New Racemic Planar-Chiral Metalloligands Derived from Donor-Substituted Indenes: A Synthetic, Structural, and Catalytic Investigation

Dominik Wechsler,[†] Matthew A. Rankin,[†] Robert McDonald,[‡] Michael J. Ferguson,[‡] Gabriele Schatte,[§] and Mark Stradiotto*,[†]

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada, X-Ray Crystallography Laboratory, Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada, and Saskatchewan Structural Sciences Centre, University of Saskatchewan, Saskatoon, SK S7N 5C9, Canada

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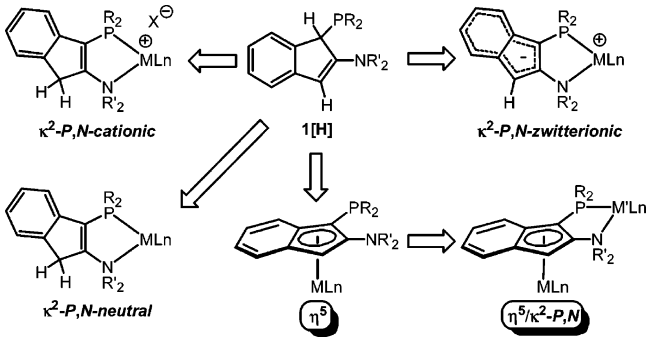
The synthesis and characterization of a new family of (η^5-indenyl)ML_n complexes (ML_n = $Mn(CO)_3$, Cp*Ru, or Cp*Fe; Cp* = η^5-C_5Me_5) derived from 3-P^{i}Pr$_2$-indene, 1-P^{i}Pr$_2$-2-NMe$_2$-indene (**1a[H]**), or 1-P(S)^{i}Pr$_2$-2-NMe$_2$-indene (**1b[H]**) are described. Lithiation of **1b[H]** followed by treatment with $BrMn(CO)_5$, 0.25 equiv of $[Cp^*RuCl]_4$, or Cp*Li/$FeCl_2$ provided the corresponding (η^5-**1b**)ML_n complexes (ML_n = $Mn(CO)_3$, **2a**, 96%; Cp*Ru, **2b**, 87%; or Cp*Fe, **2c**, 55%). Similarly, treatment of **1a[Li]** with 0.25 equiv of $[Cp^*RuCl]_4$ or Cp*Li/$FeCl_2$ provided the corresponding (η^5-**1a**)ML_n complexes (ML_n = Cp*Ru, **3b**, 74%; or Cp*Fe, **3c**, 62%). Whereas combination of **3b** and 0.5 equiv of $[(COD)RhCl]_2$ afforded [(COD)Rh(κ^2-*P*,*N*-**3b**)]$^+Cl^-$ (**[4b]$^+$Cl$^-$**; 49% isolated yield), under similar conditions **3c** was observed to undergo a decomposition reaction resulting in the formation of the zwitterionic complex (COD)Rh(κ^2-*P*,*N*-**1a**) (**5**; COD = η^4-1,5-cyclooctadiene). Each of **3a**−**c** was observed to react cleanly with $[(COD)Rh(THF)_2]^+BF_4^-$ (prepared in situ) to give the corresponding [(COD)Rh(κ^2-*P*,*N*-**3a**−**c**)]$^+BF_4^-$ complex (**[4a**−**c]$^+$BF$_4^-$**; 87%, 96%, and 89% isolated yield, respectively). Whereas lithiation of 3-P^{i}Pr$_2$-indene followed by the addition of $BrMn(CO)_5$ generated a complex mixture of products, similar reactions employing 0.25 equiv of $[Cp^*RuCl]_4$ or Cp*Li/$FeCl_2$ afforded **6b** or **6c** in 98% and 43% yield, respectively. Treatment of **6b** with 0.5 equiv of $[(COD)RhCl]_2$ allowed for the isolation of (COD)RhCl(κ^1-*P*-**6b**) **7** in 96% isolated yield. Each of **[4a**−**c]$^+$BF$_4^-$** proved to be an active catalyst for addition of pinacolborane to styrene, with the observed regioselectivity being dependent on the nature of the η^5-coordinated metal fragment, as well as the solvent employed. Single-crystal X-ray diffraction data for **2a**, **2b**, **2c**, **3b**, **[4c]$^+$BF$_4^-$**, and **7** are provided.

Introduction

In the quest to identify new classes of metal complexes that are capable of mediating synthetically useful substrate transformations involving the activation of E−H bonds (E = main group fragment),[1] we are exploring the coordination chemistry of various donor-substituted indene ligands, including 1-PR_2-2-NR′$_2$-indenes (**1[H]**, Scheme 1). Thus far, ligands of type **1-[H]** have proven to be remarkably versatile, providing access to a range of neutral, cationic, and formally zwitterionic κ^2-*P*,*N* late metal complexes that exhibit interesting stoichiometric and catalytic reactivity with E−H bonds.[2] Such zwitterionic complexes are unusual in that the indenide unit functions as an uncoordinated anionic charge reservoir to counterbalance the κ^2-*P*,*N*-coordinated cationic ML_n fragment, rather than as a locale for metal binding.[3]

Scheme 1. Coordination Complexes Derived from P,N-Substituted Indene Ligands



Given the unusual coordination chemistry exhibited by **1[H]** in the formation of zwitterionic κ^2-*P*,*N* complexes, we became interested in surveying the feasibility of preparing more conventional η^5-indenylmetal derivatives of **1[H]**. From a fundamental perspective, the successful synthesis of analogous (η^5-indenyl)ML_n and κ^2-*P*,*N*-ML_n derivatives of **1[H]** would allow for the relative stability of such linkage isomers to be evaluated. Furthermore, we envisioned that η^5-ML_n species derived from **1[H]**, once resolved, could be employed as a new class of enantiopure planar-chiral metalloligands (PCMs) for use in the construction of chiral dinuclear η^5/κ^2-*P*,*N* catalyst

* Corresponding author. Tel.: (902) 494-7190. Fax: (902) 494-1310. E-mail: mark.stradiotto@dal.ca.
† Dalhousie University.
‡ University of Alberta.
§ University of Saskatchewan.

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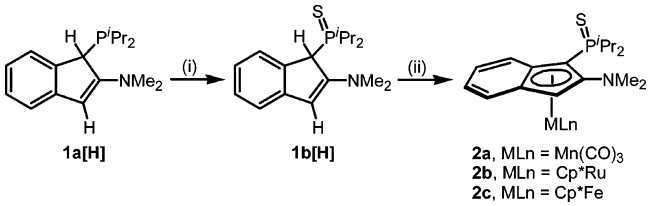
complexes. While PCMs featuring P,N-donors built upon a ferrocenyl core have proven to be effective in promoting high activity and enantioselectivity in a range of metal-mediated asymmetric transformations,[4] the development of alternative half-sandwich P,N-ligands of this type has received relatively little attention.[5−9] However, comparative studies reported thus far suggest that such alternative PCMs can, in some catalytic applications, offer performance that is on par with, and even superior to,[7b,9a,b,d] more traditional ferrocenyl-based PCMs. In this context, we anticipated that the successful preparation of structurally diverse η^5-ML_n derivatives of **1[H]** would allow for the facially bound metal ML_n fragment in such complexes to serve as a control element in tuning the steric and electronic properties of the κ^2-*P*,*N*-coordinated $M'L_n$ fragment (Scheme 1). Herein, we report the synthesis and characterization of a new family of (η^5-indenyl)ML_n complexes (ML_n = $Mn(CO)_3$, Cp*Ru, or Cp*Fe; Cp* = η^5-C_5Me_5) derived from 3-P^{i}Pr$_2$-indene, 1-P^{i}Pr$_2$-2-NMe$_2$-indene (**1a[H]**), or 1-P(S)^{i}Pr$_2$-2-NMe$_2$-indene (**1b[H]**). Also described is the use of the racemic (η^5-**1a**)ML_n species (**3a**−**c**) as κ^2-*P*,*N*-metalloligands toward $[(COD)Rh]^+$ (COD = η^4-1,5-cyclooctadiene) to give isolable dinuclear Mn/Rh, Ru/Rh, and Fe/Rh complexes (**[4a**−**c]$^+$BF$_4^-$**). The preliminary catalytic studies reported herein employing **[4a**−**c]$^+$BF$_4^-$** revealed that altering the η^5-coordinated metal fragment in such dinuclear catalysts can lead to modest changes in the regioselectivity observed in the hydroboration of alkenes.

Scheme 2. Synthesis of the (η^5-1b)ML_n Complexes 2a, 2b, and 2c[a]



[a] Reagents: (i) 0.125 equiv of S_8; (ii) *n*-BuLi, followed by $BrMn(CO)_5$ (for **2a**), 0.25 equiv of $[Cp^*RuCl]_4$ (for **2b**), or Cp*Li/$FeCl_2$ (for **2c**).

Results and Discussion

Our initial synthetic efforts have focused on the preparation of representative PCMs of type (η^5-**1a**)ML_n featuring $Mn(CO)_3$, Cp*Ru, and Cp*Fe metal fragments. In light of our previous observation that treatment of $BrMn(CO)_5$ with **1a[Li]** resulted in a complex distribution of products,[10] an alternative synthetic strategy starting from the corresponding phosphine sulfide **1b-[H]** was explored (Scheme 2). Lithiation of **1b[H]** followed by treatment with $BrMn(CO)_5$ led to the clean formation of **2a**, which was isolated as an analytically pure solid in 96% yield.[11] Using a similar synthetic protocol, the related Ru and Fe complexes (**2b** and **2c**) were obtained in 87% and 55% isolated yield, respectively. Data obtained from both NMR spectroscopic and X-ray crystallographic studies involving **2a**−**c** support the assignment of these products as (η^5-**1b**)ML_n species. An ORTEP[12] diagram for each of **2a**, **2b**, and **2c** is provided in Figure 1, while X-ray experimental data and selected metrical parameters for all of the crystallographically characterized complexes reported herein are collected in Tables 1 and 2, respectively. While the structural features observed within the η^5-**1b** ligands of **2a**−**c** do not differ importantly, some significant structural differences are observed with respect to the way in which the $Mn(CO)_3$, Cp*Ru, and Cp*Fe fragments coordinate to **1b**.[13] Deviation from ideal η^5-coordination is observed in **2a**, with progressive lengthening of the Mn−C_{ind} distances noted as follows: Mn−C1 ≈ Mn−C3 < Mn−C2 < Mn−C3a ≈ Mn−C7a. Whereas a significant distortion from η^5-binding is also observed in the Cp*Fe complex **2c** (Fe−C3a ≈ Fe−C7a > Fe−C1 ≈ Fe−C2 ≈ Fe−C3), the Ru−C_{ind} distances in **2b** are statistically equivalent (ca. 2.23 Å), with the exception of the contracted Ru−C1 contact (2.181(2) Å).

