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# Cationic and Formally Zwitterionic Rhodium(I) and Iridium(I) Derivatives of a P,N-Substituted Indene: A Comparative Synthetic, Structural, and Catalytic Investigation

Judy Cipot,[†] Robert McDonald,[‡] Michael J. Ferguson,[‡] Gabriele Schatte,[§] and Mark Stradiotto*[,†]

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

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A family of neutral, cationic, and formally zwitterionic Rh(I) and Ir(I) complexes featuring 1-$P^iPr_2$-2-$NMe_2$-indene (**3a**), 3-$P^iPr_2$-2-$NMe_2$-indene (**3b**), or 3-$P^iPr_2$-2-$NMe_2$-indenide (**3c**) ligands have been prepared and structurally characterized. Whereas treatment of **3a** with 0.5 equiv of $[(COD)RhCl]_2$ afforded (COD)RhCl($\kappa^1$-*P*,N-**3a**) (**4a**) in 96% isolated yield, [(COD)M($\kappa^2$-*P*,*N*-**3a**)]$^+$X$^-$ ([**5a**]$^+$$PF_6^-$, M = Rh; [**6a**]$^+$$SO_3CF_3^-$, M = Ir) complexes were obtained in 14% and 41% isolated yield from **3a** and the appropriate in-situ-prepared $[(COD)M(THF)_2]^+X^-$ precursor. The isomeric complexes [(COD)M($\kappa^2$-*P*,*N*-**3b**)]$^+$X$^-$ ([**5b**]$^+$X$^-$, M = Rh; [**6b**]$^+$X$^-$, M = Ir) were prepared using a similar protocol employing $NEt_3$, with isolated yields ranging from 37% to 94% depending on the identity of M and X. The zwitterionic complexes (COD)M($\kappa^2$-*P*,*N*-**3c**) (**5c**, M = Rh; **6c**, M = Ir) were prepared in 89% and 93% isolated yield, either upon treatment of [**5b**]$^+$X$^-$ or [**6b**]$^+$X$^-$ with $NaN(SiMe_3)_2$ or via addition of 0.5 equiv of $[(COD)MCl]_2$ to [**3c**]Li. The Rh(I) complexes (CO)(Cl)Rh($\kappa^2$-*P*,*N*-**3b**) (**7**) and $[(CO)_2$Rh($\kappa^2$-*P*,*N*-**3b**)]$^+$$PF_6^-$ (**8**) were prepared in 43% and 66% isolated yield. Single-crystal X-ray diffraction data were obtained for **4a**·$CH_2Cl_2$, [**5b**]$^+$$BF_4^-$, **5c**, [**6b**]$^+$$SO_3CF_3^-$, [**6b**]$^+$$PF_6^-$, **6c**, and **7**, the analysis of which revealed an effectively isostructural relationship among the metal coordination environments in [**5b**]$^+$X$^-$, [**6b**]$^+$X$^-$, **5c**, and **6c**. Despite the structural similarities that are apparent within the cation/zwitterion pairs [**5b**]$^+$X$^-$/**5c** and [**6b**]$^+$X$^-$/**6c**, reactivity studies involving these complexes highlighted important distinctions within and between these pairs of complexes. While both the $\kappa^2$-*P*,*N*-**3b** and the COD ligands in [**5b**]$^+$$BF_4^-$ were displaced upon exposure to excess $PMePh_2$, under similar conditions only the COD ligand in **5c** underwent substitution, affording $(PMePh_2)_2$Rh($\kappa^2$-*P*,*N*-**3c**) (**9**) in 66% isolated yield. Temperature-dependent $^1H$ NMR line shape changes observed for **9** were rationalized in terms of the operation of at least one dynamic process in this complex ($\Delta G^{\ddagger}_{298} \approx 14$ kcal/mol). Further reactivity differences were observed when [**5b**]$^+$$PF_6^-$, [**6b**]$^+$$PF_6^-$, **5c**, and **6c** were employed as catalysts for the hydrogenation and hydrosilylation of alkenes. While [**6b**]$^+$$PF_6^-$ proved to be the most effective styrene hydrogenation catalyst in $CH_2Cl_2$ or THF, similarly high conversion to ethylbenzene was achieved by use of **5c** as a catalyst in benzene, a solvent in which [**5b**]$^+$$PF_6^-$ and [**6b**]$^+$$PF_6^-$ are not soluble. The catalytic utility of **5c** and **6c** was demonstrated further in hydrosilylation reactions employing triethylsilane and styrene, wherein these zwitterionic complexes were observed to outperform their cationic relatives. While nearly quantitative yields were obtained by use of either **5c** (toluene or THF) or **6c** (1,2-dichloroethane or THF) as a catalyst, these complexes were found to exhibit remarkably high, but divergent, selectivity for *E*-1-triethylsilyl-2-phenylethene (**10b**) and 1-triethylsilyl-2-phenylethane (**10a**), respectively. By comparison, **10a** and **10b** were produced in a 1.3:1 ratio in reactions employing Crabtree's catalyst ($[(COD)Ir(PCy_3)(Py)]^+PF_6^-$, COD = $\eta^4$-1,5-cyclooctadiene, Cy = cyclohexyl, Py = pyridine; **1**) under similar conditions. When catalytic activity/selectivity and solvent compatibility are considered, the results of these catalytic studies suggest that zwitterionic species such as **5c** and **6c** represent an effective class of catalyst complexes for the addition of E−H bonds to unsaturated substrates, whose properties are in some cases complementary to those of more traditional Rh(I) and Ir(I) [(COD)M($\kappa^2$-*P*,*N*)]$^+$X$^-$ salts.

## Introduction

Building on the seminal investigations by Schrock and Osborn,[1] and later by Crabtree,[2] the development of cationic square-planar complexes of the heavier group 9 metals has emerged as an important theme in modern organometallic research, since such species are among the most active and widely used classes of homogeneous catalysts for the addition of E−H and E−E bonds (E = main group element) to

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* Author to whom correspondence should be addressed. Fax: 1-902-494-1310. Tel: 1-902-494-7190. E-mail: mark.stradiotto@dal.ca.

[†] Dalhousie University.

[‡] University of Alberta.

[§] University of Saskatchewan.

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10.1021/om060758c CCC: $37.00

unsaturated substrates.[3] The groundbreaking work of Knowles[4] and more recent discoveries by Pfaltz[5] demonstrate that the rational development of such catalysts can enable significant advancements in metal-mediated synthesis. However, the range of experimental conditions under which such cationic group 9 species can be employed is limited, since these catalysts commonly exhibit poor solubility in low-polarity media and can be rendered inactive in strongly coordinating solvents.[6] Furthermore, the systematic design of cationic catalysts is complicated by the fact that the choice of accompanying outer-sphere counteranion in such discrete salts can influence catalytic performance (i.e., activity, selectivity, lifetime, etc.), with some of the most effective counteranions (e.g., tetrakis(3,5-(trifluoromethyl)phenyl)borate, $BAr_F^-$) being relatively costly to obtain from commercial sources and/or hazardous to prepare.[7] In principle, the use of less polar neutral catalyst complexes represents a way in which to circumvent the aforementioned drawbacks associated with cationic species; however, neutral group 9 catalysts can be less active than their cationic relatives. This trend is particularly evident in the case of Ir(I) alkene hydrogenation catalysts. While Crabtree's catalyst ($[(COD)Ir(PCy_3)(Py)]^+PF_6^-$, COD = $\eta^4$-1,5-cyclooctadiene, Cy = cyclohexyl, Py = pyridine; **1**)[2] is capable of hydrogenating a much wider range of alkene substrates than can be reduced by use of Wilkinson's catalyst ($(PPh_3)_3RhCl$, **2**),[8] the related neutral Ir(I) complex $(PPh_3)_3IrCl$ is inactive for alkene hydrogenation.[9]

