	4830/0/262	4856/0/262
R1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0338	0.0350	0.0281	0.0217
wR2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0887	0.0978	0.0770	0.0544
GOF	1.064	1.057	1.020	1.029
largest peak, hole (e·Å^{-3})	0.433, −0.178	0.721, −0.190	0.734, −0.274	1.040, −0.415

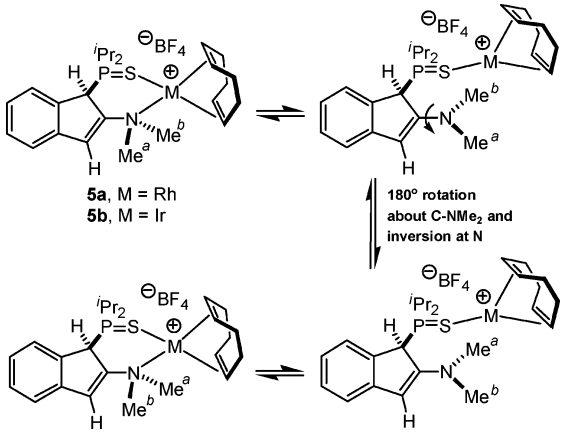
Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **4a**, **4b**, **6a**, and **6b**

	4a	4b	6a	6b
P−S	1.9665(6)	1.9657(5)	2.0127(8)	2.019(1)
P−C_{ind}	1.873(2)	1.803(1)	1.783(2)	1.799(3)
N−C2	1.392(2)	1.351(2)	1.407(3)	1.406(4)
C1−C2	1.533(2)	1.519(2)	1.504(3)	1.507(4)
C2−C3	1.351(2)	1.388(2)	1.364(4)	1.362(5)
M−S	−	−	2.3811(7)	2.3653(8)
M−C1	−	−	2.233(2)	2.214(3)
M−C11	−	−	2.116(2)	2.108(3)
M−C12	−	−	2.137(3)	2.122(3)
M−C15	−	−	2.135(2)	2.112(3)
M−C16	−	−	2.153(3)	2.137(3)
C2−N−Me^a	114.9(1)	120.3(2)	119.2(2)	119.7(3)
C2−N−Me^b	116.3(1)	123.7(1)	115.5(2)	115.6(3)
Me^a−N−Me^b	110.9(1)	113.0(1)	110.7(2)	110.6(3)
M−C1−P	−	−	90.9(1)	92.2(1)
C1−P−S	−	−	104.30(8)	102.1(1)
P−S−M	−	−	81.41(3)	82.63(4)
S−M−C1	−	−	81.07(6)	80.88(8)

an equimolar mixture of $[(COD)M(PPh_3)_2]^+BF_4^-$,[12] **4a**, and unreacted **5a** or **5b** was generated (^{31}P NMR).

Neutral *κ*²-*C,S* Complexes Derived from 4a. In the pursuit of neutral κ^2-N,S relatives of the formally zwitterionic complexes **3a,b**, the κ^2-N,S cations **5a,b** were separately treated with $NaN(SiMe_3)_2$. In each case, clean conversion to a single new phosphorus-containing compound was detected by use of ^{31}P NMR techniques, and these products were isolated as analytically pure yellow (**6a**) and orange (**6b**) solids in 70% and 86% yield, respectively. Both complexes yielded combustion analysis data consistent with the anticipated (κ^2-*N,S*-1-P(*S*)^{i}Pr$_2$-2-*N*Me$_2$-indenyl)M(COD) product, and for the reaction involving **5a**, the observation of Rh−P coupling ($^2J_{RhP}$ = 15 Hz) provided evidence for Rh−S bonding in **6a**. However, the existence of Rh−C1 coupling ($^1J_{RhC}$ = 11 Hz) seemed to rule out κ^2-N,S connectivity in **6a**. The identity of **6a** and **6b** as κ^2-C,S isomers of the targeted κ^2-N,S compounds was confirmed on the basis of the analysis of X-ray diffraction data. The crystallographically determined structures of **6a** and **6b** are given in Figures 2 and 3, respectively. Complex **6a** is the first reported complex featuring a Rh−C−P−S ring system,[13] as well as the first η^1-indenylrhodium species to be crystal-

Scheme 3. Proposed Mechanism for the Dynamic Interconversion of the NMe_2 Enviroments in **5a** or **5b**



(12) Elsevier: C. J.; Kowall, B.; Kragten, H. *Inorg. Chem.* **1995**, *34*, 4836.

(13) For examples of related complexes featuring M−C−P−S rings, see: (a) Avis, M. W.; Goosen, M.; Elsevier, C. J.; Veldman, N.; Kooijman, H.; Spek, A. L. *Inorg. Chim. Acta* **1997**, *264*, 43. (b) Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; López-de-Luzuriaga, J. M.; Olmos, E. *J. Chem. Soc., Dalton Trans.* **1997**, 3515. (c) Berry, D. E.; Browning, J.; Dixon, K. R.; Hilts, R. W.; Pidcock, A. *Inorg. Chem.* **1992**, *31*, 1479. (d) Browning, J.; Dixon, K. R.; Hilts, R. W. *Organometallics* **1989**, *8*, 552. (e) Murray, H. H.; Garzón, G.; Raptis, R. G.; Mazany, A. M.; Porter, L. C.; Fackler, J. P., Jr. *Inorg. Chem.* **1988**, *27*, 836. (f) Browning, J.; Bushnell, G. W.; Dixon, K. R.; Pidcock, A. *Inorg. Chem.* **1983**, *22*, 2226. (g) Mazany, A. M.; Fackler, J. P., Jr. *Organometallics* **1982**, *1*, 752.