We have reported previously that **2a** is transformed into the P,N-metalloligand **3a** (56% isolated yield) upon treatment with $Cl_3SiSiCl_3$ at 85 °C over the course of 14 d.[10] In an effort to identify more convenient routes to **3a**, some alternative reduction

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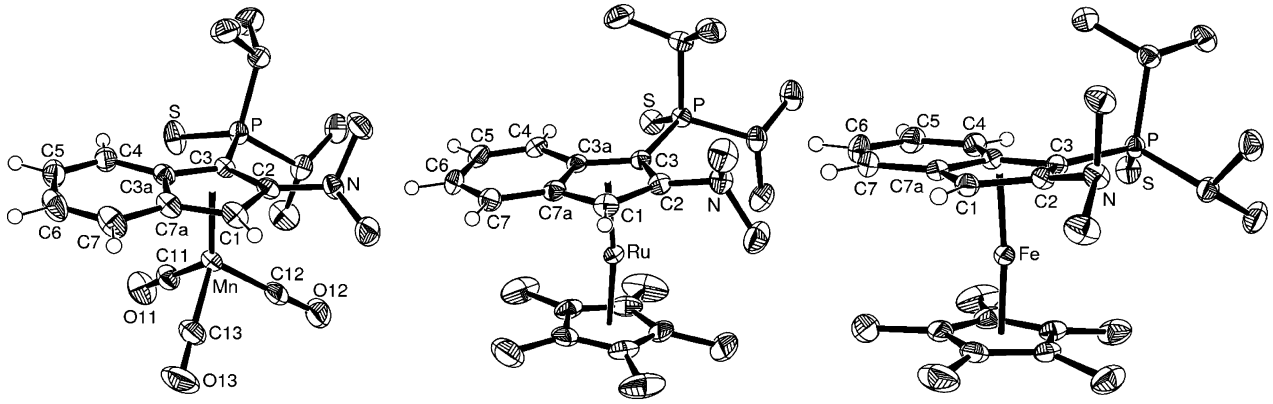


Figure 1. ORTEP diagrams for **2a**, **2b**, and **2c**, shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted. Selected hydrogen atoms have been omitted for clarity.

Table 1. Crystallographic Data for 2a, 2b, 2c, 3b, [4c]$^+$BF$_4^-$, and 7

	2a	**2b**	**2c**	**3b**	**[4c]$^+$BF$_4^-$**	**7**
empirical formula	$C_{20}H_{25}Mn_1N_1O_3P_1S_1$	$C_{27}H_{40}Ru_1N_1P_1S_1$	$C_{27}H_{40}Fe_1N_1P_1S_1$	$C_{27}H_{40}Ru_1N_1P_1$	$C_{35}H_{52}B_1F_4Fe_1N_1P_1Rh_1$	$C_{33}H_{47}Cl_1P_1Rh_1Ru_1$
formula weight	445.38	542.70	497.48	510.64	763.32	714.11
crystal dimensions	0.46 × 0.39 × 0.32	0.35 × 0.32 × 0.11	0.60 × 0.29 × 0.29	0.51 × 0.47 × 0.20	0.15 × 0.10 × 0.10	0.05 × 0.05 × 0.05
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$
a (Å)	9.688(2)	15.0636(7)	11.599(1)	11.5111(8)	11.4520(3)	8.2280(7)
b (Å)	15.570(4)	10.1395(5)	9.824(1)	9.8759(7)	14.8950(4)	18.737(2)
c (Å)	13.898(3)	17.1950(8)	22.447(2)	22.979(2)	19.7890(5)	20.574(2)
α (deg)	90	90	90	90	90	79.373(5)
β (deg)	91.494(4)	96.1692(8)	102.364(2)	103.242(1)	90	88.354(4)
γ (deg)	90	90	90	90	90	79.595(5)
V (Å^3)	2095.8(8)	2611.1(2)	2498.7(4)	2542.9(3)	3375.6(2)	3066.2(5)
Z	4	4	4	4	4	4
ρ_{calcd} (g cm^{-3})	1.412	1.381	1.322	1.334	1.502	1.547
μ (mm^{-1})	0.825	0.756	0.766	0.693	1.014	1.191
2θ limit (deg)	52.78	52.76	52.82	52.80	54.94	52.74
	$-12 \le h \le 12$	$-18 \le h \le 18$	$-14 \le h \le 14$	$-14 \le h \le 14$	$-14 \le h \le 14$	$-10 \le h \le 10$
	$-19 \le k \le 19$	$-12 \le k \le 12$	$-12 \le k \le 12$	$-12 \le k \le 12$	$-19 \le k \le 19$	$-23 \le k \le 23$
	$-17 \le l \le 17$	$-21 \le l \le 21$	$-28 \le l \le 28$	$-28 \le l \le 28$	$-25 \le l \le 25$	$-25 \le l \le 24$
total data collected	16 327	17 659	18 496	19 661	7698	20 189
independent reflections	4273	5333	5112	5200	7698	12 349
R_{int}	0.0252	0.0290	0.0225	0.0231	N/A	0.0708
observed reflections	3966	4696	4506	4761	6635	9540
range of transmission	0.7781−0.7027	0.9214−0.7777	0.8083−0.6563	0.8738−0.7189	0.9054−0.8628	0.9429−0.9429
data/restraints/parameters	4273/0/244	5333/0/285	5112/0/285	5200/0/276	7698/0/408	12 349/838/785
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0273	0.0244	0.0314	0.0223	0.0441	0.0603
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0764	0.0657	0.0865	0.0610	0.0979	0.1344
GOF	1.043	1.071	1.032	1.043	1.066	1.035

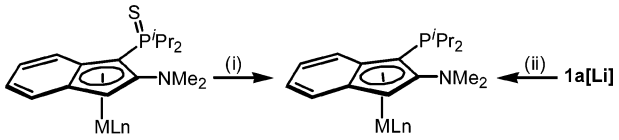
protocols were surveyed (Scheme 3). Whereas the use of Raney Ni resulted in the rapid decomposition of **2a**, Cp_2ZrHCl proved to be a more useful reducing agent for the conversion of **2a** to **3a** at ambient temperatures, thereby allowing for the isolation of **3a** in 83% yield. However, in optimizing the synthetic protocol, a total of 6 equiv of Cp_2ZrHCl delivered over the course of 42 h was found to be necessary to effect the complete conversion of **2a** to **3a** at ambient temperature, and efforts to accelerate the reduction by heating of the reaction mixture (60 °C) resulted in the formation of multiple phosphorus-containing byproducts. While the clean reduction of **2b** to **3b** (^{31}P NMR) was also achieved by use of excess Cp_2ZrHCl over the course of 15 d at ambient temperature, a mixture of products (including **1a[H]**) was observed in the attempted reduction of **2c** with Cp_2ZrHCl under similar conditions. However, in contrast to the complex reactivity observed between **1a[Li]** and $BrMn(CO)_5$,[10] compounds **3b** and **3c** were prepared conveniently from **1a[Li]** and 0.25 equiv of $[Cp^*RuCl]_4$ or $Cp^*Li/FeCl_2$ in 74% and 62% isolated yield, respectively. Solution NMR spectroscopic data support fully the formulation of **3b** and **3c** as facially bound (η^5-**1a**)ML_n complexes, including the observation of relatively low-frequency ^{31}P NMR chemical shifts in comparison to related κ^2-*P*,*N* complexes of **1a**,[2] and the observation of one ^{1}H NMR and one ^{13}C NMR resonance attributable to the NMe_2 unit in **3b** or **3c**, resulting from a rotation/inversion process involving the uncoordinated N-donor fragment that is rapid on the NMR time scale at 300 K. Furthermore, the connectivity in **3b** was confirmed by use of single-crystal X-ray diffraction methods; an ORTEP[12] diagram for **3b** is provided in Figure 2. The overall structural characteristics of **3b** compare well with those found in **3a**,[10] and the related phosphine sulfide **2b** (vide supra). We have reported previously on the reactivity of Cp*Ru(κ^2-*P*,*N*-**1a**), a formally zwitterionic linkage isomer of **3b** that rearranges rapidly to a hydridocarbene complex via double

Table 2. Selected Interatomic Distances (Å) for 2a, 2b, 2c, 3a, 3b, [4c]$^+$BF$_4^-$, and 7

	2a	2b	2c	3a[a]	3b	[4c]$^+$BF$_4^-$ [b]	7[c]	7[d]
P−S	1.9575(6)	1.9651(7)	1.9659(6)					
P−C3	1.828(1)	1.808(2)	1.813(2)	1.837(2)	1.824(2)	1.802(5)	1.807(6)	1.822(6)
N−C2	1.417(2)	1.432(3)	1.434(2)	1.377(2)	1.428(2)	1.460(6)		
C1−C2	1.415(2)	1.420(3)	1.421(2)	1.428(2)	1.430(2)	1.433(5)	1.410(9)	1.405(9)
C2−C3	1.460(2)	1.457(3)	1.452(2)	1.454(2)	1.447(2)	1.447(6)	1.444(9)	1.444(8)
C3−C3a	1.466(2)	1.455(3)	1.458(2)	1.456(2)	1.452(2)	1.449(6)	1.471(8)	1.453(8)
C3a−C4	1.429(2)	1.433(3)	1.434(2)	1.433(2)	1.432(2)	1.428(6)	1.437(9)	1.426(9)
C4−C5	1.370(2)	1.358(3)	1.362(2)	1.360(2)	1.360(3)	1.364(8)	1.36(1)	1.373(9)
C5−C6	1.416(3)	1.429(3)	1.423(3)	1.421(3)	1.426(3)	1.425(9)	1.44(1)	1.42(1)
C6−C7	1.356(3)	1.351(3)	1.358(3)	1.361(3)	1.359(3)	1.362(8)	1.34(1)	1.36(1)
C7−C7a	1.432(2)	1.426(3)	1.432(2)	1.423(2)	1.432(2)	1.419(7)	1.426(9)	1.430(9)
C1−C7a	1.429(2)	1.424(3)	1.425(2)	1.432(2)	1.429(2)	1.425(7)	1.433(9)	1.422(9)
C3a−C7a	1.431(2)	1.446(3)	1.440(2)	1.430(2)	1.444(2)	1.463(7)	1.423(9)	1.455(8)
M−C1	2.138(2)	2.181(2)	2.059(2)	2.135(2)	2.189(2)	2.056(5)	2.186(6)	2.185(6)
M−C2	2.158(1)	2.225(2)	2.068(2)	2.238(2)	2.204(2)	2.058(5)	2.198(6)	2.202(6)
M−C3	2.131(2)	2.228(2)	2.063(2)	2.181(2)	2.206(2)	2.078(5)	2.252(6)	2.243(6)
M−C3a	2.203(2)	2.229(2)	2.106(2)	2.192(2)	2.217(2)	2.134(4)	2.259(6)	2.243(6)
M−C7a	2.190(2)	2.222(2)	2.118(2)	2.170(2)	2.228(2)	2.121(5)	2.224(6)	2.221(6)
Rh−P						2.350(1)	2.339(2)	2.351(2)
Rh−N or Cl						2.186(3)	2.373(2)	2.380(2)
Rh−$C_{alkene1}$[e]						2.229(5)	2.218(7)	2.198(7)
Rh−$C_{alkene2}$[e]						2.270(4)	2.251(7)	2.215(7)
Rh−$C_{alkene3}$[f]						2.141(5)	2.116(6)	2.118(6)
Rh−$C_{alkene4}$[f]						2.148(5)	2.143(6)	2.148(6)

[a] Data from ref 10 herein included for comparison purposes. [b] The Rh···Fe distance in the final refined structure is 4.24 Å. [c,d] Within the first and second independent molecules of **7**, respectively. [e] The Rh−cyclooctadiene distances trans to phosphorus. [f] The Rh−cyclooctadiene distances trans to nitrogen or chloride.