Zwitterionic group 9 complexes that feature formal charge separation between a cationic metal fragment and an associated anionic ancillary ligand represent appealing candidates for catalytic studies, since in principle such species espouse the desirable traits of discrete salts and traditional neutral complexes in offering a formally cationic metal fragment within an overall neutral molecular framework.[10] However, formally zwitterionic group 9 complexes are much less common than their cationic relatives, as a result of the challenges associated with constructing such charge-separated species. The first zwitterionic Rh(I) complexes to be explored in catalytic applications were those supported by $\eta^6$-coordinated tetraphenylborate and related ligands.[11] While such zwitterions have proven capable of mediating a wide range of substrate transformations involving E−H and/or E−E bond activation under mild conditions and with a high degree of selectivity,[11] it has been shown that these complexes can be transformed into conventional cationic $[L_4Rh]^+BPh_4^-$ species upon substitution of the $\eta^6$-boratoarene ligand by more strongly coordinating Lewis bases.[12] Other classes of Rh(I) zwitterions featuring *homo*bidentate or *homo*tridentate anionic ancillary ligands based on either P or N donors have also emerged, including those in which the anionic charge carrier is a substituted carborane,[13] sulfate,[14] or borate[15] fragment. Notably, Betley and Peters[15b,c] have demonstrated that zwitterionic square-planar Rh(I) complexes featuring either $\kappa^2$-$[Ph_2B(CH_2PR_2)_2]^-$ or $\kappa^2$-$[Ph_2B(CH_2NR_2)_2]^-$ ancillary ligands are active catalysts for various E−H bond additions to alkenes in the presence of both high- and low-polarity solvents. However, a more recent report by Tilley and co-workers[15a] highlights the fact that this general class of zwitterions are also susceptible to decomposition by way of B−C bond cleavage to yield nonzwitterionic bis(phosphino)borane Rh(I) derivatives.[16] By comparison, zwitterionic complexes featuring formally cationic Ir centers are much less common than their Rh relatives, and while the synthetic utility of cationic Ir(I) catalysts such as **1** is well-established,[2,5] the reactivity properties of related Ir(I) zwitterions have not been explored systematically.[17]

In this context, we have established recently synthetic routes to an entirely new class of zwitterionic metal complexes derived from donor-substituted indenes.[18] In contrast to the facial ($\eta^5$) binding of metal fragments that is commonly observed in indenylmetal chemistry,[19,20] these unusual zwitterions can be

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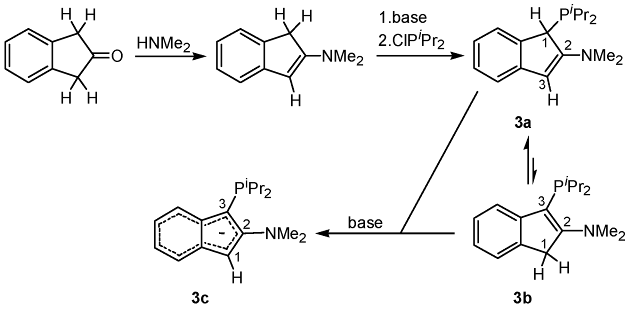
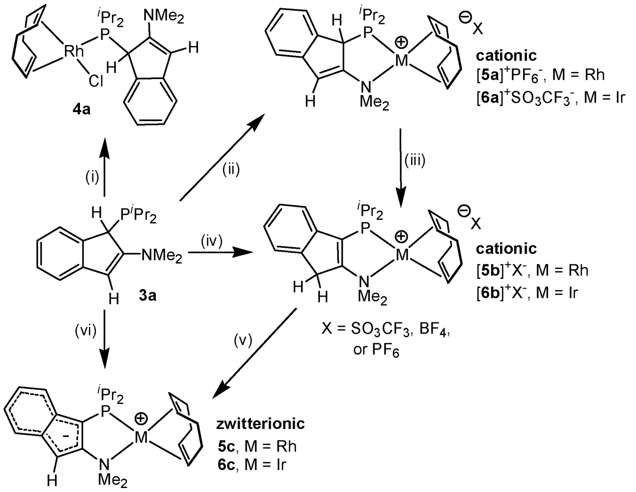
**Scheme 1. Modular Synthesis of the P,N Ligands 3a, 3b, and 3c**



viewed as comprising a formally cationic metal fragment whose charge is counterbalanced by a sequestered, uncoordinated 10$\pi$-electron indenide unit that is built into the backbone of a bidentate ancillary ligand.[21] In light of the superior catalytic properties commonly exhibited by platinum-group metal complexes featuring $\kappa^2$-*P*,*N* ancillary ligands compared to analogous P,P or N,N species,[2,22] and given the lack of published synthetic routes to *hetero*bidentate group 9 zwitterions, we identified P,N-substituted indenides as particularly important ligand targets. As outlined in Scheme 1 for 1-P$^i$Pr$_2$-2-NMe$_2$-indene (**3a**), the indene precursors to such indenide ligands are prepared easily in a high-yielding and modular fashion via condensation of the commercially available reagents 2-indanone and HNR$_2$, followed by deprotonation of the ensuing 2-aminoindene and quenching with a chlorophosphine. While in solution the first-formed allylic indene **3a** evolves slowly to an equilibrium mixture of **3a** and the vinylic isomer **3b**,[23] both are readily deprotonated to afford cleanly the desired P,N-indenide **3c**, which has proven to be an effective ancillary ligand for supporting $\kappa^2$-*P*,*N* zwitterionic complexes.[18]

In an effort to assess the extent to which group 9 zwitterions supported by $\kappa^2$-*P*,*N*-**3c** compare with more conventional square-planar Rh(I) and Ir(I) cationic complexes, we have carried out a series of synthetic and structural studies in which cations supported by $\kappa^2$-*P*,*N*-**3b** were compared with zwitterionic relatives that feature the anionic ligand $\kappa^2$-*P*,*N*-**3c**.[24,25] So as to correlate these structural results with experimentally observed reactivity, the hydrogenation and hydrosilylation of alkenes were exploited as representative E−H bond addition reactions. The synthetic utility of these new group 9 complexes was confirmed during the course of this catalytic survey, and their performance was benchmarked against those of the prototypical group 9 catalysts, **1** and **2**. When catalytic activity/selectivity and solvent compatibility are considered, the results of these catalytic studies suggest that zwitterionic Rh(I) and Ir(I) species supported by $\kappa^2$-*P*,*N*-**3c** represent an effective class of catalyst complexes for the addition of E−H bonds to unsaturated substrates, whose properties are in some cases complementary to those of more traditional Rh(I) and Ir(I) [(COD)M($\kappa^2$-*P*,*N*)]$^+$X$^-$ salts. Herein we report the findings of this multifaceted study involving $\kappa^2$-*P*,*N* Rh(I) and Ir(I) derivatives of **3c**, the first formally zwitterionic analogues of ubiquitous heterobidentate $\kappa^2$-*P*,*N* square-planar group 9 cations. A portion of these results has been communicated previously.[18c,d]

**Scheme 2. Synthesis of Rh(I) and Ir(I) Complexes Derived from 3a**[a]



[a]Reagents: (i) 0.5 [(COD)RhCl]$_2$; (ii) 0.5 [(COD)MCl]$_2$, AgX (M = Rh, X = PF$_6$; M = Ir, X = SO$_3$CF$_3$); (iii) NEt$_3$; (iv) 0.5 [(COD)MCl]$_2$, AgX (X = SO$_3$CF$_3$, BF$_4$, or PF$_6$) then NEt$_3$ (except for M = Rh and X = BF$_4$); (v) NaN(SiMe$_3$)$_2$; (vi) *n*-BuLi, then 0.5 [(COD)MCl]$_2$ (COD = $\eta^4$-1,5-cyclooctadiene).