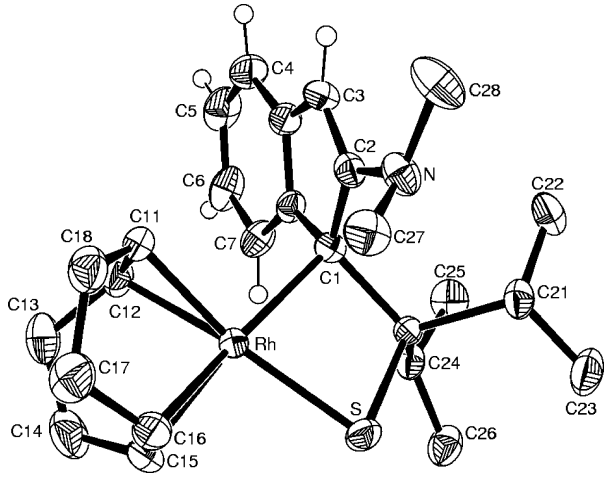


Figure 2. ORTEP diagram for **6a**, shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms have been omitted for clarity.

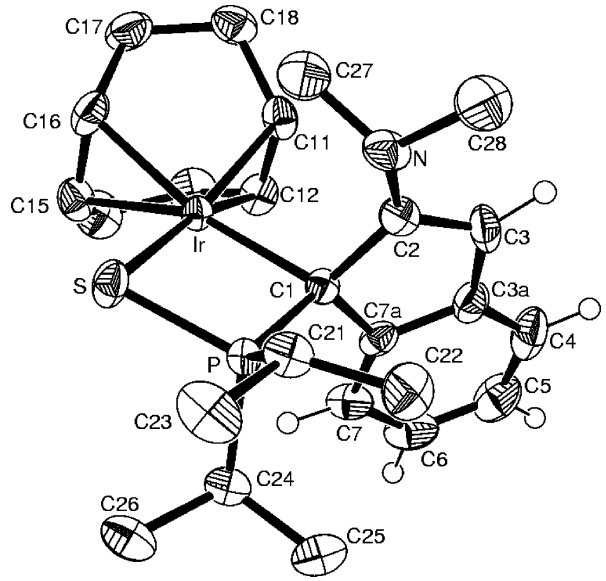
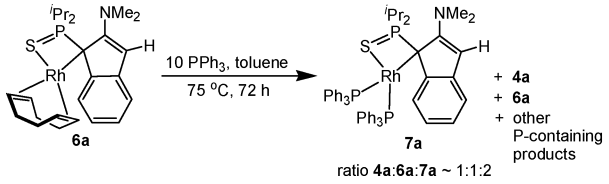


Figure 3. ORTEP diagram for **6b**, shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms have been omitted for clarity.

lographically characterized,[5c] while **6b** represents the first crystallographically characterized complex containing an Ir−C−P−S ring.[14] The metrical parameters associated with **6a** and **6b** are nearly identical and will be discussed collectively. Complexes **6a,b** feature Group 9 metals that exist within nearly planar M−C−P−S rings (mean deviation < 0.2 Å). The equidistant M−COD linkages exhibited by **6a,b** suggest a similar trans influence for the indenyl-C1 and S donors in these complexes. As well, the P−C1 distances in **6a,b** are contracted significantly relative to **4a**, whereas the P−S distances are elongated, suggesting partial delocalization of the anionic charge along the C−P−S unit in **6a,b**, as has been observed in some other structurally related complexes featuring anionic phosphine sulfide ligands.[15] Complex **6b** can also be prepared cleanly via lithiation of **4a** with *n*-BuLi followed by the addition of 0.5 equiv of $[(COD)IrCl]_2$. In using a similar protocol employing $[(COD)RhCl]_2$, **6a** was formed as the major product, along with varying amounts (≤20%) of a new product which gave rise to a singlet $^{31}P\{^1H\}$ NMR shift at 61 ppm; we have thus far been unable to isolate and characterize this minor product. By comparison, lithiation of **4a** with *n*-BuLi followed by the addition of $BrMn(CO)_5$ affords the corresponding η^5-$Mn(CO)_3$ complex in nearly quantitative isolated yield.[3h]

The reactivity of complexes **6a,b** with PPh_3 was compared with that of **5a,b**. Unlike **5a,b**, no reaction was observed (^{31}P NMR) for either of **6a** or **6b** upon exposure to 10 equiv of PPh_3 at 22 °C over the course of 1 week, suggesting that the anionic κ^2-C,S ligand in **6a,b** is coordinated more strongly than the neutral κ^2-*N*,*S*-**4a** ligand in the cations **5a,b**. Whereas a similar experiment involving **6b** conducted at 75 °C generated a complex mixture of products over 72 h, under analogous conditions, **6a** reacted with excess PPh_3 to generate a mixture containing **4a**, unreacted **6a**, and **7a** as the major



phosphorus-containing species (eq 2).[16]

Catalytic Addition of Triethylsilane to Styrene. Vinylsilanes represent useful organic synthons that can be prepared directly via the hydrosilylation of alkynes, although achieving high regioselectivity in such addition reactions can be challenging.[17,18] The selective dehydrogenative silylation of olefins provides an alternative route to vinysilanes,[17,19] and Group 9 catalysts including Wilkinson's catalyst ($(PPh_3)_3$-RhCl; **8**) have proven capable of mediating such transformations.[3j,20] In this context, the metal-mediated addition of triethylsilane to styrene was selected as a prototypical E−H bond activation reaction for use in benchmarking the catalytic

(14) One Ir(III) complex featuring an Ir−C−P−S ring has been characterized spectroscopically: Valderrama, M.; Contreras, R. *J. Organomet. Chem.* **1996**, *513*, 7.