Scheme 3. Synthesis of Complexes 3a, 3b, and 3c[a]



2a, MLn = Mn(CO)$_3$
2b, MLn = Cp*Ru
2c, MLn = Cp*Fe

3a, MLn = Mn(CO)$_3$
3b, MLn = Cp*Ru
3c, MLn = Cp*Fe

[a] Reagents: (i) 1.4 equiv of $Cl_3SiSiCl_3$, 85 °C, 14 d or 6 equiv of Cp_2ZrHCl, 24 °C, 42 h (for **2a**); 6 equiv of Cp_2ZrHCl, 24 °C, 15 d (for **2b**); (ii) 0.25 equiv of $[Cp^*RuCl]_4$ (for **3b**) or Cp*Li/$FeCl_2$ (for **3c**).

geminal C−H bond activation.[2f] In monitoring the stability of **3b** in solution over the course of 96 h at 65 °C, no evidence for the rearrangement of **3b** to Cp*Ru(κ^2-*P*,*N*-**1a**), or the derived hydridocarbene, was observed (^{31}P NMR).

Having established viable synthetic routes to **3a**−**c**, we then proceeded to examine the Rh coordination chemistry of these racemic PCMs. In preliminary studies involving $[(COD)RhCl]_2$, divergent reactivity behavior was observed for the structurally related Ru (**3b**) and Fe (**3c**) metalloligands (Scheme 4). Treatment of **3b** with 0.5 equiv of $[(COD)RhCl]_2$ in THF resulted in the formation of a yellow precipitate, which in turn was isolated and identified as [(COD)Rh(κ^2-*P*,*N*-**3b**)]$^+$Cl$^-$ (**[4b]$^+$Cl$^-$**; 49% isolated yield). In contrast, under similar conditions, **3c** was transformed cleanly into the known zwitterionic Rh species, **5**.[2c] The apparent ability of **3c** to serve as a transfer agent for the anionic **1a** fragment, when placed in the context of the facile *rac*/*meso* isomerization of (3-PPh$_2$-η^5-C_9H_6)$_2$Fe at ambient temperature in THF solution that has been reported by Curnow and co-workers,[13c] suggests that such Cp*Fe-based metalloligands may be less well-suited for some catalytic applications. However, a report by Fang and co-workers,[13a] in which resolved Cp*Fe(4-PR$_2$-η^5-C_9H_6) complexes are shown to resist racemization, highlights that the substitution pattern in such donor-substituted η^5-indenyl species can influence the overall stability of the metalloligand architecture.

In contrast to the differing reactivity patterns observed between **3b** and **3c** with $[(COD)RhCl]_2$, each of **3a**−**c** was observed to react cleanly with $[(COD)Rh(THF)_2]^+BF_4^-$ (prepared in situ) to give the corresponding [(COD)Rh(κ^2-*P*,*N*-**3a**−**c**)]$^+$BF$_4^-$ complex (**[4a**−**c]$^+$BF$_4^-$**; 87%, 96%, and 89% isolated yield, respectively; Scheme 5). The observation of a single downfield-shifted ^{31}P NMR resonance (versus **3a**−**c**) that exhibits coupling to Rh provided support for the existence of a Rh−P linkage in **[4a**−**c]$^+$BF$_4^-$**. In addition, while a single ^{1}H NMR resonance and a single ^{13}C NMR resonance attributable to the NMe$_2$ unit is observed for each of **3a**−**c** (vide supra), coordination of the amino moiety to Rh in **[4a**−**c]$^+$BF$_4^-$** results in the observation of two distinct NMe signals in each of the ^{1}H NMR and ^{13}C NMR spectra, in keeping with the C_1-symmetric nature of these dinuclear complexes. For **[4c]$^+$BF$_4^-$**, the connectivity was confirmed by use of X-ray diffraction techniques; an ORTEP[12] diagram for **[4c]$^+$BF$_4^-$** is provided in Figure 2. The structural features observed in the **1a** fragment of **[4c]$^+$BF$_4^-$** mirror those found within the Ru-metalloligand **3b**, with the exception of a modest shortening of the P−C3 distance and a lengthening of the N−C2 distance in **[4c]$^+$BF$_4^-$**. As was noted in **2c**, the Cp*Fe unit is not bound in a symmetrical fashion to the C_5-ring of the **1a** unit in **[4c]$^+$BF$_4^-$**, and instead exhibits a tendency toward η^3-coordination. The interatomic distances found within the Rh coordination sphere of **[4c]$^+$BF$_4^-$** are strikingly similar to those observed in the related mononuclear complex [(COD)Rh(κ^2-3-*P*^{i}Pr$_2$-2-*N*Me$_2$-indene)]$^+$BF$_4^-$,[2c] including the observation of Rh−alkene distances trans to P that are significantly longer than those trans to N, in keeping with established structural trends in coordination chemistry. Whereas the restricted conformational flexibility associated with the P,N chelate in **[4c]$^+$BF$_4^-$** holds the Cp*Fe and [(COD)Rh]$^+$ fragments in relatively close proximity, the Rh···Fe distance (4.24 Å) precludes any significant metal−metal bonding interactions.

In light of the increasing utility of bulky monodentate phosphine ligands in asymmetric catalysis,[14] we sought to extend our synthetic efforts to the preparation of η^5-ML$_n$ derivatives

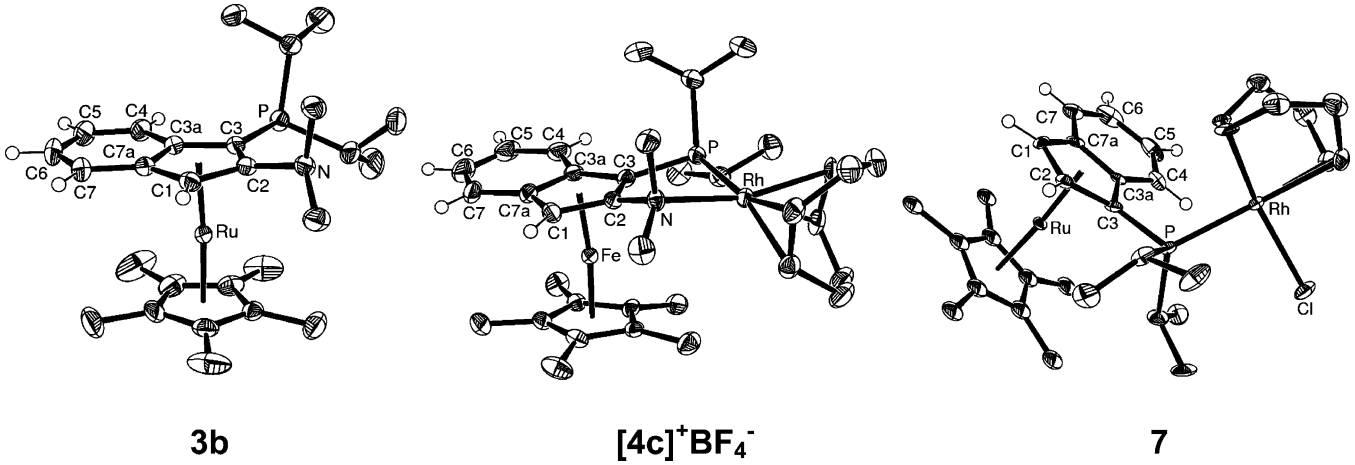
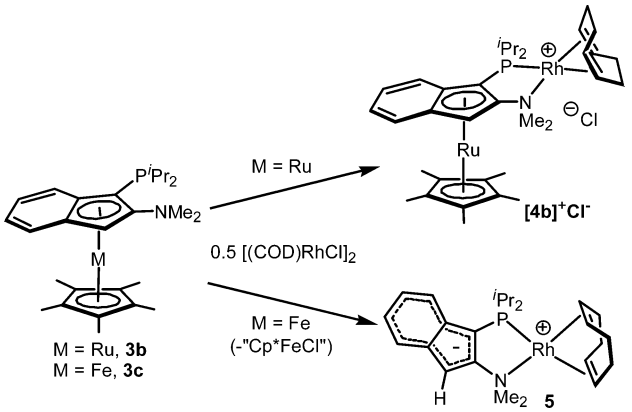
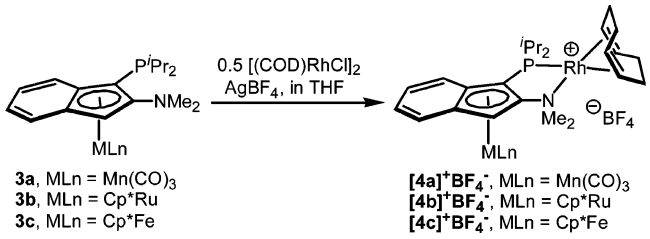


Figure 2. ORTEP diagrams for **3b**, **[4c]**$^+$**BF**$_4^-$, and **7**, shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted. Selected hydrogen atoms, as well as the tetrafluoroborate anion in **[4c]**$^+$**BF**$_4^-$, have been omitted for clarity. Only one of the two crystallographically independent molecules of **7** is shown.