## Results and Discussion

**Synthesis and Characterization of Neutral and Cationic Complexes of 3a.** In a preliminary synthetic survey, the ability of **3a** to support neutral and cationic Rh(I) and Ir(I) species was examined. Addition of **3a** to 0.5 equiv of [(COD)RhCl]$_2$ afforded (COD)RhCl($\kappa^1$-*P*,N-**3a**) (**4a**) in 96% isolated yield (Scheme 2). Data obtained from NMR spectroscopic studies indicated that the connectivity within the monodentate ligand **3a** is retained in the square-planar complex **4a**. This was confirmed through the crystallographic characterization of **4a**·CH$_2$Cl$_2$; an ORTEP[26] diagram is provided in Figure 1, while salient X-ray experimental data and selected metrical parameters are collected in Tables 1 and 2, respectively. In **4a** the Rh−alkene distances *trans* to P are significantly longer than those *trans* to Cl, in keeping with established structural trends in

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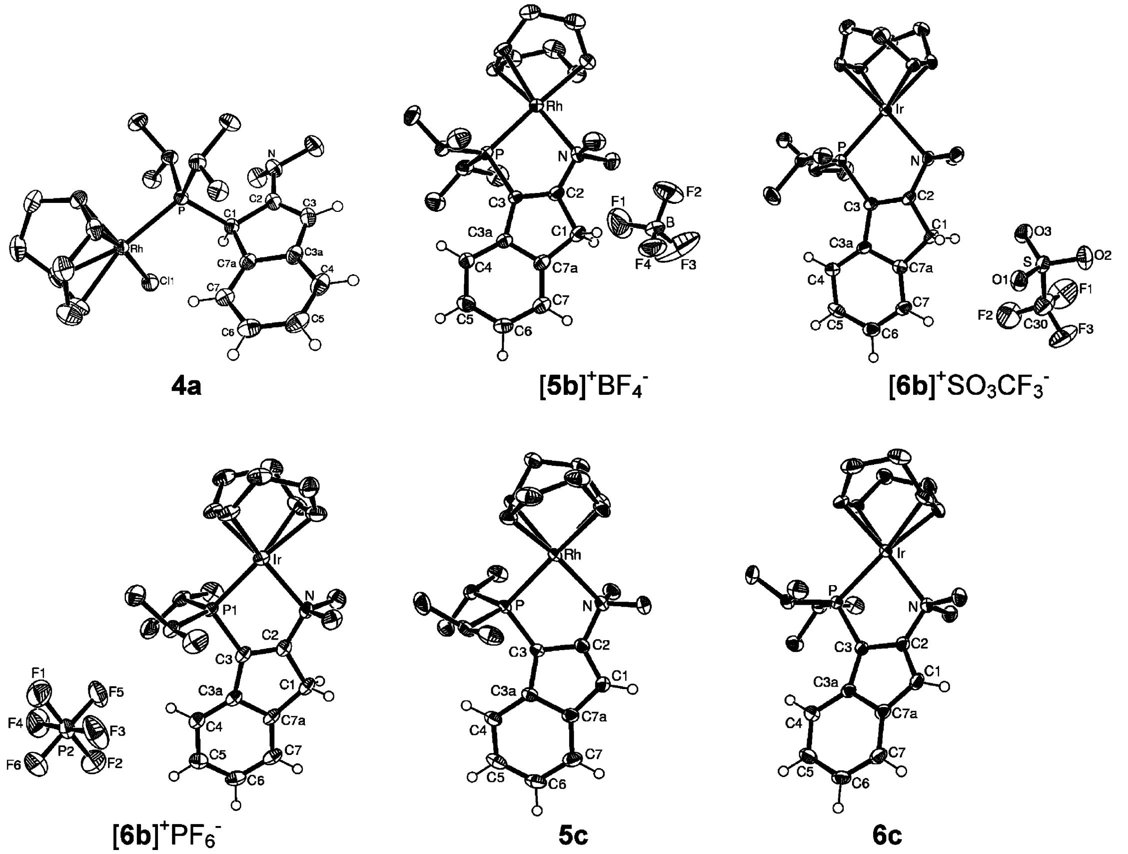

**4a** **[5b]$^+$BF$_4^-$** **[6b]$^+$SO$_3$CF$_3^-$**

**[6b]$^+$PF$_6^-$** **5c** **6c**

**Figure 1.** ORTEP diagrams for **4a**·CH$_2$Cl$_2$, [**5b**]$^+$BF$_4^-$, **5c**, [**6b**]$^+$SO$_3$CF$_3^-$, [**6b**]$^+$PF$_6^-$, and **6c**, shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted. The dichloromethane solvate and selected hydrogen atoms have been omitted for clarity. Only one of the two crystallographically independent molecules of [**6b**]$^+$PF$_6^-$ is shown.

coordination chemistry. As well, the somewhat short N−C2 distance (1.398(3) Å) suggests that the uncoordinated NMe$_2$ fragment in **4a** is in partial conjugation with the adjacent indene framework. In contrast to the rearrangement of **3a** to **3b** that is observed both for uncoordinated **3a** in solution[23] and for **3a** within the coordination sphere of cationic Rh(I) and Ir(I) complexes (vide infra), the corresponding isomerization of **4a** to (COD)RhCl($\kappa^1$-*P*,N-**3b**) was not detected. Analogous reactions employing [(COD)IrCl]$_2$ resulted in the consumption of **3a**, along with the clean formation of two phosphorus-containing products ($\delta$ $^{31}$P = 6.8 and 36.1). We have thus far not been able to isolate and unequivocally identify these products, which may correspond to a (COD)IrCl($\kappa^1$-*P*,N-**3a,b**) mixture. However, the high-frequency $^{31}$P NMR resonance is also consistent with the formation of [(COD)Ir($\kappa^2$-*P*,*N*-**3b**)]$^+$Cl$^-$ ([**6b**]$^+$Cl$^-$, vide infra).

In the pursuit of [(COD)M($\kappa^2$-*P*,*N*-**3a**)]$^+$X$^-$ ([**5a**]$^+$X$^-$, M = Rh; [**6a**]$^+$X$^-$, M = Ir; X = SO$_3$CF$_3$, BF$_4$, or PF$_6$) complexes, appropriate [(COD)M(THF)$_2$]$^+$X$^-$ precursors (prepared in-situ) were treated with **3a** at 24 °C, and the progress of each reaction was monitored by use of $^{31}$P NMR methods. Notably, the nature of the metal/counteranion combination was found to figure importantly in determining the course of these transformations. For reactions featuring SO$_3$CF$_3^-$ or PF$_6^-$ counterions, [**5a**]$^+$X$^-$ or [**6a**]$^+$X$^-$ and the corresponding [(COD)M($\kappa^2$-*P*,*N*-**3b**)]$^+$X$^-$ ([**5b**]$^+$X$^-$, M = Rh; [**6b**]$^+$X$^-$, M = Ir) isomer were observed in various proportions as the only products in the crude reaction mixture, even after short reaction times (minutes). While a similar isomeric [**6a,b**]$^+$X$^-$ mixture was detected spectroscopically in reactions employing the BF$_4^-$ counteranion, under analogous conditions the Rh(I) cation [**5b**]$^+$X$^-$ was observed exclusively. Only for [**5a**]$^+$PF$_6^-$ (14%) and [**6a**]$^+$SO$_3$CF$_3^-$ (41%) were we successful in exploiting the differing solubilities of the $\kappa^2$-*P*,*N*-**3a** and $\kappa^2$-*P*,*N*-**3b** isomers as a means of isolating pure samples of these complexes (Scheme 2). Data obtained from $^1$H and $^{13}$C NMR experiments are in keeping with the $C_1$-symmetric nature of [**5a**]$^+$PF$_6^-$ and [**6a**]$^+$SO$_3$CF$_3^-$ and confirm the allylic structure of the bound **3a** ligand in these complexes. It is evident that [**5a**]$^+$X$^-$ and [**6a**]$^+$X$^-$ represent kinetic products in these reactions and that the net 1,3-proton shift within the indene backbone of **3a**, leading to thermodynamically favored [**5b**]$^+$X$^-$ or [**6b**]$^+$X$^-$ products featuring $\kappa^2$-*P*,*N*-**3b** ligands, is facilitated upon coordination to [(COD)M]$^+$ fragments in this system. We have observed that while in solution the isomerization of isolated [**5a**]$^+$PF$_6^-$ or [**6a**]$^+$SO$_3$CF$_3^-$ to the corresponding $\kappa^2$-*P*,*N*-**3b** complex is slow and does not proceed to completion after several days at 24 °C. under similar conditions such transformations are rendered rapid (hours) and quantitative in the presence of NEt$_3$. In contrast, we have demonstrated previously that uncoordinated **3a** is not transformed cleanly into **3b** upon treatment with amine.[23]