(15) (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.

(16) We have yet to obtain **7a** in pure form, and as such, full characterization data for this complex are lacking; the connectivity of **7a** is proposed on the basis of ^1H and $^{31}P\{^1H\}$ NMR data. $^{31}P\{^1H\}$ NMR (toluene) for **7a**: δ 81.3 (d of d, P_a, $^2J_{RhPa}$ = 18.6 Hz, $^3J_{PaPb}$ = 7.4 Hz), 46.4 (d of d of d, P_b, $^1J_{RhPb}$ = 202.9 Hz, $^2J_{PbPc}$ = 39.1 Hz, $^3J_{PaPb}$ = 7.4 Hz), 43.2 (d of d, P_c, $^1J_{RhPc}$ = 156.4 Hz, $^2J_{PbPc}$ = 39.1 Hz).

(17) For selected reviews, see: (a) Marciniec, B.; Guliñski, J. *J. Organomet. Chem.* **1993**, *446*, 15. (b) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, p 763. (c) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(18) For a recent example of alkyne hydrosilylation mediated by Group 9 complexes, see: Field, L. D.; Ward, A. J. *J. Organomet. Chem.* **2003**, *681*, 91.

(19) Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374.

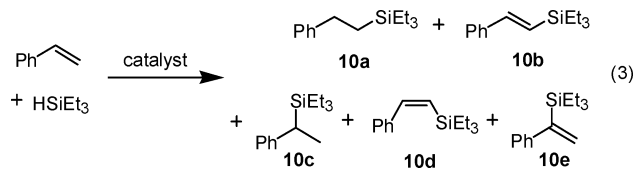
(20) For selected examples, see: (a) Takeuchi, R.; Yasue, H. *Organometallics* **1996**, *15*, 2098, and references therein. (b) Kakiuchi, F.; Nogami, K.; Chatani, N.; Seki, Y.; Murai, S. *Organometallics* **1993**, *12*, 4748. (c) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1984**, *49*, 3389. (d) Onopchenko, A.; Sabourin, E. T.; Beach, D. L. *J. Org. Chem.* **1983**, *48*, 5101.

Table 3. Addition of Triethylsilane to Styrene[a]

entry	catalyst	styrene: Et_3SiH	solvent	yield [%][b]	**10a**[c]	**10b**[c]	**10c**[c]	other[c]
1	**5a**	1:1	DCE	21	4	2	15	<1
2	**5a**	5:1	DCE	19	5	8	6	<1
3	**5b**	1:1	DCE	22	9	11	2	<1
4	**5b**	5:1	DCE	70	29	36	3	2
5	**9**	5:1	DCE	>99	7	41	52	<1
6	**6a**	1:1	DCE	78	29	40	9	<1
7	**6a**	5:1	DCE	96[d]	15	81	<1	<1
8	**6a**	5:1	DCE	>99	15	83	2	<1
9	**8**	5:1	DCE	>99[d]	3	93	4	<1
10	**6a**	1:1	C_6H_6	94	27	61	6	<1
11	**6a**	5:1	C_6H_6	98[d]	8	90	<1	<1
12	**6a**	5:1	C_6H_6	>99	8	91	1	<1
13	**8**	5:1	C_6H_6	>99[d]	1	94	5	<1
14	**6b**	1:1	DCE	34	9	18	7	<1
15	**6b**	5:1	DCE	64	24	33	6	1
16	**6b**	1:1	C_6H_6	26	5	11	7	3
17	**6b**	5:1	C_6H_6	36	9	14	8	5

[a] Reactions employing 5.5 mol% catalyst at 60 °C; DCE = 1,2-dichloroethane; control experiments confirmed that solutions of **5a,b** and **6a,b** are stable upon heating at 60 °C for a minimum of 24 h (^{31}P NMR). [b] Based on the consumption of triethylsilane at 24 h, except where noted. [c] Product distribution based on GC-MS and GC-FID data, rounded to the nearest percent; other silicon-containing products include **10d** and **10e**. [d] Yield quoted at 4 h.

abilities of **5a,b** and **6a,b** against those of **8**, as well as Crabtree's catalyst, $[(COD)Ir(PCy_3)(Py)]^+PF_6^-$ (Cy = cyclohexyl, Py = pyridine; **9**). The predominant silicon-containing products of this reaction are given in eq 3, and include the addition products **10a** and **10c**, as well as the



(3)

vinylsilanes **10b**, **10d**, and **10e**. The results of catalytic experiments conducted at 60 °C using a 5.5 mol% catalyst loading are collected in Table 3. Reactions mediated by the cations **5a,b** were restricted to 1,2-dichloroethane due to the poor solubility of these complexes in alternative media. In the presence of either an equimolar (entry 1) or an excess (entry 2) amount of styrene relative to triethylsilane, **5a** performed poorly as a catalyst, with only ~20% silane conversion noted after 24 h. This contrasts the efficient and selective transformation of these substrates into **10b** mediated by the $[Rh(COD)_2]^+BF_4^-$/2 PPh_3 catalyst system in diethyl ketone under similar conditions.[20a] Low conversion was also obtained for the 1:1 reaction of styrene with triethylsilane in the presence of a catalytic amount of **5b** (entry 3). However, 70% conversion was achieved after 24 h by use of **5b** and a 5:1 ratio of these substrates, albeit with very poor selectivity (entry 4). Under similar conditions employing **9** as a catalyst, >99% silane conversion was obtained with similarly poor product selectivity (entry 5). Throughout, an equimolar amount of ethylbenzene compared to **10b** was detected, which confirms that the excess styrene employed acts as a dihydrogen acceptor in this catalytic system.