Scheme 4. Divergent Reactivity of 3b and 3c with [(COD)RhCl]$_2$

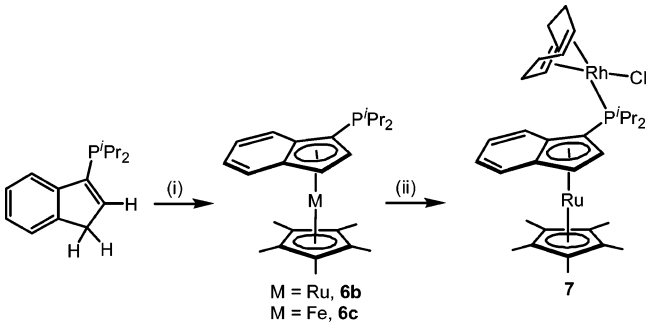


Scheme 5. Synthesis of the [(κ^2-*P*,*N*-3a−c)Rh(COD)]$^+$BF**$_4^-$ Complexes ([4a−c]$^+$**BF**$_4^-$)**



of 3-P^{i}Pr$_2$-indene.[15] Lithiation of 3-P^{i}Pr$_2$-indene followed by the addition of BrMn(CO)$_5$ generated a complex mixture of products, from which the desired complex (3-P^{i}Pr$_2$-η^5-C$_9$H$_6$)-Mn(CO)$_3$ (**6a**) could not be isolated. However, similar reactions employing 0.25 equiv of [Cp*RuCl]$_4$ or Cp*Li/FeCl$_2$ in place of BrMn(CO)$_5$ afforded **6b** or **6c** in 98% and 43% yield, respectively (Scheme 6). The ability of **6b** to function as a monophosphine ligand was demonstrated upon treatment with 0.5 equiv of [(COD)RhCl]$_2$, thereby allowing for the isolation of (COD)RhCl(κ^1-*P*-**6b**) **7** in 96% yield. Each of **6b**,**c** and **7**

Scheme 6. Synthesis of the Metalloligands 6b,c and the Dinuclear Ru/Rh Complex 7[a]



[a] Reagents: (i) *n*-BuLi, followed by 0.25 equiv of [Cp*RuCl]$_4$ (for **6b**) or Cp*Li/FeCl$_2$ (for **6c**); (ii) 0.5 equiv of [(COD)RhCl]$_2$.

were characterized spectroscopically, and, in the case of **7**, data from crystallographic studies provided confirmation of the atomic connectivity; an ORTEP[12] diagram for **7** is provided in Figure 2. The metrical features found in **7** can be compared to those of **2b**, **3b**, and the related complex (COD)RhCl(3-P^{i}Pr$_2$-indene).[15]

The addition of pinacolborane (HBpin) to styrene mediated by **[4a−c]**$^+$**BF**$_4^-$ was chosen as a test reaction with which to survey the potential influence of the η^5-coordinated organometallic moiety on the catalytic properties of the associated (κ^2-*P*,*N*)Rh fragment in these dinuclear complexes.[16−18] As well as representing a widely employed chemical transformation that provides access to organoboron synthons, metal-catalyzed alkene

(14) For selected reviews, see: (a) Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651. (b) de Vries, J. G.; Lefort, L. *Chem.-Eur. J.* **2006**, *12*, 4722. (c) Jerphagnon, T.; Renaud, J. L.; Bruneau, C. *Tetrahedron: Asymmetry* **2004**, *15*, 2101. (d) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131. (e) Komarov, I. V.; Börner, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 1197.

(15) Cipot, J.; Wechsler, D.; Stradiotto, M.; McDonald, R.; Ferguson, M. J. *Organometallics* **2003**, *22*, 5185.

(16) For selected reviews pertaining to alkene hydroboration, see: (a) Carroll, A.-M.; O'Sullivan, T. P.; Guiry, P. J. *Adv. Synth. Catal.* **2005**, *347*, 609. (b) Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, 4695. (c) Reference 1f herein.

(17) Whereas the catecholborane (HBcat) has traditionally been employed in such hydroboration reactivity surveys, HBpin was chosen specifically for the studies herein because HBpin is significantly more stable to air and nucleophiles than is HBcat, and the greater steric bulk of HBpin provides an increased challenge in terms of attaining branched selectivity. For further details, see: (a) Crudden, C. M.; Hleba, Y. B.; Chen, A. C. *J. Am. Chem. Soc.* **2004**, *126*, 9200. (b) Reference 16b herein.

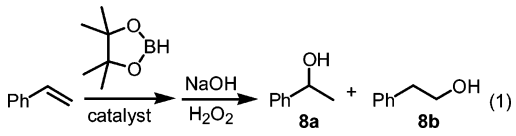
(18) For selected reports in which regioselectivity and enantioselectivity in alkene hydroboration employing HBcat are used in the evaluation of PCM design, see: (a) Kloetzing, R. J.; Lotz, M.; Knochel, P. *Tetrahedron: Asymmetry* **2003**, *14*, 255. (b) Reetz, M. T.; Beuttenmüller, E. W.; Goddard, R.; Pastó, M. *Tetrahedron Lett.* **1999**, *40*, 4977. (c) Schnyder, A.; Hintermann, L.; Togni, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 931. (d) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062. (e) Reference 9c herein.

Table 3. Rhodium-Catalyzed Addition of Pinacolborane to Styrene[a]

entry	catalyst	solvent	branched:linear[b] (**8a**:**8b**)
1	**[4a]**$^+$**BF$_4^-$**	THF	62:38
2	**[4a]**$^+$**BF$_4^-$**	DCE	71:29
3	**[4b]**$^+$**BF$_4^-$**	THF	35:65
4	**[4b]**$^+$**BF$_4^-$**	DCE	56:44
5	**[4c]**$^+$**BF$_4^-$**	THF	50:50
6	**[4c]**$^+$**BF$_4^-$**	DCE	54:46

[a] Conditions: 24 °C; 5.0 mol % catalyst; 24 h; pinacolborane-to-styrene ratio of 1.2:1; DCE = 1,2-dichloroethane. In all experiments listed, >90 % conversion of the styrene starting material was achieved, and no hydroboration products were observed in control experiments employing **3a**−**c**. [b] Product ratio on the basis of GC-FID data, rounded to the nearest percent. In all cases, alternative boron-containing products represented <3 % of the total product distribution.

hydroboration can serve as a prototype for E−H addition reactions in which product selectivity can be a challenge.[16] In addition to the possible branched and linear regioisomers that can arise from simple B−H addition (**8a** and **8b**, eq 1), unsaturated species formed via dehydrogenative borylation, and products of net diboration, are also observed commonly.



The preliminary results of our alkene hydroboration survey are collected in Table 3. Notably, each of **[4a**−**c]**$^+$**BF$_4^-$** proved to be an active catalyst for this transformation, with the observed regioselectivity, albeit modest,[19] being dependent on the nature of the η^5-coordinated metal fragment, as well as the solvent employed. While the Mn/Rh complex **[4a]**$^+$**BF$_4^-$** demonstrated selectivity for the branched product **8a** in both THF (entry 1) and 1,2-dichloroethane (entry 2), the related Ru/Rh species **[4b]**$^+$**BF$_4^-$** exhibited linear selectivity in THF (entry 3), but almost no selectivity in 1,2-dichloroethane (entry 4). As well, the Fe/Rh complex **[4c]**$^+$**BF$_4^-$** exhibited poor selectivity in both of these solvents (entries 5 and 6).

Summary and Conclusions

In summary, we have established modular synthetic pathways to new pentahapto complexes of the donor-substituted indenyl ligands 3-P^{i}Pr$_2$-indenyl, **1a**, and **1b**. Comparative reactivity studies featuring three examples of these (η^5-**1a**)ML$_n$ complexes (i.e., ML$_n$ = Mn(CO)$_3$, Cp*Ru, or Cp*Fe; **3a**−**c**) underscored some important differences in the behavior of such metalloligands. Whereas **3b** reacted cleanly with [(COD)RhCl]$_2$ to give the Ru/Rh species **[4b]**$^+$**Cl**$^-$, the congeneric Fe complex **3c** served as a source of **1a**, leading to the generation of the mononuclear zwitterionic Rh complex **5**. In contrast, each of **3a**−**c** was observed to react cleanly with [(COD)Rh(THF)$_2$]$^+$BF$_4^-$, thereby allowing for the isolation of the corresponding planar-chiral (racemic) dinuclear η^5/κ^2-*P*,*N* catalyst complexes **[4a**−**c]**$^+$**BF$_4^-$** in high isolated yield. The preliminary alkene hydroboration results described herein establish the viability of **[4a**−**c]**$^+$**BF$_4^-$** as catalysts for the addition of B−H bonds to unsaturated substrates, although we are presently unable to comment as to whether the source of the differing regioselectivity displayed by **[4a**−**c]**$^+$**BF$_4^-$** is primarily steric or electronic in origin. However, the observation of divergent selectivity in transformations mediated by **[4a**−**c]**$^+$**BF$_4^-$** suggests that the introduction of structural changes to the η^5-coordinated metal fragment may provide a systematic way in which to modify the steric and electronic properties of the κ^2-*P*,*N*-ligated metal fragment in these complexes.

(19) By comparison, Crudden and co-workers have demonstrated that [(COD)$_2$Rh]$^+$BF$_4^-$/bisphosphine mixtures can provide >96% branched selectivity. See ref 17a herein.

Experimental Section

General Considerations. All manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an mBraun glovebox apparatus, utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Celite and Florisil each were oven-dried for 5 d and then evacuated for 24 h prior to use. The non-deuterated solvents tetrahydrofuran, diethyl ether, toluene, 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 and diethyl ether were purified over two alumina-packed columns, while toluene, hexanes, and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. All solvents used within the glovebox were stored over activated 4 Å molecular sieves. CD_2Cl_2 (Cambridge Isotopes) was degassed by using three repeated freeze−pump−thaw cycles, dried over CaH_2 for 7 days, distilled in vacuo, and stored over 4 Å molecular sieves for 24 h prior to use. 1,2-Dichloroethane (Aldrich), C_6D_6 (Cambridge Isotopes), and pinacolborane (HBpin) were each degassed by using three repeated freeze−pump−thaw cycles and then dried over 4 Å molecular sieves for 24 h prior to use; styrene (Aldrich, containing 10−15 ppm 4-*tert*-butylcatechol as inhibitor) was degassed in a similar manner, but was not stored over molecular sieves. Compounds **1a-[H]** (now available commercially from Strem Chemicals Inc.),[20a] **1b[H]**,[20b] **1a[Li]**,[20a] 3-P^{i}Pr$_2$-indene,[15] and [Cp*RuCl]$_4$[21] were prepared employing literature procedures, while [(COD)RhCl]$_2$ was purchased from Strem Chemicals Inc. (Cp* = C_5Me_5; COD = η^4-1,5-cyclooctadiene). Cp$_2$ZrHCl (Cp = η^5-C_5H_5), BrMn(CO)$_5$, $FeCl_2$, and $AgBF_4$ were obtained from Aldrich. All of the aforementioned purchased and prepared solid reagents were dried in vacuo for 24 h prior to use. Otherwise, all other commercial reagents were obtained from Aldrich (except for 2.9 M *n*-BuLi in hexanes, Alfa Aesar) and were used as received. Unless otherwise stated, ^{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, and ^{1}H−^{13}C HMBC NMR experiments. In some cases, fewer than expected unique ^{13}C NMR resonances were observed, despite prolonged acquisition times. IR data were collected on a Bruker VECTOR 22 FT-IR instrument. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada.

Synthesis of 2a. A 1.6 M hexanes solution (precooled to −35 °C) of *n*-BuLi (0.20 mL, 0.32 mmol) was added dropwise via syringe to a glass vial containing a magnetically stirred solution (precooled to −35 °C) of **1b[H]** (0.099 g, 0.32 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

(20) (a) Stradiotto, M.; Cipot, J.; McDonald, R. *J. Am. Chem. Soc.* **2003**, *125*, 5618. (b) Wechsler, D.; Myers, A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Inorg. Chem.* **2006**, *45*, 4562.