**Synthesis and Characterization of the Cationic Complexes [5b]$^+$X$^-$ and [6b]$^+$X$^-$.** The incomplete rearrangement of **3a** to **3b** in solution prevents the direct use of the latter in the synthesis of $\kappa^2$-*P*,*N*-**3b** metal complexes. However, we have discovered that the target complexes [**5b**]$^+$X$^-$ and [**6b**]$^+$X$^-$ are formed quantitatively ($^{31}$P NMR) upon addition of **3a** to [(COD)M(THF)$_2$]$^+$X$^-$ (prepared in-situ), followed by treatment with NEt$_3$ (Scheme 2); [**5b**]$^+$BF$_4^-$ is generated cleanly from [(COD)Rh(THF)$_2$]$^+$BF$_4^-$ and **3a**, even in the absence of added amine (vide supra). After workup, [**5b**]$^+$X$^-$ (X = SO$_3$CF$_3$, 87%; BF$_4$, 94%; PF$_6$, 73%) or [**6b**]$^+$X$^-$ (X = SO$_3$CF$_3$, 89%; BF$_4$, 37%; PF$_6$, 78%) were

**Table 1. Crystallographic Data for 4a, $[\mathbf{5b}]^+BF_4^-$, $[\mathbf{6b}]^+SO_3CF_3^-$, $[\mathbf{6b}]^+PF_6^-$, 5c, 6c, and 7**

| | **4a**·$CH_2Cl_2$ | $[\mathbf{5b}]^+BF_4^-$ | $[\mathbf{6b}]^+SO_3CF_3^-$ | $[\mathbf{6b}]^+PF_6^-$ | **5c** | **6c** | **7** |
|---|---|---|---|---|---|---|---|
| empirical formula | $C_{26}H_{40}Cl_3NPRh$ | $C_{25}H_{38}BF_4NPRh$ | $C_{26}H_{38}F_3O_3NPSIr$ | $C_{25}H_{38}F_6NP_2Ir$ | $C_{25}H_{37}NPRh$ | $C_{25}H_{37}NPIr$ | $C_{18}H_{26}ClNOPRh$ |
| fw | 606.82 | 573.25 | 724.80 | 720.70 | 485.44 | 574.73 | 652.55 |
| cryst dimens | 0.61 × 0.31 × 0.17 | 0.26 × 0.24 × 0.23 | 0.22 × 0.14 × 0.08 | 0.53 × 0.13 × 0.13 | 0.28 × 0.25 × 0.10 | 0.36 × 0.18 × 0.13 | 0.08 × 0.08 × 0.05 |
| cryst syst | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P2_1/m$ | $P2_1/n$ | $P2_1/n$ | $P2_1$ |
| $a$ (Å) | 15.773(1) | 9.893(1) | 9.9608(6) | 14.535(1) | 9.7054(6) | 9.6714(5) | 9.4380(4) |
| $b$ (Å) | 8.2243(6) | 18.375(2) | 20.270(1) | 9.9545(9) | 16.985(1) | 16.9783(9) | 10.7550(7) |
| $c$ (Å) | 20.994(2) | 14.129(1) | 14.0988(9) | 18.506(2) | 14.5743(9) | 14.5080(7) | 9.7100(6) |
| $\beta$ (deg) | 91.688(1) | 90.911(2) | 103.575(1) | 91.182(1) | 109.392(1) | 109.4177(7) | 102.118(3) |
| $V$ (Å$^3$) | 2722.2(3) | 2568.1(5) | 2767.2(3) | 2677.0(4) | 2266.2(2) | 2246.8(2) | 963.7(1) |
| $Z$ | 4 | 4 | 4 | 4 | 4 | 4 | 2 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.481 | 1.483 | 1.740 | 1.788 | 1.423 | 1.699 | 1.522 |
| $\mu$ (mm$^{-1}$) | 0.996 | 0.770 | 5.007 | 5.164 | 0.835 | 6.025 | 1.111 |
| $2\theta$ limit (deg) | 52.74 | 52.86 | 52.82 | 52.84 | 52.76 | 52.72 | 54.94 |
| | $-19 \leq h \leq 16$ | $-10 \leq h \leq 12$ | $-12 \leq h \leq 12$ | $-18 \leq h \leq 18$ | $-12 \leq h \leq 12$ | $-12 \leq h \leq 12$ | $-12 \leq h \leq 12$ |
| | $-10 \leq k \leq 10$ | $-22 \leq k \leq 20$ | $-25 \leq k \leq 25$ | $-12 \leq k \leq 12$ | $-21 \leq k \leq 17$ | $-21 \leq k \leq 21$ | $-13 \leq k \leq 13$ |
| | $-26 \leq l \leq 26$ | $-17 \leq l \leq 17$ | $-17 \leq l \leq 17$ | $-23 \leq l \leq 23$ | $-17 \leq l \leq 18$ | $-18 \leq l \leq 18$ | $-12 \leq l \leq 12$ |
| total no. of data collected | 15 470 | 14 027 | 19 876 | 20 721 | 12 397 | 17 112 | 4198 |
| no. of indep reflns | 5548 | 5224 | 5676 | 5809 | 4611 | 4579 | 4198 |
| $R_{int}$ | 0.0205 | 0.0310 | 0.0621 | 0.0370 | 0.0321 | 0.0254 | NA |
| no. of obsd reflns | 5091 | 4661 | 4270 | 5030 | 4033 | 4273 | 3818 |
| range of transmn | 0.8490−0.5818 | 0.8428−0.8249 | 0.6902−0.4055 | 0.5533−0.1706 | 0.9212−0.7998 | 0.5081−0.2203 | 0.9465−0.9164 |
| no. of data/restraints/params | 5548/0/289 | 5224/0/298 | 5676/0/325 | 5809/0/571 | 4611/0/253 | 4579/0/253 | 4198/1/214 |
| $R_1$ $[F_o^2 \geq 2\sigma(F_o^2)]$ | 0.0328 | 0.0510 | 0.0315 | 0.0290 | 0.0329 | 0.0174 | 0.0398 |
| $wR_2$ $[F_o^2 \geq -3\sigma(F_o^2)]$ | 0.0874 | 0.1415 | 0.0654 | 0.0740 | 0.0861 | 0.0426 | 0.0849 |
| goodness-of-fit | 1.019 | 1.147 | 1.002 | 1.088 | 1.083 | 1.086 | 1.078 |

**Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 4a, [5b]$^+$BF$_4^-$, [6b]$^+$SO$_3$CF$_3^-$, [6b]$^+$PF$_6^-$, 5c, and 6c**

| | **4a**·$CH_2Cl_2$ | [**5b**]$^+$BF$_4^-$ | [**6b**]$^+$SO$_3$CF$_3^-$ | [**6b**$^a$]$^+$PF$_6^-$ | [**6b**$^b$]$^+$PF$_6^-$ | **5c** | **6c** |
|---|---|---|---|---|---|---|---|
| M−P | 2.3474(6) | 2.305(1) | 2.299(1) | 2.301(2) | 2.32(1) | 2.3173(6) | 2.3171(6) |
| M−N | | 2.211(4) | 2.192(4) | 2.203(6) | 2.231(8) | 2.242(2) | 2.216(2) |
| M−$C_{alkene1}$$^c$ | 2.202(3) | 2.239(5) | 2.212(4) | 2.17(1) | 2.22(1) | 2.275(2) | 2.201(3) |
| M−$C_{alkene2}$$^c$ | 2.216(3) | 2.232(5) | 2.184(4) | 2.22(1) | 2.170(9) | 2.238(2) | 2.231(3) |
| M−$C_{alkene3}$$^d$ | 2.113(3) | 2.140(5) | 2.152(4) | 2.14(3) | 2.122(8) | 2.123(3) | 2.127(2) |
| M−$C_{alkene4}$$^d$ | 2.138(3) | 2.136(5) | 2.108(5) | 2.13(3) | 2.13(1) | 2.123(3) | 2.116(2) |
| P−$C_{ind}$ | 1.877(2) | 1.809(4) | 1.807(5) | 1.812(5) | 1.810(7) | 1.758(2) | 1.755(2) |
| N-C2 | 1.398(3) | 1.459(6) | 1.475(6) | 1.462(8) | 1.460(9) | 1.479(3) | 1.478(3) |
| C1−C2 | 1.533(3) | 1.508(6) | 1.500(6) | 1.519(7) | 1.491(7) | 1.386(3) | 1.381(3) |
| C2−C3 | 1.352(4) | 1.340(7) | 1.339(6) | 1.321(7) | 1.346(7) | 1.419(3) | 1.413(3) |
| C3−C3a | 1.451(4) | 1.486(6) | 1.491(6) | 1.486(7) | 1.466(8) | 1.446(3) | 1.435(3) |
| C3a-C4 | 1.393(4) | 1.384(7) | 1.380(7) | 1.391(8) | 1.380(8) | 1.412(3) | 1.406(3) |
| C4−C5 | 1.396(5) | 1.396(7) | 1.396(7) | 1.388(8) | 1.387(8) | 1.387(4) | 1.374(4) |
| C5−C6 | 1.385(5) | 1.384(8) | 1.381(7) | 1.381(8) | 1.364(9) | 1.398(4) | 1.411(4) |
| C6−C7 | 1.400(4) | 1.390(7) | 1.383(7) | 1.394(9) | 1.403(9) | 1.383(4) | 1.370(4) |
| C7−C7a | 1.386(4) | 1.382(7) | 1.390(6) | 1.379(7) | 1.382(9) | 1.414(4) | 1.412(4) |
| C1−C7a | 1.528(3) | 1.502(7) | 1.498(6) | 1.510(8) | 1.508(8) | 1.430(4) | 1.424(4) |
| C3a−C7a | 1.406(4) | 1.411(6) | 1.404(7) | 1.406(7) | 1.394(7) | 1.442(4) | 1.440(3) |
| M···C2$^e$ | 2.974 | 3.074 | 3.072 | 3.060 | 3.060 | 3.088 | 3.070 |
| M···C3$^e$ | 3.889 | 3.198 | 3.199 | 3.192 | 3.192 | 3.190 | 3.189 |
| P−M−N | | 84.2(1) | 84.3(1) | 84.2(2) | 83.1(4) | 83.92(5) | 83.90(5) |
| M−N−C2 | | 112.1(3) | 112.4(3) | 111.6(5) | 111.3(6) | 110.5(2) | 110.8(1) |
| N−C2−C3 | | 124.2(4) | 123.8(4) | 124.5(5) | 124.2(5) | 120.6(2) | 121.0(2) |
| C2−C3−P | | 117.4(3) | 117.1(3) | 116.9(4) | 117.1(4) | 118.2(2) | 117.5(2) |
| C3−P−M | | 101.3(2) | 101.7(2) | 101.1(2) | 101.1(5) | 102.15(8) | 102.23(8) |

[a,b] Within the first and second independent molecules of [**6b**]$^+$PF$_6^-$, respectively. [c] The metal−cyclooctadiene distances *trans* to phosphorus. [d] The metal−cyclooctadiene distances *trans* to nitrogen or chloride. [e] Transannular distance measured in the final refined structure.

isolated as analytically pure orange solids.[27] The $^1$H, $^{13}$C, and $^{31}$P NMR data obtained for [**5b**]$^+$X$^-$ and [**6b**]$^+$X$^-$ are in each case consistent with a square-planar [(COD)M($\kappa^2$-*P*,*N*-**3b**)]$^+$X$^-$ complex possessing $C_s$ symmetry. As well, NMR signals associated with the respective Rh(I) and Ir(I) cations are not influenced by the nature of the accompanying counteranion, in keeping with the proposed outer-sphere nature of X in these salts. For [**5b**]$^+$BF$_4^-$, [**6b**]$^+$SO$_3$CF$_3^-$, and [**6b**]$^+$PF$_6^-$, the solution structural characterization of these complexes was confirmed on the basis of data obtained from single-crystal X-ray diffraction experiments (Figure 1; Tables 1 and 2). The metrical parameters associated with the cationic fragments in these complexes differ only modestly, and no short contacts are observed between M and X,[28] or between M and the adjacent C2═C3 unit. As well, the interatomic distances within the metal coordination sphere of these complexes fall within the range of those observed in related group 9 complexes,[29] with the M−alkene distances *trans* to P being significantly longer than those *trans* to N.

**Synthesis and Characterization of the Formally Zwitterionic Complexes 5c and 6c.** While the ability of the indenyl fragment to coordinate metals in an $\eta^5$ fashion is well-known,[19] other indenyl−metal binding modes are also commonly observed, and entirely new coordination motifs for this versatile ligand are continuing to emerge.[30] Alternatively, we envisioned the use of donor-substituted variants of this anionic hydrocarbon in the construction of zwitterionic $\kappa^2$-*P*,*N* group 9 metal complexes, in which the uncoordinated indenide unit serves as a sequestered anionic charge reservoir, rather than as a site for metal binding. Having successfully prepared cationic square-planar group 9 complexes supported by $\kappa^2$-*P*,*N*-**3b**, we turned our attention to the synthesis of structurally analogous zwitterions featuring $\kappa^2$-*P*,*N*-**3c** ligation. Upon exposure to NaN(SiMe$_3$)$_2$, both [**5b**]$^+$X$^-$ and [**6b**]$^+$X$^-$ are transformed quantitatively ($^{31}$P NMR) into the desired $\kappa^2$-*P*,*N*-**3c** complexes **5c** and **6c**, respectively (Scheme 2). These zwitterionic species are also generated cleanly from [**3c**]Li and 0.5 equiv of [(COD)MCl]$_2$ and can be isolated as analytically pure orange-red solids in high yield (M = Rh, 89%; M = Ir, 93%). The exclusive formation of **5c** and **6c** in these transformations is unusual, given the established propensity of [(COD)M]$^+$ fragments for $\eta^5$ binding to indenyl ligands.[20] The connectivity in **5c** and **6c** that was initially determined by use of $^1$H, $^{13}$C, and $^{31}$P NMR methods was confirmed subsequently by use of X-ray crystallographic techniques (Figure 1; Tables 1 and 2). Interestingly, the metal−ligand contacts within **5c** and **6c** differ only modestly from those found in the corresponding cations [**5b**]$^+$X$^-$ and [**6b**]$^+$X$^-$, thereby confirming the nearly isosteric relationship between the $\kappa^2$-*P*,*N*-**3b** and $\kappa^2$-*P*,*N*-**3c** ligands in these complexes with respect to the metal coordination sphere. However, while pronounced bond length alternation is observed within the indene portion of the $\kappa^2$-*P*,*N*-**3b** ancillary ligands in these cationic complexes, the indenide moiety of the $\kappa^2$-*P*,*N*-**3c** ligand in each of **5c** and **6c** exhibits a more delocalized structure, consistent with a 10$\pi$-electron indenide framework. In fact, the extent of delocalization observed within the carbocyclic backbone of the $\kappa^2$-*P*,*N*-**3c** ligands in these zwitterionic complexes

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(27) Attempts to prepare [**6b**]$^+$B(C$_6$F$_5$)$_4^-$ by employing Li(Et$_2$O)$_{2.5}$B(C$_6$F$_5$)$_4$ as the halide-abstracting reagent under analogous conditions produced dark solids that exhibited numerous $^{31}$P NMR resonances and from which no pure Ir(I) complexes could be isolated.