Improved catalytic performance was noted for the neutral *κ*²-*C,S*-Rh complex, **6a**, relative to the cations **5a,b**. For reactions conducted in 1,2-dichloroethane, 78% silane conversion was observed after 24 h when using a 1:1 ratio of styrene and triethylsilane (entry 6). Further increases in the silane conversion (96%), as well as improved selectivity for the dehydrogenative silylation product **10b**, were achieved after only 4 h when a 5:1 substrate ratio was employed (entry 7), and after 24 h, the triethylsilane was completely consumed (entry 8). In switching to benzene as the reaction medium, additional gains in conversion and selectivity were achieved when employing **6a** in combination with either a 1:1 (entry 10) or 5:1 (entries 11 and 12) ratio of styrene and triethylsilane. While the performance of complex **8** in 1,2-dichloroethane is superior to that of **6a** under similar reaction conditions (entry 9), the difference in selectivity is somewhat less pronounced for reactions conducted in benzene (entry 13). By comparison, the catalytic abilities of the *κ*²-*C,S*-Ir complex **6b** proved to be vastly inferior to those of **6a** in both 1,2-dichloroethane (entries 14 and 15) and benzene (entries 16 and 17).[21]

Summary and Conclusions

Despite the apparent structural similarities between 1-P^{i}Pr$_2$-2-NMe$_2$-indene (**1a**) and its oxidized relative 1-^{i}Pr$_2$P(S)-2-NMe$_2$-indene (**4a**), the observations described herein reveal that these species, as well as their monoanionic derivatives, can differ considerably in their coordination chemistry. Although we have shown previously that **1a** rapidly isomerizes to **1b** upon *κ*²-P,N coordination to $[(COD)M]^+$ fragments, the indene **4a** is not transformed into **4b** within the coordination sphere of the analogous *κ*²-N,S cations, **5a,b**. It is possible that the relief of steric strain associated with the five-membered chelate ring in $[(COD)M(\kappa^2\text{-}P,N\text{-}\mathbf{1a})]^+$ is somehow achieved upon isomerization to $[(COD)M(\kappa^2\text{-}P,N\text{-}\mathbf{1b})]^+$ (i.e., **2a,b**), whereas the six-membered chelate ring in **5a,b** lacks such a driving force to promote a similar rearrangement. We have also reported previously that upon deprotonation complexes **2a,b** are cleanly converted into the formally zwitterionic *κ*²-P,N species, **3a,b**. In contrast, we have demonstrated herein that *κ*²-N,S binding is not retained upon treatment of **5a,b** with $NaN(SiMe_3)_2$; instead, the putative (κ^2-*N,S*-1-P(*S*)^{i}Pr$_2$-2-*N*Me$_2$-indenyl)M(COD) intermediate rearranges to the corresponding *κ*²-C,S complex, **6a,b**. These observations appear to underscore the importance of maintaining a rigid five-membered chelate ring as a means of enforcing *κ*² coordination in **3a,b** and related formally zwitterionic complexes. In a preliminary catalytic survey, the ability of **5a,b** and **6a,b** to mediate the addition of triethylsilane to styrene was evaluated. While the cationic complexes and **6b** exhibited rather poor catalytic performance, the activity and selectivity exhibited by **6a** approached that of Wilkinson's catalyst under some conditions. We are currently assessing the utility of **5a,b**, **6a,b**, and related metal complexes as catalysts for

(21) For examples of alkene hydrosilylation mediated by neutral Ir(I) complexes, see: (a) Oro, L. A.; Fernandez, M. J.; Esteruelas, M. A.; Jimenez, M. S. *J. Mol. Catal.* **1986**, *37*, 151. (b) Apple, D. C.; Brady, K. A.; Chance, J. M.; Heard, N. E.; Nile, T. A. *J. Mol. Catal.* **1985**, *29*, 55.