(21) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

cap and left to stir for 1.5 h at ambient temperature; the clean lithiation of **1b[H]** was monitored in situ by the disappearance of a ^{31}P NMR signal corresponding to **1b[H]** and the appearance of a single new resonance at 54 ppm. A mixture of $BrMn(CO)_5$ (0.089 g, 0.32 mmol) in toluene (5 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 3 d 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 **2a** as an analytically pure, orange solid (0.14 g, 0.31 mmol, 96%). Anal. Calcd for $C_{20}H_{25}PSNO_3Mn$: C, 53.93; H, 5.66; N, 3.14. Found: C, 53.61; H, 5.72; N, 3.26. ^{1}H NMR (C_6D_6): δ 9.42 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4-H or C7-H), 7.06 (d, $^3J_{HH}$ = 8.1 Hz, 1H, C7-H or C4-H), 6.80−6.72 (m, 2H, C5-H and C6-H), 4.46 (s, 1H, C1-H), 3.16 (m, 1H, P(C*H*Me$_2$)), 2.18 (m, 1H, P(C*H*Me$_2$)), 2.09 (s, 6H, NMe$_2$), 1.77 (d of d, $^3J_{PH}$ = 18.6 Hz, $^3J_{HH}$ = 6.0 Hz, 3H, P(CHMe*Me*)), 1.31 (d of d, $^3J_{PH}$ = 17.3 Hz, $^3J_{HH}$ = 5.7 Hz, 3H, P(CHMe*Me*)), 1.08 (d of d, $^3J_{PH}$ = 17.9 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, P(CHMe*Me*)), 1.77 (d of d, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 6.7 Hz, 3H, P(CHMe*Me*)). ^{13}C{^{1}H} NMR (C_6D_6): δ 223.7 (CO), 138.7 (C2), 129.0 (C4 or C7), 127.1 (C5 or C6), 126.1 (C6 or C5), 124.7 (C7 or C4), 105.5 (d, J = 7.3 Hz, C7a or C3a), 100.0 (d, J = 7.6 Hz, C3a or C7a), 61.5 (C1), 46.2 (NMe$_2$), 30.7 (m, P(*C*HMe$_2$)), 28.0 (m, P(*C*HMe$_2$)), 19.6 (P(CHMe*Me*)), 19.2 (P(CHMe*Me*)), 18.5 (P(CHMe*Me*)), 17.2 (P(CHMe*Me*)). ^{31}P{^{1}H} NMR (C_6D_6): δ 64.4. FTIR (cm^{-1}) ν(CO): 2014, 1945, 1931. Crystals of **2a** suitable for single-crystal X-ray diffraction analysis were grown from diethyl ether at −35 °C.

Synthesis of 2b. A glass vial charged with a stir bar, **1b[H]** (0.28 g, 0.91 mmol), and diethyl ether (2 mL) was cooled to −35 °C. To the vial was added dropwise a 1.6 M hexanes solution of *n*-BuLi (0.57 mL, 0.91 mmol; precooled to −35 °C) via Eppendorf pipet, and the mixture was stirred for 1 h. The resulting slurry was cooled to −35 °C, to which a suspension of [Cp*RuCl]$_4$ (0.25 g, 0.23 mmol) in diethyl ether (2 mL) (precooled to −35 °C) was added slowly. The reaction mixture was stirred for an additional 1.5 h at ambient temperature, and subsequently filtered through a plug of Celite. The filtrate was collected, and the solvent and other volatile materials were removed in vacuo to leave **2b** as an analytically pure, dark yellow solid (0.43 g, 0.79 mmol, 87%). Anal. Calcd for $C_{27}H_{40}PSNRu$: C, 59.75; H, 7.43; N, 2.58. Found: C, 59.71; H, 7.49; N, 2.48. ^{1}H NMR (C_6D_6): δ 8.40 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C7-H or C4-H), 7.13−7.18 (m, 2H, aryl H), 7.05−7.08 (m, 1H, aryl H), 5.23 (s, 1H, C1-H), 3.35 (m, 1H, P(C*H*Me$_c$Me$_d$)), 2.76 (s, 6H, NMe$_2$), 2.45 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.73 (d of d, $^3J_{PH}$ = 18.3 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.70 (s, 15H, C$_5$Me$_5$), 1.46 (d of d, $^3J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_d$*Me$_c$)), 1.32 (d of d, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me$_b$*Me$_a$)), 1.05 (d of d, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, P(CH*Me$_a$*Me$_b$)). ^{13}C{^{1}H} NMR (C_6D_6): δ 129.3 (aryl CH), 124.0 (aryl CH), 123.1 (aryl CH), 122.6 (d, $^2J_{PC}$ = 9.3 Hz, C2), 120.6 (aryl CH), 92.1 (d, J_{PC} = 8.3 Hz, C3a or C7a), 91.8 (d, J_{PC} = 10.2 Hz, C7a or C3a), 83.5 (*C*$_5$Me$_5$), 67.8 (d, $^1J_{PC}$ = 77.2 Hz, C3), 64.7 (d, $^3J_{PC}$ = 7.2 Hz, C1), 49.1 (NMe$_2$), 31.6 (d, $^1J_{PC}$ = 50.5 Hz, P(*C*HMe$_a$Me$_b$)), 27.8 (d, $^1J_{PC}$ = 51.5 Hz, P(*C*HMe$_c$Me$_d$)), 19.8 (P(CH*Me*Me)), 17.6 (P(CH*Me*Me)), 17.6 (P(CH*Me*Me)), 16.1 (P(CH*Me*Me)), 9.9 (C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (C_6D_6): δ 65.3. Crystals of **2b** suitable for single-crystal X-ray diffraction analysis were grown from pentane at −35 °C.

Synthesis of 2c. A vial was charged with a stir bar, Cp*H (0.049 mL, 0.31 mmol), and THF (2 mL). To the vial was added a precooled (−35 °C) solution of *n*-BuLi (0.11 mL of a 2.9 M hexanes solution, 0.31 mmol) via Eppendorf pipet, at which point a white precipitate formed immediately. The mixture was stirred magnetically at ambient temperature for 2 h and then cooled to −35 °C. This mixture was then added dropwise to a suspension of $FeCl_2$ (0.039 g, 0.31 mmol) in THF (1.5 mL) that had been precooled to −35 °C. The resulting lime-green mixture (**A**, containing "Cp*FeCl") was stirred magnetically for 2 h. A separate vial was charged with a stir bar, **1b[H]** (0.095 g, 0.31 mmol), and THF (2 mL), and the mixture was cooled to −35 °C, at which point a precooled 2.9 M hexanes solution of *n*-BuLi (0.11 mL, 0.31 mmol) was added dropwise via Eppendorf pipet. The mixture was stirred magnetically at ambient temperature for 2 h, after which the solvent and other volatile materials were removed in vacuo. The residue was washed with hexanes and dried in vacuo. To the remaining solid was added THF (2 mL), and this mixture (**B**) was cooled to −35 °C. Mixture **A** was also cooled to −35 °C, at which point mixture **B** was added slowly to mixture **A**, giving a burgundy-colored mixture. This combined reaction mixture was allowed to react for 18 h at ambient temperature under the influence of magnetic stirring, after which the reaction mixture was filtered through Celite and the filtrate was dried in vacuo. The residue was then extracted with pentane (5 mL), and the resulting pentane mixture was filtered through a short plug of Celite. The filtrate was collected, and the solvent and other volatile materials were removed in vacuo. Any decamethylferrocene that was produced during the synthesis was then removed via sublimation to leave **2c** as an analytically pure, purple solid (0.085 g, 0.17 mmol, 55%). Anal. Calcd for $C_{27}H_{40}PSNFe$: C, 65.18; H, 8.11; N, 2.82. Found: C, 65.07; H, 8.06; N, 2.75. ^{1}H NMR (C_6D_6): δ 9.33 (d, $^3J_{HH}$ = 8.3 Hz, 1H, C7-H), 7.12 (d of d, $^3J_{HH}$ = 8.3 Hz, J = 1.1 Hz, 1H, C4-H), 6.96−7.06 (m, 2H, C5-H and C6-H), 4.26 (s, 1H, C1-H), 3.13 (m, 1H, P(C*H*Me$_c$Me$_d$)), 2.34 (s, 6H, NMe$_2$), 2.06 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.90 (d of d, $^3J_{PH}$ = 18.2 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, P(CH*Me$_c$*Me$_d$)), 1.54 (s, 15H, C$_5$Me$_5$), 1.37 (d of d, $^3J_{PH}$ = 16.7 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me$_d$*Me$_c$)), 1.16 (d of d, $^3J_{PH}$ = 17.3 Hz, $^3J_{HH}$ = 6.7 Hz, 3H, P(CH*Me$_b$*Me$_a$)), 0.63 (d of d, $^3J_{PH}$ = 16.8 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, P(CH*Me$_a$*Me$_b$)). ^{13}C-{^{1}H} NMR (C_6D_6): δ 132.5 (C7), 126.8 (C4), 125.0 (C5 or C6), 123.1 (C6 or C5), 118.9 (d, $^2J_{PC}$ = 8.4 Hz, C2), 89.3 (C3a or C7a), 89.2 (C7a or C3a), 78.2 (*C*$_5$Me$_5$), 63.6 (d, $^1J_{PC}$ = 77.2 Hz, C3), 58.8 (d, $^3J_{PC}$ = 7.0 Hz, C1), 48.2 (NMe$_2$), 30.5 (d, $^1J_{PC}$ = 50.3 Hz, P(*C*HMe$_c$Me$_d$)), 29.5 (d, $^1J_{PC}$ = 24.6 Hz, P(*C*HMe$_a$Me$_b$)), 20.8 (P(CH*Me*Me)), 17.8 (P(CH*Me*Me)), 17.4 (P(CH*Me*Me)), 17.3 (P(CH*Me*Me)), 10.1 (C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (C_6D_6): δ 65.2. Crystals of **2c** suitable for single-crystal X-ray diffraction analysis were grown from pentane at −35 °C.

Protocol for the Reduction of 2a to 3a Using Cp$_2$ZrHCl. To a solution of **2a** (0.13 g, 0.29 mmol) in THF (5 mL) was added 3 equiv of Cp$_2$ZrHCl, followed by stirring for 18 h. Analysis of the reaction mixture (^{31}P NMR) revealed the incomplete conversion of **2a** to **3a**. The reaction mixture was filtered through Celite, an additional 3 equiv of Cp$_2$ZrHCl was added to the fitrate, and the mixture was stirred magnetically for an additional 24 h. Analysis of the reaction mixture (^{31}P NMR) at this stage revealed the quantitative conversion to **3a**. The reaction mixture was filtered through Celite, and the solvent was removed in vacuo. The residue was taken up in pentane or hexanes (10 mL) and filtered through Celite, followed by removal of the solvent in vacuo, affording **3a** (0.10 g, 0.24 mmol, 83%).