(28) The shortest cation−anion contacts: (a) [**5b**]$^+$BF$_4^-$, 2.78 Å between F and C1(*H*)$_2$; (b) [**6b**]$^+$SO$_3$CF$_3^-$, 2.44 Å between F and C1(*H*)$_2$; (c) [**6b**]$^+$PF$_6^-$, 2.48 Å between F and C4-*H*.

(29) For a selection of crystallographically characterized Rh(I) and Ir(I) [(COD)M($\kappa^2$-*P*,*N*)]$^+$X$^-$ complexes, see: (a) Phillips, A. D.; Bolaño, S.; Bosquain, S. S.; Daran, J.-C.; Malacea, R.; Peruzzini, M.; Poli, R.; Gonsalvi, L. *Organometallics* **2006**, *25*, 2189. (b) Dahlenburg, L.; Götz, R. *Eur. J. Inorg. Chem.* **2004**, 888. (c) Brauer, D. J.; Kottsieper, K. W.; Rossenbach, S.; Stelzer, O. *Eur. J. Inorg. Chem.* **2003**, 1748. (d) Hou, D.-R.; Reibenspies, J.; Colacot, T. J.; Burgess, K. *Chem.*−*Eur. J.* **2001**, *7*, 5391. (e) Kataoka, Y.; Imanishi, M.; Yamagata, T.; Tani, K. *Organometallics* **1999**, *18*, 3563. (f) Yang, H.; Lugan, N.; Mathieu, R. *Organometallics* **1997**, *16*, 2089. (g) Berger, H.; Nesper, R.; Pregosin, P. S.; Rüegger, H.; Wörle, M. *Helv. Chim. Acta* **1993**, *76*, 1520. (h) McKay, I. D.; Payne, N. C. *Can. J. Chem.* **1986**, *64*, 1930. (i) Reference 7b herein.

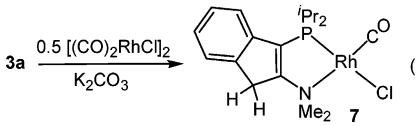
(30) (a) Bradley, C. A.; Lobkovsky, E.; Keresztes, I.; Chirik, P. J. *J. Am. Chem. Soc.* **2005**, *127*, 10291. (b) Bradley, C. A.; Keresztes, I.; Lobkovsky, E.; Young, V. G.; Chirik, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 16937. (c) Zargarian, D. *Coord. Chem. Rev.* **2002**, *233*−234., 157. (d) Stradiotto, M.; McGlinchey, M. J. *Coord. Chem. Rev.* **2001**, *219-221*, 311.

equals that observed in some discrete "naked" indenide salts.[31] Although **5c** and **6c** formally lack a conventional resonance contributor that places the anionic charge onto either of the pnictogen donor groups, the short P−C3 and C1−C2 distances in these complexes, when compared with those found in the analogous cations [**5b**]$^+$X$^-$ and [**6b**]$^+$X$^-$, suggest that a methylene phosphide-type resonance structure featuring a $^i$Pr$_2$P=C3 linkage and a formal anionic charge on phosphorus may also figure prominently in **5c** and **6c**.[32]

**Solubility Studies and Stoichiometric Reactivity with E−H Bonds.** The solubility of the discrete salts [**5b**]$^+$X$^-$ and [**6b**]$^+$X$^-$, and the neutral complexes **5c** and **6c**, in various organic media was assessed, so as to determine the scope of solvents in which such complexes may be utilized as catalysts.[33] All complexes were found to be fully soluble in either $CH_2Cl_2$ or THF with the exception of [**6b**]$^+$X$^-$, which exhibited only limited solubility in the latter solvent. In contrast, while these cationic species proved insoluble in all hydrocarbons, complexes **5c** and **6c** were observed to dissolve fully in benzene or toluene, and even proved soluble to a limited extent in hexanes or pentane.

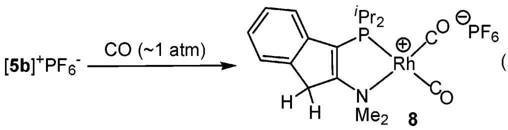
The reactivity of the cationic and zwitterionic complexes reported herein toward E−H bond containing small molecules was surveyed prior to catalytic studies; unfortunately, such reactions proved rather uninformative. Exposure of [**5b**]$^+$X$^-$, [**6b**]$^+$X$^-$, **5c**, or **6c** to $Et_3SiH$ or $Ph_2SiH_2$ (1 or 10 equiv in THF) at 24 or 60 °C led to the formation of a complex mixture of products, including in some cases **3a** and **3b** ($^{31}$P NMR). Similarly, though exposure of **1** to an atmosphere of $H_2$ is known to generate the trinuclear cluster $[Ir_3H_7(PCy_3)_3(Py)_3]^{2+}$,[2] treatment of **6c** in $C_6D_6$ with $H_2$ produced an intractable dark brown precipitate.

**Pursuit of Rh Carbonyl Complexes.** With an aim toward utilizing infrared spectroscopic techniques to compare the electron-donating abilities of the $\kappa^2$-*P*,*N*-ligands **3b** and **3c** in these cationic and zwitterionic complexes (respectively), we sought to prepare carbonyl-containing relatives of [**5b**]$^+$X$^-$ and **5c**. In exploring the reactivity of **3a** with 0.5 equiv of $[(CO)_2RhCl]_2$ in THF, complete consumption of **3a** was noted after 10 min, along with the formation of multiple phosphorus-containing products ($^{31}$P NMR). However, subsequent treatment of this reaction mixture with anhydrous $K_2CO_3$ resulted in the clean formation of a single phosphorus-containing species (**7**, $\delta$ $^{31}$P = 72), which was isolated as an analytically pure yellow-orange solid in 43% yield (eq 1). The crystallographic characterization of **7** (see Supporting Information and Table 1) reveals *trans*-disposed phosphorus and chloride ligands in this square-planar complex, a bonding motif that has been observed in related crystallographically characterized ($\kappa^2$-*P*,*N*)Rh(CO)Cl species.[34]



(1)

Initial attempts to prepare $[(CO)_2Rh(\kappa^2\text{-}P,N\text{-}\mathbf{3b})]^+PF_6^-$ (**8**) via treatment of **3a** with 0.5 equiv of $[(CO)_2RhCl]_2$ in the presence of $AgPF_6$ generated a complex mixture of products. While similarly complex product distributions were obtained upon exposure of a THF solution of [**5b**]$^+$PF$_6^-$ to an atmosphere of CO, clean conversion to a single phosphorus-containing species (**8**, $\delta$ $^{31}$P = 63) was achieved under similar conditions in $CH_2Cl_2$, allowing for the subsequent isolation of **8** in 66% yield (eq 2). The structure proposed for **8** is supported by elemental analysis data as well as NMR spectroscopic ($^1$H, $^{13}$C, and $^{31}$P) data, with the exception that $^{13}$C NMR resonances attributable to the CO groups were not observed, despite prolonged data acquisition times. Moreover, while only two IR-active CO vibrations are predicted for **8**, three vibrations (2100, 2030, and 1990 cm$^{-1}$) were detected for this complex. Although definitive experimental data needed to unequivocally confirm the connectivity in **8** and to rationalize such IR-spectroscopic observations are currently lacking, it is possible that the third IR band arises from the coexistence of a dimeric or other oligomeric relative of **8** that possesses linear OC−M−CO linkages.[35] The absence of NMR evidence in support of multiple Rh species in solution requires that the NMR spectroscopic signature of such an oligomeric relative of **8** be identical to that of **8** itself and/or that such monomeric and oligomeric species must undergo rapid exchange on the NMR time scale.



(2)

The preparation of the zwitterionic complex $(CO)_2Rh(\kappa^2\text{-}P,N\text{-}\mathbf{3c})$ was examined subsequently. Whereas the combination of [**3c**]Li and 0.5 equiv of $[(COD)RhCl]_2$ afforded **5c** cleanly (vide supra), under similar conditions employing $[(CO)_2RhCl]_2$ a complicated mixture of products was generated ($^{31}$P NMR). Similarly complex product distributions were observed upon exposure of THF, $CH_2Cl_2$, or toluene solutions of **5c** to an atmosphere of CO, and all efforts to isolate Rh-containing products from these reactions have thus far not been fruitful.