other substrate transformations involving E−H bond activation and will describe the results of these studies in 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 (130 °C) for 5 days and then evacuated for 24 h prior to use. The nondeuterated solvents tetrahydrofuran, dichloromethane, diethyl ether, toluene, benzene, 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, dichloromethane, and diethyl ether were purified over two alumina-packed columns, while toluene, benzene, and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. The solvents used within the glovebox were stored over activated 3 Å molecular sieves. 1,2-Dichloroethane (Aldrich), C_6D_6 (Aldrich), styrene (Aldrich, containing 10−15 ppm 4-*tert*-butylcatechol as inhibitor), and Et_3SiH (Aldrich) were each degassed by using three repeated freeze−pump−thaw cycles and then dried over 3 Å molecular sieves for 24 h prior to use; $CDCl_3$ (Aldrich) was degassed in a similar manner, dried over CaH_2 for 7 days, distilled in vacuo, and stored over 3 Å molecular sieves for 24 h prior to use. $AgBF_4$ (Aldrich) was dried in vacuo for 48 h prior to use, while sulfur powder, *n*-BuLi (1.6 M in hexanes), and $NaN(SiMe_3)_2$ were obtained from Aldrich and were used as received. Compounds **1a**,[3j] 1-P^{i}Pr$_2$-indene,[3i] [(COD)RhCl]$_2$,[22a] [(COD)IrCl]$_2$,[22b] and $(PPh_3)_3$RhCl (**8**)[23] were prepared using literature methods and dried in vacuo for 24 h prior to use, while $[(COD)Ir(PCy_3)(Py)]^+PF_6^-$ (**9**) was obtained from Strem. Unless otherwise stated, ^{1}H, ^{13}C, and ^{31}P NMR 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 ppm downfield of $SiMe_4$ (for ^{1}H and ^{13}C) or 85% H_3PO_4 in D_2O (for ^{31}P). In some cases, slightly fewer than expected independent ^{1}H and/or ^{13}C NMR resonances were observed, despite prolonged data acquisition times. ^{1}H and ^{13}C NMR chemical shift assignments are based on data obtained from ^{1}H−^{13}C HSQC and ^{1}H−^{13}C HMBC or 1D ^{1}H nOe NMR experiments. Variable-temperature NMR studies involving **5a** and **5b** were conducted on a Bruker AC-250 spectrometer with temperature calibrations carried out using an external MeOH/MeOD standard.[24] The $\Delta G^{\ddagger}$ values quoted for the dynamic processes involving **5a** and **5b** were determined at 279 and 284 K, respectively, by use of the Gutowsky−Holm approximation.[10] GC-MS and GC-FID were performed on a Perkin-Elmer AutoSystem XL gas chromatograph equipped with a TurboMass mass spectrometer. GC-MS analyses were performed using a Supelco 30 m × 0.25 mm MDN-5S 5% phenyl methylsiloxane, film thickness 0.50 μm, temperature programmed: 60 °C, 1 min; 20 °C/min to 200 °C; 200 °C, 7 min. GC-FID analyses were done in a similar way except on a Supelco DB200 column. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada. Single-crystal X-ray diffraction experiments were performed by Dr. R. McDonald and Dr. M. J. Ferguson at the X-ray Crystallography Laboratory, University of Alberta, Department of Chemistry, Edmonton, Alberta.

Preparation of 3-^{i}Pr$_2$P(S)-indene. A Schlenk flask containing a magnetic stir bar was charged with elemental sulfur (0.14 g, 4.5 mmol) and dried under vacuum for 2.5 h. To this flask was then added a solution of 1-P^{i}Pr$_2$-indene (1.0 g, 4.3 mmol) in 15 mL of diethyl ether. Upon completion of the transfer, the resulting mixture was stirred for 1 h, after which the diethyl ether and other volatile materials were removed in vacuo. The resulting solid was found to be a mixture of 1- and 3-^{i}Pr$_2$P(S)-indene (~5:95, respectively; ^{1}H and ^{31}P NMR) corresponding to a crude yield of 97%. Selective crystallization from diethyl ether afforded pure 3-^{i}Pr$_2$P(S)-indene as a light yellow solid (0.82 g, 3.5 mmol, 81%). Anal. Calcd for $C_{15}H_{21}PS$: C 68.15; H 8.00; N 0.00. Found: C 68.05; H 8.13; N <0.3. ^{1}H NMR (C_6D_6): δ 7.74 (d, $^3J_{HH}$ = 7.9 Hz, 1H, C4−H), 7.30 (d, $^3J_{HH}$ = 9.8 Hz, 1H, C2−H), 7.18 (m, 2H, C7−H, and C5−H or C6−H), 7.09 (t, $^3J_{HH}$ = 7.1 Hz, 1H, C6−H or C5−H), 2.93 (broad t, J = 2 Hz, 2H, CH_2), 2.17 (m, 2H, P(C*H*Me$_2$)$_2$), 3.09 (d of d, $^3J_{PH}$ = 17.3 Hz, $^3J_{HH}$ = 6.8 Hz, 6H, P(CH*Me*Me)$_2$), 0.94 (d of d, $^3J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe*Me*)$_2$); ^{13}C{^{1}H} NMR (C_6D_6): δ 150.3 (d, $^2J_{PC}$ = 8.3 Hz, C2), 145.0 (d, J_{PC} = 8.8 Hz, C3a or C7a), 142.9 (d, J_{PC} = 10.5 Hz, C7a or C3a), 136.1 (d, $^1J_{PC}$ = 68.1 Hz, C3), 126.5 (aryl-CH), 125.4 (aryl-CH), 124.3 (aryl-CH), 122.3 (C7), 39.0 (d, $^3J_{PC}$ = 12.0 Hz, C1), 28.4 (d, $^1J_{PC}$ = 52.3 Hz, P(*C*HMe$_2$)), 17.0 (d, $^2J_{PC}$ = 2.0 Hz, P(CH*Me*Me)$_2$), 16.4 (d, $^2J_{PC}$ = 1.4 Hz, P(CHMe*Me*)$_2$); ^{31}P{^{1}H} NMR (C_6D_6): δ 60.3.