Synthesis of 3b. A glass vial charged with a stir bar, excess **1a[Li]** (1.13 mmol), and THF (2 mL) was cooled to −35 °C. A separate vial charged with [Cp*RuCl]$_4$ (0.24 g, 0.22 mmol) and diethyl ether (2 mL) was cooled to −35 °C, and subsequently was added slowly to the solution of **1a[Li]**. The resulting mixture was stirred magnetically at ambient temperature for 18 h. The solvent and other volatile materials were removed in vacuo, and the residue was taken up in a mixture of pentane (5 mL) and diethyl ether (2 mL) and passed through a Florisil column and eluted with pentane. The filtrate was then concentrated and dried in vacuo affording analytically pure **3b** as a yellow solid (0.33 g, 0.65 mmol, 74%). Anal. Calcd for $C_{27}H_{40}PNRu$: C, 63.50; H, 7.89; N, 2.74. Found: C, 63.25; H, 7.99; N, 2.74. ^{1}H NMR (C_6D_6): δ 7.55 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C7-H or C4-H), 6.94 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C4-H or

C7-H), 6.86−6.81 (m, 2H, C5-H and C6-H), 4.67 (s, 1H, C1-H), 2.58 (s, 6H, NMe_2), 2.57−2.43 (m, 2H, P(C*H*$Me_c$$Me_d$) and P(C*H*$Me_a$$Me_b$)), 1.57 (s, 15H, C_5Me_5), 1.36 (d of d, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_c$$Me_d$)), 1.33−1.25 (m, 6H, P(CH*Me*$_a$*Me*$_b$)), 1.18 (d of d, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me*$_d$$Me_c$)). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 128.0 (C4 or C7), 127.3 (d, $^2J_{PC}$ = 6.5 Hz, C2), 124.7 (C7 or C4), 121.9 (C5 or C6), 120.6 (C6 or C5), 94.0 (d, J_{PC} = 10.1 Hz, C3a or C7a), 91.3 (C7a or C3a), 82.1 (C_5Me_5), 70.6 (d, $^1J_{PC}$ = 31.8 Hz, C3), 63.3 (C1), 46.8 (d, $^4J_{PC}$ = 6.7 Hz, NMe_2), 24.3 (d, $^1J_{PC}$ = 13.1 Hz, P(*C*H$Me_c$$Me_d$)), 23.7 (d, $^1J_{PC}$ = 13.1 Hz, P(*C*H$Me_a$$Me_b$)), 23.3 (d, $^2J_{PC}$ = 23.1 Hz, P(CH*Me*$_d$$Me_c$)), 22.9 (d, $^2J_{PC}$ = 20.8 Hz, P(CHMe_a*Me*$_b$)), 21.5 (d, $^2J_{PC}$ = 18.9 Hz, P(CH*Me*$_a$$Me_b$)), 20.7 (d, $^2J_{PC}$ = 11.1 Hz, P(CHMe_d*Me*$_c$)), 10.8 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −0.3. Crystals of **3b** suitable for single-crystal X-ray diffraction analysis were grown from pentane at −35 °C.

Synthesis of 3c. A vial charged with a stir bar and a solution of Cp*FeCl (1.10 mmol) in THF (2 mL) (prepared in a manner analogous to that described for the synthesis of **2c**) was cooled to −35 °C. To this solution was added slowly a solution of **1a[Li]** (1.10 mmol) and THF (2 mL) (precooled to −35 °C), and the mixture was stirred magnetically at ambient temperature for 2 h. The solvent and other volatile materials were removed in vacuo, and the residue was taken up in pentane (5 mL) followed by filtration through a short plug of Celite. The filtrate was collected, and the solvent and other volatile materials were removed in vacuo. Any decamethylferrocene that was produced during the synthesis was then removed via sublimation to leave **3c** as an analytically pure, purple solid (0.31 g, 0.68 mmol, 62%). Anal. Calcd for $C_{27}H_{40}PNFe$: C, 69.57; H, 8.66; N, 3.01. Found: C, 69.57; H, 8.50; N, 2.96. ^1H NMR (C_6D_6): δ 7.77 (d, $^3J_{HH}$ = 8.4 Hz, 1H, C7-H or C4-H), 7.22 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C4-H or C7-H), 6.95−7.02 (m, 2H, C5-H and C6-H), 4.24 (s, 1H, C1-H), 2.63 (s, 6H, NMe_2), 2.53−2.62 (m, 2H, P(C*H*$Me_c$$Me_d$) and P(C*H*$Me_a$$Me_b$)), 1.58 (s, 15H, C_5Me_5), 1.58 (d of d, $^3J_{PH}$ = 10.3 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_a$$Me_b$)), 1.30 (d of d, $^3J_{PH}$ = 13.7 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me*$_b$$Me_a$)), 1.19 (d of d, $^3J_{PH}$ = 11.3 Hz, $^3J_{HH}$ = 7.4 Hz, 3H, P(CH*Me*$_c$$Me_d$)), 1.15 (d of d, $^3J_{PH}$ = 7.1 Hz, $^3J_{HH}$ = 2.6 Hz, 3H, P(CH*Me*$_d$$Me_c$)). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 130.1 (C4 or C7), 123.5 (C5 or C6), 122.3 (C6 or C5), 120.6 (d, $^2J_{PC}$ = 4.4 Hz, C2), 89.8 (d, J_{PC} = 12.2 Hz, C3a or C7a), 87.8 (C7a or C3a), 76.8 (C_5Me_5), 63.3 (d, $^1J_{PC}$ = 31.1 Hz, C3), 75.7 (C1), 46.3 (d, $^4J_{PC}$ = 6.4 Hz, NMe_2), 23.6 (d, $^1J_{PC}$ = 25.7 Hz, P(CH*Me*$_c$$Me_d$) or P(CH$Me_c$*Me*$_d$)), 23.3 (d, $^1J_{PC}$ = 13.8 Hz, P(*C*H$Me_a$$Me_b$) or P(*C*H$Me_c$$Me_d$)), 22.9 (d, $^1J_{PC}$ = 11.9 Hz, (P(*C*H$Me_d$$Me_c$) or P(*C*H$Me_a$$Me_b$)), 22.7 (d, $^2J_{PC}$ = 4.0 Hz, P(CHMe_c*Me*$_d$) or P(CH*Me*$_c$$Me_d$)), 21.5 (d, $^2J_{PC}$ = 19.1 Hz, P(CH*Me*$_b$$Me_a$)), 20.2 (d, $^2J_{PC}$ = 8.0 Hz, P(CHMe_b*Me*$_a$)), 10.2 (C_5Me_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −2.5.

Synthesis of [4b]$^+$Cl$^-$. To a glass vial charged with a stir bar, **3b** (0.12 g, 0.24 mmol), and THF (2 mL) was added a solution of $[(COD)RhCl]_2$ (0.059 g, 0.12 mmol) in THF (4 mL). The mixture was stirred for 4 h at ambient temperature, and during this time a precipitate formed. The supernatant was decanted, and the precipitate was washed with THF (5 mL). The residue was then dried in vacuo, affording analytically pure **[4b]$^+$Cl$^-$** as a yellow solid (0.088 g, 0.12 mmol, 49%). Anal. Calcd for $C_{35}H_{52}PNRuRhCl$: C, 55.50; H, 6.93; N, 1.85. Found: C, 55.22; H, 6.77; N, 1.53. ^1H NMR (CD_2Cl_2): δ 7.17 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C7-H or C4-H), 7.12−7.00 (m, 3H, aryl CH), 5.38 (br s, 1H, COD), 5.24 (s, 1H, C1-H), 4.82 (br s, 1H, COD), 4.55 (br s, 1H, COD), 3.84 (br s, 1H, COD), 3.20−2.80 (br m, 6H, NMe_2), 2.69−2.45 (m, 4H, P(C*H*$Me_c$$Me_d$), P(C*H*$Me_a$$Me_b$) and COD), 2.40−2.21 (m, 4H, COD), 1.96 (d of d, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 17.5 Hz, 3H, P(CH*Me*$_d$$Me_c$)), 1.99−1.82 (m, 2H, COD), 1.59 (d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 14.0 Hz, 3H, P(CHMe$_d$*Me*$_c$)), 1.55 (s, 15H, C_5Me_5), 1.15 (d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 15.0 Hz, 3H, P(CH*Me*$_b$Me$_a$)), 0.94 (d of d, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 17.5 Hz, 3H, P(CHMe$_b$*Me*$_a$)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 131.2 (d, $^2J_{PC}$ = 24.3 Hz, C2), 125.4 (C7 or C4), 125.0 (aryl CH), 124.5 (aryl CH), 123.9 (aryl CH), 106.6 (br s, COD), 101.8 (br s, COD), 96.9 (d, J_{PC} = 3.9 Hz, C3a or C7a), 88.1 (C7a or C3a), 84.8 (C_5Me_5), 76.2 (m, COD), 69.6 (COD), 69.2 (d, $^1J_{PC}$ = 52.5 Hz, C3), 61.1 (d, $^3J_{PC}$ = 8.8 Hz, C1), 54.8 (br s, NMe_2) 34.4 (br s, COD), 30.4 (br s, COD), 26.2−26.1 (P(*C*H$Me_a$$Me_b$) and COD), 25.5 (d, $^1J_{PC}$ = 26.0 Hz, P(*C*H$Me_c$$Me_d$)), 20.8 (P(CH*Me*$_d$$Me_c$)), 20.1 (d, $^2J_{PC}$ = 4.0 Hz, P(CH*Me*$_a$$Me_b$)), 19.4 (d, $^2J_{PC}$ = 3.7 Hz, P(CHMe$_d$*Me*$_c$)), 18.2 (P(CHMe$_a$*Me*$_b$)), 10.1 (C_5Me_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 42.4 (d, $^1J_{PRh}$ = 150.6 Hz).