**Treatment of [5b]$^+$X$^-$ and 5c with PMePh$_2$.** In a further effort to qualitatively assess the binding affinity of the neutral $\kappa^2$-*P*,*N*-**3b** ligand in [**5b**]$^+$BF$_4^-$ relative to the anionic $\kappa^2$-*P*,*N*-**3c** ligand in **5c**, these Rh(I) complexes were each treated with an excess of $PMePh_2$. Addition of 10 equiv of $PMePh_2$ to [**5b**]$^+$BF$_4^-$ resulted in the quantitative consumption of the starting Rh(I) complex, with concomitant formation of $[Rh(PMePh_2)_4]^+$,[36] **3a**, and **3b** as the only phosphorus-containing products (eq 3). Whereas both the neutral $\kappa^2$-*P*,*N*-**3b** ligand and COD in [**5b**]$^+$BF$_4^-$ were displaced by $PMePh_2$, under similar experimental conditions employing the zwitterionic **5c**, *only the COD ligand* underwent substitution, affording $(PMePh_2)_2Rh(\kappa^2\text{-}P,N\text{-}\mathbf{3c})$, **9** (eq 4). Complex **9** was obtained subsequently as an analytically pure light brown powder in 66% isolated yield. In the absence of significant steric differences between $\kappa^2$-*P*,*N*-**3b** and $\kappa^2$-*P*,*N*-**3c** (vide supra), and given the possible hemilabile character of these P,N-ligands whereby the P-donor may serve as an anchor to the group 9 metal,[37] it is plausible that the divergent reactivity of [**5b**]$^+$BF$_4^-$ and **5c** with $PMePh_2$ may be attributable in part to the ease with which the N-donor can dissociate from the formally cationic Rh(I) center, presuming that such a process is of relevance to the reaction pathway

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[31] For crystallographically characterized indenide salts, see: (a) Boche, G.; Ledig, B.; Marsch, M.; Harms, K. *Acta Crystallogr.* **2001**, *E57*, m570. (b) Marder, T. B.; Williams, I. D. *Chem. Commun.* **1987**, 1478.

[32] Izod, K. *Coord. Chem. Rev.* **2002**, *227*, 153.

[33] A combination of 6 mg of complex and 0.8 mL of solvent was utilized in these qualitative visual solubility tests. The solubility of [**5b**]$^+$X$^-$ and [**6b**]$^+$X$^-$ complexes was not found to vary significantly for X = $SO_3CF_3$, $BF_4$, and $PF_6$.

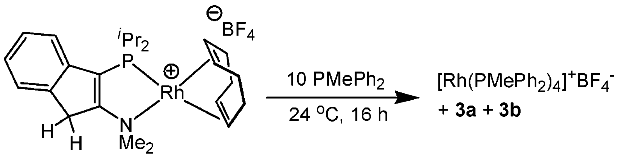
[34] For a recent example, see: Dennett, J. N. L.; Bierenstiel, M.; Ferguson, M. J.; McDonald, R.; Cowie, M. *Inorg. Chem.* **2006**, *45*, 3705.

[35] Andrieu, J.; Camus, J.-M.; Richard, P.; Poli, R.; Gonslavi, L.; Vizza, F.; Peruzzini, M. *Eur. J. Inorg. Chem.* **2006**, 51.

[36] Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.

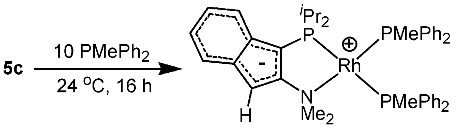
[37] Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233.

leading to substitution of the P,N-ligand in these complexes. In this vein, and consistent with the observed reluctance of the $\kappa^2$-*P*,*N*-**3c** ligand in **5c** to undergo substitution by $PMePh_2$, the dissociation of a ligand arm in [**5b**]$^+$ to give a [(COD)M($\kappa^1$-*P*,N-**3b**)]$^+$ intermediate is anticipated to be more facile than an analogous dechelation process involving **5c**, given the heightened attractive electrostatic forces that are likely to exist between the formally anionic P,N-indenide ligand and the formally cationic [(COD)M]$^+$ fragment in **5c**, relative to those in [**5b**]$^+$. The retention of the anionic ancillary ligand in **5c** following treatment with $PMePh_2$ contrasts the previously documented loss of $BPh_4^-$ from zwitterionic ($\eta^6$-$PhBPh_3$)$RhL_2$ species upon exposure to phosphines.[12]



[**5b**]$^+BF_4^-$

(3)



**9**

(4)

In the course of characterizing **9** at 300 K, the $^1H$ and $^{13}C\{^1H\}$ NMR resonances associated with the $PPh_2$, $P^iPr_2$, and $NMe_2$ fragments were found to be broadened significantly relative to the indenide and the P*MePh₂* signals. Furthermore, the observation of two unique P(*CHMe₂*)₂ resonances in both the $^1H$ and $^{13}C\{^1H\}$ NMR spectra at this temperature is consistent with **9** adopting an effective $C_1$-symmetric solution structure on the NMR time scale, in contrast to the apparent $C_s$ symmetry exhibited by [**5b**]$^+$X, [**6b**]$^+$X$^-$, **5c**, and **6c**. The $^1H$ NMR line shape changes that occur on going from 240 to 350 K, including the apparent simplification of the $PPh_2$ and $P^iPr_2$ regions of the spectrum as well as coalescence ($T_c = 298$ K) of the initially well-resolved $NMe_2$ resonances at 240 K, are consistent with a dynamic process involving restricted rotation about the Rh−$PMePh_2$ bonds in **9**. Although signal overlap within the $PPh_2$ and $P^iPr_2$ regions of the $^1H$ NMR spectrum rendered these resonances too complex to interpret in terms of line shape analysis, evaluation of the temperature-dependent $^1H$ NMR line shape changes for the $NMe_2$ unit employing the Gutowsky−Holm approximation[38] yielded a value for $\Delta G^{\ddagger}_{Tc}$ of ca. 14 kcal/mol. It is unclear whether the calculated $\Delta G^{\ddagger}_{Tc}$ based on the coalescence of the $NMe_2$ signals provides a measure of the barrier associated with the proposed Rh−$PMePh_2$ restricted rotation process, and/or the barrier to an alternative dynamic process involving Rh−N dissociation, rotation about the C2−$NMe_2$ linkage, inversion at N, and recoordination to Rh, which would also render equivalent the two N-*Me* environments in **9** if rapid on the NMR time scale.[39] However, such a process involving N-dissociation alone cannot account for the temperature-dependent line shape changes that are observed within the $PPh_2$ and $P^iPr_2$ regions of the $^1H$ NMR spectra of **9**.

**Alkene Hydrogenation Studies.** In an initial effort to compare and contrast the catalytic abilities of the Rh(I) and Ir(I) cations [**5b**]$^+PF_6^-$ and [**6b**]$^+PF_6^-$, with those of the structurally related zwitterionic complexes **5c** and **6c**, the metal-mediated hydrogenation of styrene (24 °C, ∼1 atm $H_2$) was examined; selected catalytic results are collected in Table 3.