Preparation of 4a. A Schlenk flask containing a magnetic stir bar was charged with **1a** (0.73 g, 2.7 mmol) and then was sealed with a septum. Magnetic stirring was initiated and then a suspension of sulfur (0.12 g, 3.8 mmol) in dichloromethane (20 mL) was transferred via cannula to the Schlenk flask containing **1a**. Upon completion of the slurry transfer, the resulting mixture was stirred for 1 h; at this stage, ^{31}P NMR data obtained from an aliquot of the reaction mixture indicated clean conversion to **4a**. The dichloromethane and other volatile materials were then removed in vacuo. Within the glovebox, the residual solid was dissolved in toluene (15 mL) and passed down an alumina column (0.5 cm × 5 cm). Removal of the toluene and other volatile materials in vacuo yielded **4a** as an analytically pure yellow solid (0.71 g, 2.3 mmol, 85%). Anal. Calcd for $C_{17}H_{26}PSN$: C 66.44; H 8.52; N 4.56. Found: C 66.46; H 8.59; N 4.72. ^{1}H NMR (C_6D_6): δ 7.61 (d, $^3J_{HH}$ = 7.4 Hz, 1H, C4−H), 7.19 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H), 7.06 (d, $^3J_{HH}$ = 7.4 Hz, 1H, C7−H), 6.92 (t, $^3J_{HH}$ = 7.7 Hz, 1H, C6−H), 5.44 (s, 1H, C3−H), 4.19 (d, $^2J_{PH}$ = 17.6 Hz, 1H, C1−H), 2.49 (s, 6H, NMe_2), 2.28−2.16 (m, 2H, 2 P(C*H*Me$_2$)), 1.19 (d of d, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_a$Me$_b$)), 0.99 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, P(CH*Me*$_c$Me$_d$)), 0.93 (d of d, $^3J_{PH}$ = 16.7 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CHMe$_a$*Me*$_b$)), 0.79 (d of d, $^3J_{PH}$ = 16.6 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me*$_d$)); ^{13}C{^{1}H} NMR (C_6D_6): δ 158.6 (d, $^2J_{PC}$ = 5.0 Hz, C2), 146.5 (d, $^3J_{PC}$ = 3.8 Hz, C3a), 135.4 (d, $^2J_{PC}$ = 4.6 Hz, C7a), 127.5 (C5), 125.2 (d, $^4J_{PC}$ = 2.7 Hz, C4), 121.3 (d, $^4J_{PC}$ = 1.9 Hz, C6), 118.5 (C7), 105.7 (d, $^3J_{PC}$ = 3.8 Hz, C3), 50.6 (d, $^1J_{PC}$ = 30.2 Hz, C1), 43.5 (NMe_2), 26.4 (d, $^1J_{PC}$ = 45.5 Hz, P(*C*HMe$_2$)), 26.3 (d, $^1J_{PC}$ = 47.4 Hz, P(*C*HMe$_2$)), 18.4 (d, $^2J_{PC}$ = 1.9 Hz, P(CH*Me*$_c$Me$_d$)), 17.2 (d, $^2J_{PC}$ = 2.3 Hz, P(CH*Me*$_a$-Me$_b$)), 16.8 (d, $^2J_{PC}$ = 2.7 Hz, P(CHMe$_c$*Me*$_d$)), 16.5 (d, $^2J_{PC}$ = 1.9 Hz, P(CHMe$_a$*Me*$_b$)); ^{31}P{^{1}H} NMR (C_6D_6): δ 72.8. Crystals of **4a** suitable for single-crystal X-ray diffraction analysis were grown from toluene at −35 °C. A crystal of **4b** suitable for single-crystal X-ray diffraction analysis was grown from a diethyl ether solution of **4a** stored at −35 °C.

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Preparation of 5a. To a glass vial containing a magnetically stirred suspension of $[(COD)RhCl]_2$ (0.094 g, 0.19 mmol) in THF (2 mL) was added a suspension of $AgBF_4$ (0.075 g, 0.38 mmol) in THF (3 mL); a yellow solution was generated immediately along with a white precipitate. The supernatant solution was separated from the precipitate by filtration through Celite, and the solution was transferred to a glass vial containing a magnetically stirred solution of **4a** (0.12 g, 0.38 mmol) in THF (3 mL). After 30 s, a dark orange-red precipitate started to form, and after 3 additional hours, the reaction supernatant solution was decanted and the remaining solid (**5a**) was washed with pentane (3 mL). Any remaining solvent or other volatile materials were then removed in vacuo, yielding **5a** as an analytically pure orange-red solid (0.18 g, 0.29 mmol, 76%). Anal. Calcd for $C_{25}H_{38}PSNRhBF_4$: C 49.61; H 6.33; N 2.31. Found: C 49.78; H 6.54; N 2.34. ^{1}H NMR ($CDCl_3$): δ 7.20−7.15 (m, 2H, aryl-Hs), 7.10 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C4−H or C7−H), 6.96 (m, 1H, C5−H or C6−H), 5.21 (d, $^2J_{PH}$ = 8.6 Hz, 1H, C1−H), 4.37 (m, 2H, COD), 4.08 (m, 2H, COD), 3.31 (broad s, 6H, NMe_2), 2.82 (m, 1H, P(C*H*Me_2)), 2.53 (m, 1H, P(C*H*Me_2) or COD), 2.41 (m, 2H, P(C*H*Me_2) and/or COD), 2.18 (broad m, 2H, COD), 1.98 (broad m, 2H, COD), 1.70 (broad m, 2H, COD), 1.44 (d of d, $^3J_{PH}$ = 18.4 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me*Me)), 1.39−1.32 (m, 6H, P(CH*Me*$_2$)), 0.96 (d of d, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*Me)); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 145.8 (C3a or C7a or C2), 131.0 (C7a or C3a or C2), 129.4 (aryl-CH), 124.6 (aryl-CH), 123.7 (aryl-CH), 119.8 (aryl-CH), 84.6 (m, COD), 82.2 (m, COD), 47.8 (d, $^1J_{PC}$ = 26.8 Hz, C1), 44.6 (broad m, NMe_2), 32.6 (broad m), 30.8, (d, J = 40.0 Hz), 30.0 (d, J = 36.1 Hz), 29.9−29.5 (broad m), 17.8 (P(CH-*Me*Me)), 17.5 (P(CH*Me*Me)), 17.4 (P(CH*Me*Me)), 16.5 (P(CH-*Me*Me)); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 103.5 (broad s).