Synthesis of [4b]$^+$BF$_4^-$. To a glass vial containing a magnetically stirred suspension of $[(COD)RhCl]_2$ (0.025 g, 0.050 mmol) in THF (2 mL) was added a suspension of $AgBF_4$ (0.020 g, 0.10 mmol) in THF (2 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 **3b** (0.051 g, 0.10 mmol) in THF (3 mL). The reaction mixture was stirred for an additional 3 h at ambient temperature, during which time the solution developed a yellow-orange coloration. The reaction mixture was then filtered through a plug of Celite, followed by removal of the solvent and other volatiles in vacuo yielding **[4b]$^+$BF$_4^-$** as a orange solid (0.078 g, 0.096 mmol, 96%). Anal. Calcd for $C_{35}H_{52}PNRuRhBF_4$: C, 51.96; H, 6.48; N, 1.73. Found: C, 51.84; H, 6.45; N, 1.75. ^1H NMR (CD_2Cl_2): δ 7.19 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C7-H or C4-H), 7.14−7.05 (m, 3H, aryl CH), 5.42 (br s, 1H, COD), 5.19 (s, 1H, C1-H), 4.87 (m, 1H, COD), 4.53 (m, 1H, COD), 3.90 (m, 1H, COD), 3.21 (s, 3H, NMe), 2.80 (s, 3H, NMe), 2.75−2.20 (m, 9H, P(C*H*$Me_c$$Me_d$), P(C*H*$Me_a$$Me_b$), and COD), 2.01 (d of d, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me*$_c$$Me_d$)), 1.95 (m, 1H, COD), 1.63 (d of d, $^3J_{PH}$ = 14.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_c$*Me*$_d$)), 1.59 (s, 15H, C_5Me_5), 1.19 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me*$_a$$Me_b$)), 0.99 (d of d, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me*$_b$)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 131.1 (d, $^2J_{PC}$ = 24.3 Hz, C2), 125.5 (C4 or C7), 125.0 (aryl CH), 124.6 (aryl CH), 124.0 (aryl CH), 106.7 (m, COD), 101.7 (m, COD), 97.0 (C3a or C7a), 88.2 (C7a or C3a), 84.9 (C_5Me_5), 76.1 (d, J = 12.7 Hz, COD), 69.7 (d, J = 12.0 Hz, COD), 69.2 (d, $^1J_{PC}$ = 32.5 Hz, C3), 60.8 (d, J = 8.8 Hz, C1), 55.1 (NMe), 54.0 (NMe), 34.4 (COD), 30.4 (COD), 26.2 (d, $^1J_{PC}$ = 23.0 Hz, P(*C*H$Me_c$$Me_d$)), 26.1 (COD), 25.5 (d, $^1J_{PC}$ = 25.8 Hz, P(*C*H$Me_a$$Me_b$)), 20.8 (P(CH*Me*$_c$$Me_d$)), 20.1 (P(CHMe$_a$*Me*$_b$)), 19.4 (P(CHMe$_c$*Me*$_d$)), 18.2 (P(CH*Me*$_aMe_b$)), 10.0 ($C_5Me_5$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 42.5 (d, $^1J_{PRh}$ = 150.4 Hz).

Synthesis of [4a]$^+$BF$_4^-$. A procedure analogous to that described for the synthesis of **[4b]$^+$BF$_4^-$** was employed, using **3a** (0.015 g, 0.037 mmol) in THF (1 mL). Complex **[4a]$^+$BF$_4^-$** was isolated as a dark yellow solid (0.023 g, 0.032 mmol, 87%). Anal. Calcd for $C_{28}H_{37}PNMnO_3RhBF_4$: C, 47.25; H, 5.24; N, 1.97. Found: C, 47.41; H, 5.62; N, 1.83. ^1H NMR (CD_2Cl_2): δ 7.72 (d, $^3J_{HH}$ = 8.3 Hz, 1H, C7-H or C4-H), 7.49−7.42 (m, 2H, aryl CH), 7.29 (t, $^3J_{HH}$ = 7.4 Hz, C6-H or C5-H), 6.05 (s, 1H, C1-H), 5.60 (br s, 1H, COD), 4.94 (br s, 1H, COD), 4.66 (br s, 1H, COD), 3.94 (br s, 1H, COD), 3.39 (s, 3H, NMe), 2.81 (s, 3H, NMe), 2.81−2.68 (m, 4H, P(C*H*$Me_c$$Me_d$), P(C*H*$Me_b$$Me_a$), and COD), 2.47 (m, 1H, COD), 2.39−2.31 (m, 2H, COD), 2.01−1.93 (m, 5H, COD and P(CHMe_c*Me*$_d$)), 1.89−1.85 (m, 4H, P(CH*Me*$_c$$Me_d$) and COD), 1.34 (d of d, $^3J_{PH}$ = 15.3 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me*$_b$)), 1.22 (d of d, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me*$_a$$Me_d$)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 223.2 (CO), 141.5 (d, $^2J_{PC}$ = 21.4 Hz, C2), 130.5 (aryl CH), 129.1 (C4 or C7), 127.3 (C5 or C6), 122.8 (aryl CH), 108.0 (t, J = 7.4 Hz, COD), 102.5 (COD), 100.9 (m, aryl C), 77.4 (d, J = 12.5 Hz, COD), 71.3 (d, J = 12.5 Hz, COD), 68.3 (d, $^3J_{PC}$ = 11.7 Hz, C1), 56.6 (NMe), 50.6 (NMe), 35.1 (COD), 30.6 (COD), 29.6 (COD), 27.6 (d, $^1J_{PC}$ = 22.6 Hz, P(*C*H$Me_c$$Me_d$) or P(*C*H$Me_a$$Me_b$)), 25.8 (P(*C*H$Me_a$$Me_b$) or P(*C*H$Me_c$$Me_d$)), 25.6 (COD), 22.7 (P(CH*Me*$_a$$Me_b$)), 20.1 (d, $^2J_{PC}$ = 3.2 Hz, (P(CHMe$_c$-

Me$_d$)), 19.3 (d, $^2J_{PC}$ = 3.5 Hz, P(CH*Me*$_c$Me$_d$)), 18.8 (P(CH-Me$_a$*Me*$_b$)). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 44.5 (d, $^1J_{PRh}$ = 151.8 Hz). FTIR (cm^{-1}) ν(CO): 2025, 1953, 1933.

Synthesis of [4c]$^+$BF$_4^-$. A procedure analogous to that described for the synthesis of **[4b]$^+$BF$_4^-$** was employed, using **3c** (0.044 g, 0.095 mmol) in THF (2 mL). Complex **[4c]$^+$BF$_4^-$** was isolated as a dark purple solid (0.068 g, 0.089 mmol, 89%). Anal. Calcd for $C_{35}H_{52}PNFeRhBF_4$: C, 55.04; H, 6.87; N, 1.83. Found: C, 54.83; H, 7.06; N, 1.52. ^{1}H NMR (CD_2Cl_2): δ 7.50 (d, $^3J_{HH}$ = 5.3 Hz, 1H, C7-H or C4-H), 7.34 (m, 1H, aryl CH), 7.31−7.27 (m, 2H, aryl CH), 5.42 (br s, 1H, COD), 4.93 (s, 1H, C1-H), 4.80 (m, 1H, COD), 4.62 (m, 1H, COD), 4.07 (m, 1H, COD), 3.06 (s, 3H, NMe), 2.98−2.91 (m, 4H, NMe and P(C*H*Me$_c$Me$_d$)), 2.67 (m, 1H, COD), 2.52 (m, 3H, COD), 2.36 (m, 2H, COD and P(C*H*Me$_b$Me$_a$)), 2.26 (m, 2H, COD), 2.11 (d of d, $^3J_{PH}$ = 15.9 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, P(CHMe$_c$*Me*$_d$)), 2.04 (m, 1H, COD), 1.74 (d of d, $^3J_{PH}$ = 23.4 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, P(CH*Me*$_c$Me$_d$)), 1.60 (s, 15H, C_5Me_5), 1.21 (d of d, $^3J_{PH}$ = 15.1 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_a$*Me*$_b$)), 0.78 (d of d, $^3J_{PH}$ = 16.1 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, P(CH*Me*$_a$Me$_b$)). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 128.5 (C4 or C7), 127.3 (aryl CH), 126.1 (aryl CH), 125.9 (aryl CH), 105.5 (t, J = 8.4 Hz, COD), 102.2 (t, J = 10.0 Hz, COD), 94.2 (quat.), 83.6 (quat.), 79.3 (*C*$_5$Me$_5$), 75.5 (d, J = 12.4 Hz, COD), 71.8 (d, J = 12.3 Hz, COD), 55.8 (d, J = 8.9 Hz, C1), 55.6 (NMe), 52.1 (NMe), 33.6 (COD), 31.0 (COD), 29.7 (COD), 27.1−26.6 (P(*C*HMe$_c$Me$_d$), P(*C*HMe$_a$Me$_b$), and COD), 22.0 (P(CHMe$_c$*Me*$_d$)), 20.6 (P(CH*Me*$_a$Me$_b$)), 19.9 (P(CH*Me*$_c$Me$_d$)), 19.5 (P(CHMe$_a$*Me*$_b$)), 9.9 (C_5*Me*$_5$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 43.8 (d, $^1J_{PRh}$ = 150.0 Hz). Crystals of **[4c]$^+$BF$_4^-$** suitable for single-crystal X-ray diffraction analysis were grown from THF at −35 °C.

Synthesis of 6b. A glass vial charged with a stir bar, 3-P^{i}Pr$_2$-indene (0.30 g, 1.29 mmol), and THF (3 mL) was cooled to −35 °C. To this vial was added dropwise via Eppendorf pipet a 1.6 M hexanes solution of *n*-BuLi (0.81 mL, 1.29 mmol; precooled to −35 °C), after which the mixture was stirred magnetically for 1 h at ambient temperature. The reaction mixture was then cooled to −35 °C, to which was added a solution of [Cp*RuCl]$_4$ (0.35 g, 0.32 mmol) in THF (2 mL) (precooled to −35 °C). The mixture was stirred magnetically at ambient temperature for 18 h, after which the solvent was removed in vacuo and the residue was taken up in diethyl ether (5 mL) followed by filtration through a plug of Celite. The filtrate was then concentrated and dried in vacuo, affording **6b** as an analytically pure, dark yellow solid (0.59 g, 1.26 mmol, 98%). Anal. Calcd for $C_{25}H_{35}PRu$: C, 64.20; H, 7.55; N, 0.00. Found: C, 64.19; H, 7.35; N < 0.3. ^{1}H NMR (C_6D_6): δ 7.52 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C4-H or C7-H), 6.95 (d, $^3J_{HH}$ = 8.2 Hz, 1H, C7-H or C4-H), 6.80−6.75 (m, 2H, C5-H and C6-H), 4.69 (d, $^3J_{HH}$ = 2.5 Hz, 1H, C1-H), 4.44 (d, $^3J_{HH}$ = 2.5 Hz, 1H, C2-H), 2.25 (m, 1H, P(C*H*MeMe)), 1.85 (m, 1H, P(C*H*MeMe)), 1.53 (s, 15H, C_5Me_5), 1.42 (d of d, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CH*Me*Me)), 1.23 (apparent t, J = 7.3 Hz, 3H, P(CH*Me*Me)), 1.08 (d of d, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*Me)), 1.08 (d of d, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*Me)). ^{13}C{^{1}H} NMR (C_6D_6): δ 126.2 (d, J_{PC} = 8.0 Hz, aryl C), 124.7 (aryl C), 121.8 (aryl C), 120.3 (aryl C), 96.4 (d, J = 23.2 Hz, C3a or C7a), 94.0 (d, J = 2.9 Hz, C7a or C3a), 82.3 (*C*$_5$Me$_5$), 77.7 (d, $^2J_{PC}$ = 4.6 Hz, C2), 76.5 (d, $^1J_{PC}$ = 21.3 Hz, C3), 70.5 (C1), 25.3 (d, $^1J_{PC}$ = 15.7 Hz, P(*C*HMeMe)), 24.0 (d, $^2J_{PC}$ = 28.6 Hz, P(CH*Me*Me)), 23.4 (d, $^1J_{PC}$ = 11.2 Hz, P(*C*HMeMe)), 21.1 (d, $^2J_{PC}$ = 20.8 Hz, P(CHMe*Me*)), 20.4 (d, $^2J_{PC}$ = 12.0 Hz, P(CHMe*Me*)), 19.5 (P(CHMe*Me*)), 10.3 (C_5*Me*$_5$). ^{31}P{^{1}H} NMR (C_6D_6): δ −10.4.