Preparation of 5b. This complex was prepared using a synthetic method analogous to that described for **5a**. Using $[(COD)IrCl]_2$ (0.17 g, 0.49 mmol), $AgBF_4$ (0.097 g, 0.49 mmol), and **4a** (0.15 g, 0.49 mmol) afforded **5b** as an analytically pure orange-red solid (0.20 g, 0.29 mmol, 59%). Anal. Calcd for $C_{25}H_{38}PSNIrBF_4$: C 43.23; H 5.51; N 2.02. Found: C 43.23; H 5.31; N 1.96. ^{1}H NMR ($CDCl_3$): δ 7.36−7.29 (m, 2H, C4−H or C7−H and C6−H or C5−H), 7.22 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C4−H or C7−H), 7.11 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5−H or C6−H), 5.58 (d, $^2J_{PH}$ = 7.4 Hz, 1H, C1−H), 4.69 (s, 1H, C3−H), 4.35 (m, 2H, COD), 4.20 (m, 2H, COD), 3.75−3.55 (m, 4H, COD), 3.53 (s, 6H, NMe_2), 2.84−2.77 (m, 2H, P(C*H*Me_2)$_2$), 2.36−2.22 (broad m, 2H, COD), 2.03−1.86 (broad m, 2H, COD), 1.68 (d of d, $^3J_{PH}$ = 18.1 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, P(CH*Me*Me)), 1.59 (d of d, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*Me)), 1.43 (d of d, $^3J_{PH}$ = 17.9 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me*Me)), 1.22 (d of d, $^3J_{PH}$ = 17.4 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, P(CH*Me*Me)); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.6 (s, C3a or C7a or C2), 129.7 (C7a or C3a or C2), 129.5 (aryl-CH), 124. 9 (m, aryl-CH), 124.1 (aryl-CH), 120.3 (aryl-CH), 70.2 (COD), 69.7 (COD), 67.7 (COD), 65.5 (COD), 58.4 (m), 47.2 (d, $^1J_{CH}$ = 23.98 Hz, C1), 44.4 (NMe_2), 34.8 (COD), 34.1 (d, $^1J_{PC}$ = 36.5 Hz, P(*C*HMe_2)), 33.5 (COD), 30.6 (COD), 29.9 (d, $^1J_{PC}$ = 34.0 Hz, P(*C*HMe_2)), 28.5 (COD), 18.5 (P(CH*Me*Me)), 18.3 (P(CH*Me*Me)), 16.9 (P(CH*Me*Me)), 15.9 (P(CH*Me*Me)); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 115.3.

Preparation of 6a. To a magnetically stirred suspension of **5a** (0.069 g, 0.11 mmol) in THF (3 mL) was added a suspension of $NaN(SiMe_3)_2$ (0.021 g, 0.11 mmol) in THF (3 mL) via Pasteur pipet. Precipitate formed upon addition, and the reaction mixture was left stirring for 3 h. A ^{31}P NMR spectrum taken of an aliquot of the reaction solution revealed the presence of a single phosphorus-containing product at 82.9 ppm (**6a**). After the solvent and other volatile materials were removed in vacuo, the residue was extracted into pentane (3 mL) and the pentane solution containing **6a** was filtered through Celite and then dried in vacuo. The residue was then taken up in toluene (3 mL) and crystallized at −35 °C, giving **6a** as an analytically pure yellow solid (0.040 g, 0.077 mmol, 70%). Anal. Calcd for $C_{25}H_{37}PSNRh$: C 58.02; H 7.21; N 2.71. Found: C 57.88; H 6.94; N 2.63. ^{1}H NMR (C_6D_6): δ 8.26 (d, $^3J_{HH}$ = 7.2 Hz, 1H, C4−H or C7−H), 7.44 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C7−H or C4−H), 7.23−7.15 (m, 2H, C5−H and C6−H), 6.16 (s, 1H, C3−H), 4.50 (broad m, 2H, COD), 4.30 (broad s, 2H, COD), 3.35 (m, 1H, P(C*H*Me_2)), 3.13 (s, 6H, NMe_2), 2.73 (m, 1H, P(C*H*Me_2)), 2.50−1.15 (m, 11H, COD and P(CH*Me*Me)), 1.07 (d of d, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, P(CH*Me*Me)), 0.82 (d of d, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, P(CH*Me*Me)), 0.67 (d of d, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, P(CH*Me*Me)); ^{13}C{^{1}H} NMR (C_6D_6): δ 161.9 (d, J = 1.8 Hz, C2), 138.2 (d, J = 9.5 Hz, C3a or C7a), 137.1 (d, J = 4.1 Hz, C7a or C3a), 120.8 (C4 or C7), 120.1 (C5 or C6), 117.4 (C7 or C4), 117.3 (C6 or C5), 103.6 (d, $^3J_{PC}$ = 8.2 Hz, C3), 80.4−77.3 (m, COD), 76.5 (d, $^1J_{RhC}$ = 13.9 Hz, COD), 45.9 (NMe_2), 31.4 (d, $^1J_{PC}$ = 31.9 Hz, P(*C*HMe_2)), 29.2−28.2 (m, COD and P(*C*HMe_2)), 26.5 (d of d, $^1J_{PC}$ = 47.4 Hz, $^1J_{RhC}$ = 11.2 Hz, C1), 15.1 (2 P(CH*Me*Me)), 14.9 (P(CH*Me*Me)), 14.4 (P(CH-*Me*Me)); ^{31}P{^{1}H} NMR (101.3 MHz, C_6D_6): δ 82.9 (d, $^2J_{RhP}$ = 14.9 Hz). Crystals of **6a** suitable for single-crystal X-ray diffraction analysis were grown from diethyl ether at −35 °C.