Synthesis of 6c. A glass vial charged with a stir bar, 3-P^{i}Pr$_2$-indene (0.13 g, 0.56 mmol), and THF (2 mL) was cooled to −35 °C. To this vial was added dropwise via Eppendorf pipet a 1.6 M hexanes solution of *n*-BuLi (0.35 mL, 0.56 mmol; precooled to −35 °C), after which the mixture was stirred magnetically for 1 h at ambient temperature. This mixture was cooled to −35 °C and then was transferred slowly to a vial containing a solution of Cp*FeCl (0.56 mmol) in THF (2 mL) (prepared in a manner analogous to that described for the synthesis of **2c**), which had been precooled to −35 °C. After the mixture had been stirred magnetically at ambient temperature for 2 h, the solvent and other volatile materials were removed in vacuo, and the residue was taken up in pentane (5 mL) followed by filtration through a short plug of Celite. The filtrate was then passed through a short Florisil plug, and the plug was washed with additional pentane (10 mL). The combined pentane eluent was then concentrated and dried in vacuo. Any decamethylferrocene that was produced during the synthesis was then removed via sublimation to leave **6c** as an analytically pure, purple-brown waxy solid (0.10 g, 0.24 mmol, 43%). Anal. Calcd for $C_{25}H_{35}PFe$: C, 71.07; H, 8.36; N, 0.00. Found: C, 71.29; H, 8.21; N < 0.3. ^{1}H NMR (CD_2Cl_2): δ 7.73 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C4-H), 7.22 (d, $^3J_{HH}$ = 8.5 Hz, 1H, C7), 6.98−6.88 (m, 2H, C5-H and C6-H), 4.35 (d, $^3J_{HH}$ = 2.5 Hz, 1H, C1-H), 3.74 (d, $^3J_{HH}$ = 2.5 Hz, 1H, C2-H), 2.55 (m, 1H, P(C*H*Me$_c$Me$_d$)), 1.83 (m, 1H, P(C*H*Me$_a$Me$_b$)), 1.59 (s, 15H, C_5Me_5), 1.53 (d of d, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHMe$_c$*Me*$_d$)), 1.29 (apparent t, J = 6.5 Hz, 3H, P(CH*Me*$_c$Me$_d$)), 1.13 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_b$Me$_a$)), 0.80 (d of d, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHMe$_b$*Me*$_a$)). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 126.8 (d, $^3J_{PC}$ = 7.6 Hz, C4), 125.4 (C7), 121.4 (C6), 119.8 (C5), 90.6 (d, $^2J_{PC}$ = 20.5 Hz, C3a), 89.1 (d, $^4J_{PC}$ = 3.1 Hz, C7a), 75.5 (*C*$_5$Me$_5$), 73.6 (d, $^2J_{PC}$ = 3.7 Hz, C2), 69.9 (d, $^1J_{PC}$ = 20.5 Hz, C3), 66.6 (C1), 22.9 (d, $^1J_{PC}$ = 16.6 Hz, P(*C*HMeMe)), 22.1 (d, $^2J_{PC}$ = 30.4 Hz, P(CH*Me*$_d$Me$_c$)), 21.1 (d, $^1J_{PC}$ = 12.1 Hz, P(*C*HMeMe)), 19.9 (d, $^2J_{PC}$ = 22.2 Hz, P(CH*Me*$_b$Me$_a$)), 19.2 (d, $^2J_{PC}$ = 12.2 Hz, P(CHMe$_b$*Me*$_a$)), 17.3 (P(CH*Me*$_c$Me$_d$)), 8.0 (C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −12.4.

Synthesis of 7. A glass vial was charged with a stir bar, **6b** (0.10 g, 0.22 mmol), and THF (2 mL). To this vial was added a solution of [(COD)RhCl]$_2$ (0.054 g, 0.11 mmol) in THF (4 mL). The combined mixture was stirred for 2 h at ambient temperature, after which the solvent and other volatile materials were removed in vacuo. To the residual solid was added pentane (5 mL), and the mixture was filtered though a plug of Celite. The filtrate was collected and dried in vacuo, affording **7** as an analytically pure, yellow-orange solid (0.15 g, 0.21 mmol, 96%). Anal. Calcd for $C_{33}H_{47}PRuRhCl$: C, 55.48; H, 6.64; N, 0.00. Found: C, 55.66; H, 6.39; N < 0.3. ^{1}H NMR (C_6D_6): δ 8.36 (br s, 1H, C4-H or C7-H), 6.88−6.83 (m, 3H, aryl CHs), 5.77 (br s, 1H, COD), 5.71 (m, 1H, COD), 4.46 (d, $^3J_{HH}$ = 2.4 Hz, 1H, C2-H), 4.31 (br s, 1H, C1-H), 3.87 (br s, 1H, COD), 3.75 (br s, 1H, COD), 2.94 (m, 1H, P(C*H*Me$_a$-Me$_b$)), 2.64 (m, 1H, P(C*H*Me$_c$Me$_d$)), 2.25−2.20 (m, 3H, COD), 2.09 (m, 1H, COD), 1.74−1.58 (m, 9H, COD and P(CH*Me*$_c$*Me*$_d$)), 1.44 (s, 15H, C_5*Me*$_5$), 1.40 (d of d, $^3J_{PH}$ = 14.9 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CH*Me*$_a$Me$_b$)), 1.33 (m, 1H, COD), 0.95 (m, 3H, P(CH-Me$_a$*Me*$_b$)). ^{13}C{^{1}H} NMR (C_6D_6): δ 128.0 (C4 or C7), 124.5 (aryl CH), 122.7 (aryl CH), 120.9 (aryl CH), 102.3−101.9 (m, COD), 95.0 (d, $^2J_{PC}$ = 11.6 Hz, C3a), 94.6 (d, $^3J_{PC}$ = 5.6 Hz, C7a), 82.9 (*C*$_5$Me$_5$), 80.9 (C1), 71.6 (d, $^2J_{PC}$ = 4.2 Hz, C2), 68.9 (d, $^1J_{RhC}$ = 13.5 Hz, COD), 68.6 (d, $^1J_{RhC}$ = 13.1 Hz, COD), 33.6 (COD), 32.9 (COD), 28.9 (COD), 27.9 (COD), 27.0 (m, P(*C*HMe$_a$Me$_b$) and P(*C*HMe$_c$Me$_d$)), 21.4 (P(CH*Me*$_c$Me$_d$)), 20.8 (P(CHMe$_a$*Me*$_b$)), 20.1 (P(CHMe$_c$*Me*$_d$)), 19.0 (br s, P(CH*Me*$_a$Me$_b$)), 10.3 (C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (C_6D_6): δ 28.2 (d, $^1J_{RhP}$ = 142.1 Hz).

General Protocol for Hydroboration Experiments. The protocols employed are based on those described by Crudden and coworkers.[17a] A solution of catalyst compound in the desired solvent (0.019 mmol in 0.95 mL to give a 0.02 M solution) was allowed to equilibrate for 5 min within a reaction vial containing a stir bar, at which point styrene (0.38 mmol) was added to the vial by use of an Eppendorf pipet. The vial was then sealed with a PTFE-lined cap and stirred for 10 min. Subsequently, pinacolborane (0.46 mmol) was added to the reaction mixture by use of an Eppendorf pipet, the vial was resealed, and the reaction mixture was left to

stir magnetically at 24 °C for 24 h. After this time, the reaction mixture was concentrated in vacuo, and hexanes (1 mL) was added to the residue. The resultant mixture was then filtered through a short silica gel column (0.6 cm × 5 cm) and eluted with 5 mL of a 20:1 hexanes:ethyl acetate solution. The eluted colorless solution was then concentrated and taken up in diethyl ether (4 mL). To convert the boronate ester products to the corresponding alcohols, the diethyl ether solution was cooled to 0 °C and NaOH (1 mL of a 3 N aqueous solution) was added, followed by H_2O_2 (1 mL of a 30% aqueous solution). After stirring at 0 °C for 1 h, then at ambient temperature for 1−2 h, the reaction mixture was diluted with diethyl ether (∼4 mL) and distilled water (∼5 mL). The organic layer was separated and retained, and the aqueous layer was extracted with diethyl ether (2 × 4 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and partially concentrated. This resulting solution was then transferred to a GC vial and sealed. Quantitative data for the derived alcohols were obtained from GC-FID analysis. Tabulated data represent the average of at least two runs. GC-FID method: temperature control, 80 °C for 15 min, then increased by 10 °C/min to 180 °C, 180 °C for 5 min. Column: Supelco 30 m × 0.25 mm BETA-DEX 120, film thickness 0.25 μm. He flowrate: 15 psi.

Crystallographic Characterization of 2a, 2b, 2c, and 3b. Crystallographic data for each of these complexes 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 a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, data reduction, and multiscan absorption correction (including SAINT and SADABS) were supplied by Bruker. The structures were solved by use of direct methods in the case of **2c** and **3b**, or a Patterson search/structure expansion in the case of **2a** and **2b**, and refined by use of full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma(F_o^2)$ and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-H atoms, and all H-atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Additional crystallographic information is provided in the accompanying CIF.

Crystallographic Characterization of [4c]$^+$BF$_4^-$ and 7. Crystallographic data for each of these complexes 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 retrieved initially by using the COLLECT software (Nonius) and refined with the HKL DENZO and SCALEPACK software.[22a] Data reduction and absorption correction were also performed with the HKL DENZO and SCALEPACK software. The structures were solved by using the direct methods package in SIR-97[22b] and refined by use of the SHELXL97-2 program,[22c] 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. For **[4c]$^+$BF$_4^-$**, the final refined value of the absolute structure parameter (−0.02(2); 3396 Friedel pairs) supported that the correct absolute structure had been chosen.[22d,e] For **7**, two crystallographically independent molecules were identified in the asymmetric unit, and during the refinement process the restraints DELU, SIMU, and ISOR were employed to restrain the anisotropic displacement parameters of the carbon atoms of the disordered C_5Me_5 ligands. 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 crystallographic information is provided in the accompanying CIF.

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Supporting Information Available: Single-crystal X-ray diffraction data in CIF format for **2a**, **2b**, **2c**, **3b**, **[4c]$^+$BF$_4^-$**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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