Preparation of 6b. A 1.6 M hexanes solution of *n*-BuLi (0.31 mL, 0.49 mmol; precooled to −35 °C) was added dropwise via syringe to a glass vial containing a magnetically stirred solution (precooled to −35 °C) of **4a** (0.15 g, 0.49 mmol) in toluene (5 mL) over 2 min, producing a faint yellow solution. The vial containing the reaction mixture was then sealed with a PTFE-lined cap and left to stir for 1 h at ambient temperature; ^{31}P NMR data obtained from an aliquot of the reaction mixture at this stage confirmed the consumption of **4a**, along with the formation of a single new phosphorus-containing product at 54 ppm. A mixture of $[(COD)IrCl]_2$ (0.17 g, 0.49 mmol) in toluene (2 mL) was then transferred to the reaction mixture via Pasteur pipet, and the reaction vial was resealed. A dark solution formed immediately, and after stirring for 1 h, the solution changed to a yellow-orange color and a white precipitate formed. The reaction mixture was then filtered through Celite and the supernatant was dried in vacuo, yielding **6b** as an analytically pure orange solid (0.25 g, 0.42 mmol, 86%). Alternatively, a protocol analogous to that described for the preparation of **6a** can be employed, in which **5b** is quantitatively deprotonated with $NaN(SiMe_3)_2$ to give **6b** (^{31}P NMR); upon purification, **6b** is obtained in similar yield to that reported above. Anal. Calcd for $C_{25}H_{37}PSNIr$: C 49.48; H 6.15; N 2.31. Found: C 49.62; H 6.36; N 2.31. ^{1}H NMR (C_6D_6): δ 8.20 (d, $^3J_{HH}$ = 7.1 Hz, 1H, C7−H), 7.40 (d, $^3J_{HH}$ = 6.9 Hz, 1H, C4−H), 7.20−7.15 (m, 2H, C5−H and C6−H), 5.91 (s, 1H, C3−H), 4.34 (m, 1H, COD), 4.15 (m, 1H, COD), 3.28 (m, 1H, P(C*H*Me_2)), 3.12 (s, 6H, NMe_2), 2.83 (m, 1H, COD), 2.77 (m, 1H, P(C*H*Me_2)), 2.43 (m, 1H, COD), 2.15−2.00 (m, 2H, COD), 1.81 (m, 2H, COD), 1.41 (m, 2H, COD), 1.23 (m, 2H, COD), 1.14 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.4 Hz, 3H, P(CH*Me*Me)), 0.83 (m, 6H, 2 P(CH*Me*Me)), 0.57 (d of d, $^3J_{PH}$ = 16.6 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, P(CH*Me*Me)); ^{13}C{^{1}H} NMR (C_6D_6): δ 163.5 (C2), 141.6 (d, J = 8.3 Hz, C3a or C7a), 141.2 (C7a or C3a), 124.6 (C7), 123.2 (C5 or C6), 119.2 (C6 or C5), 118.4 (C4), 105.6 (d, $^3J_{PC}$ = 7.6 Hz, C3), 64.9 (COD), 64.2 (COD) 60.7 (COD), 46.6 (NMe_2), 36.0 (d, $^1J_{PC}$ = 24.6 Hz, P(*C*HMe_2)), 32.5 (d, $^1J_{PC}$ = 26.0 Hz, P(*C*HMe_2)), 31.9 (COD), 31.8 (COD), 31.4 (COD), 31.3 (COD), 23.5 (d, $^1J_{PC}$ = 105.0 Hz, C1), 16.4 (P(CH*Me*Me)), 16.4 (P(CH*Me*Me)), 16.3 (P(CH*Me*Me)), 15.5

(P(CH*Me*Me)); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 98.5. Crystals of **6b** suitable for single-crystal X-ray diffraction analysis were grown from diethyl ether at −35 °C.

General Protocol for Hydrosilylation Experiments. The protocol used for the hydrosilylation reaction employing 5.5 mol% catalyst loading of **6a** (relative to Et_3SiH) in 1,2-dichloroethane with a styrene-to-silane ratio of 5:1 run at 60 °C is provided as a representative procedure. A 0.0077 M solution (3.4 mL) of **6a** in 1,2-dichloroethane was allowed to equilibrate for 5 min, at which point the alkene (226 μL) was added by use of an Eppendorf pipet. The vial was then sealed and shaken vigorously for 15 s. Subsequently, Et_3SiH (74 μL) was added to the reaction mixture by use of an Eppendorf pipet, and the vial was then sealed and shaken as before. Aliquots (0.8 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, submerged in a temperature-controlled oil bath (60 °C), 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 mixture was then filtered through a short Al_2O_3 column (3 cm) from which a clear, colorless solution eluted. The solution was then transferred to a GC vial and sealed. Products of each reaction were identified by use of GC-MS as compared to standard solutions of isolated products prepared by use of literature methods,[25] while quantitative data were obtained from GC-FID analysis; tabulated data represent the average of at least two runs.

Crystallographic Solution and Refinement Details. Crystallographic data were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using a 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. The structures were solved by use of direct methods (except in the case of **6a**, where a Patterson search/structure expansion was employed) and refined by use of full-matrix least-squares procedures (on F^2) with R1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms, and all hydrogen 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. Crystal structure diagrams were generated by use of the ORTEP-3 for Windows program.[26]

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Supporting Information Available: Single-crystal X-ray diffraction data in CIF format for **4a**, **4b**, **6a**, and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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