**Table 3. Hydrogenation of Styrene**[a]

| entry | catalyst | loading (mol %) | solvent | yield (%) | *t* (h)[b] |
|---|---|---|---|---|---|
| 3-1 | [**5b**]$^+PF_6^-$ | 1.0 | $CH_2Cl_2$ | 10 | 24 |
| 3-2 | [**5b**]$^+PF_6^-$ | 1.0 | THF | 97 | 24 |
| 3-3 | [**5b**]$^+PF_6^-$ | 5.0 | THF | >99 | 24 |
| 3-4 | **5c** | 1.0 | $CH_2Cl_2$ | 17 | 24 |
| 3-5 | **5c** | 1.0 | THF | 63 | 24 |
| 3-6 | **5c** | 5.0 | THF | 94 | 24 |
| 3-7 | **2** | 5.0 | THF | >99 | 4 |
| 3-8 | **5c** | 5.0 | benzene | >99 | 24 |
| 3-9 | [**6b**]$^+PF_6^-$ | 0.5 | $CH_2Cl_2$ | >99 | 0.5 |
| 3-10 | **1** | 0.5 | $CH_2Cl_2$ | >99 | 4 |
| 3-11 | [**6b**]$^+PF_6^-$ | 0.5 | THF | >99 | 4 |
| 3-12[c] | **1** | 0.5 | THF | 91 | 4 |
| 3-13 | **6c** | 0.5 | $CH_2Cl_2$ | 56 | 4 |
| 3-14 | **6c** | 5.0 | $CH_2Cl_2$ | 76 | 24 |
| 3-15 | **6c** | 0.5 | THF | 58 | 4 |
| 3-16 | **6c** | 0.5 | benzene | 37 | 4 |
| 3-17[c] | **6c** | 0.5 | hexanes | 17 | 4 |

[a] Conditions: 24 °C and ∼1 atm $H_2$. [b] Time at which the quoted conversion (yield) was achieved on the basis of GC-MS and GC-FID data, rounded to the nearest percent. [c] Catalyst was not completely soluble in this solvent.

The catalytic behavior of [**5b**]$^+PF_6^-$ and **5c** was found to be similar, with both of these Rh(I) catalysts exhibiting an induction period[40a] that was not observed for **2** or the Ir(I) catalysts examined in this reactivity survey (vide infra). While both [**5b**]$^+PF_6^-$ and **5c** exhibited only modest activity at the 1.0 mol % catalyst loading level in $CH_2Cl_2$ (entries 3-1 and 3-4), improved catalytic performance was noted in THF (entries 3-2 and 3-5), especially when the catalyst loading was increased to 5.0 mol % (entries 3-3 and 3-6). By comparison, Wilkinson's catalyst (**2**) proved superior to both [**5b**]$^+PF_6^-$ and **5c** in THF, affording ethylbenzene quantitatively after only 4 h (entry 3-7). Although the styrene conversions achieved by use of [**5b**]$^+PF_6^-$ in THF were consistently greater than those obtained by use of **5c** as a catalyst under similar conditions, the latter zwitterionic species provided quantitative styrene conversion in benzene (entry 3-8), a solvent in which [**5b**]$^+PF_6^-$ is not soluble.

Whereas cationic square-planar Ir(I) complexes, including Crabtree's catalyst (**1**) and related [(COD)Ir(P,N)]$^+$X$^-$ species, are among the most active homogeneous catalysts for alkene hydrogenation,[5,22a] effective neutral Ir(I) alkene hydrogenation catalysts are still very rare. In this regard, we became interested in benchmarking the catalytic abilities of the neutral and zwitterionic complex **6c** against those of the more traditional cationic complexes [**6b**]$^+PF_6^-$ and **1**.[40b] In keeping with the well-documented affinity of [(COD)Ir(P,N)]$^+$X$^-$ alkene hydrogenation catalysts for chlorocarbon reaction media,[2,22a] the reduction of styrene mediated by [**6b**]$^+PF_6^-$ or **1** (0.5 mol %) occurred quantitatively in $CH_2Cl_2$ after 0.5 h or 4 h, respectively (entries 3-9 and 3-10). The noteworthy catalytic activity displayed by [**6b**]$^+PF_6^-$ in $CH_2Cl_2$ contrasts the apparent deactivating effect that this solvent has on the related Rh(I) species, [**5b**]$^+PF_6^-$ and **5c** (vide supra). While [**6b**]$^+PF_6^-$ also

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[38] Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

[39] A similar dynamic process has been proposed to account for the temperature-dependent $^1H$ NMR line shape changes observed for [(COD)M-($\kappa^2$-1-P(*S*)$^iPr_2$-2-*N*$Me_2$-indene)]$^+BF_4^-$ (M = Rh, Ir), the analysis of which also yielded $\Delta G^{\ddagger}_{Tc}$ of ca. 14 kcal/mol: Wechsler, D.; Myers, A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Inorg. Chem.* **2006**, *45*, 4562.

[40] (a) For styrene hydrogenation reactions employing either [**5b**]$^+PF_6^-$ or **5c** as a catalyst, <1% conversion was observed after 0.5 h, and in the case of reactions employing 5.0 mol % catalyst loadings, only 5−10% conversion was achieved after 4 h. (b) In a preliminary reactivity survey, [**6b**]$^+PF_6^-$ proved to be the most effective alkene hydrogenation catalyst of the three [**6b**]$^+$X$^-$ salts reported herein (X = $SO_3CF_3$, $BF_4$, or $PF_6$); see ref 18c herein. (c) Initial rates (TOF) are defined as (moles ethylbenzene produced/moles catalyst)/time and are measured at 0.25 h for reactions employing 0.5 mol % catalyst.

**Table 4. Addition of Triethylsilane to Styrene**[a]

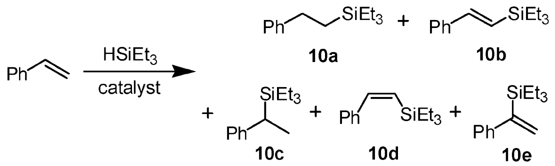
| entry | catalyst | solvent | yield (%)[b] | **10a**[c] | **10b**[c] | **10c**[c] | other[c] |
|---|---|---|---|---|---|---|---|
| 4-1 | [**5b**]$^+$PF$_6^-$ | DCE | $<$1 | $<$1 | $<$1 | $<$1 | $<$1 |
| 4-2 | **5c** | DCE | $<$1 | $<$1 | $<$1 | $<$1 | $<$1 |
| 4-3 | **2** | DCE | $>$99 | 4 | 93 | 3 | $<$1 |
| 4-4 | [**5b**]$^+$PF$_6^-$ | THF | 37 | 5 | 32 | $<$1 | $<$1 |
| 4-5 | **5c** | THF | $>$99 | 10 | 90 | $<$1 | $<$1 |
| 4-6 | **5c** | toluene | 98 | 2 | 96 | $<$1 | $<$1 |
| 4-7 | [**6b**]$^+$PF$_6^-$ | DCE | 66 | 66 | $<$1 | $<$1 | $<$1 |
| 4-8 | **6c** | DCE | $>$99 | 99 | $<$1 | $<$1 | $<$1 |
| 4-9[d] | **6c** | DCE | 86 | 86 | $<$1 | $<$1 | $<$1 |
| 4-10 | **1** | DCE | $>$99 | 51 | 40 | 7 | $<$1 |
| 4-11 | [**6b**]$^+$PF$_6^-$ | THF | $>$99 | 91 | 1 | 8 | $<$1 |
| 4-12[d] | [**6b**]$^+$PF$_6^-$ | THF | 35 | 35 | $<$1 | $<$1 | $<$1 |
| 4-13 | **6c** | THF | 98 | 94 | 2 | $<$1 | 2 |
| 4-14[d] | **6c** | THF | 88 | 88 | $<$1 | $<$1 | $<$1 |
| 4-15 | **6c** | toluene | 64 | 55 | 2 | $<$1 | 7 |

[a] Conditions: 60 °C (except where noted); 5.0 mol % catalyst; styrene-to-silane ratio of 5:1; DCE = 1,2-dichloroethane; control experiments confirmed that solutions of [**5b**]$^+$PF$_6^-$, [**6b**]$^+$PF$_6^-$, **5c**, or **6c** are each 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 for entry 4-3, where the yield is quoted after 4 h. [c] Product distribution based on GC-MS and GC-FID data, rounded to the nearest percent; other silicon-containing products including **10d** and **10e**. [d] Reaction conducted at 24 °C.

outperformed both [**5b**]$^+$PF$_6^-$ and **5c** in THF, affording ethylbenzene quantitatively after only 4 h at the 0.5 mol % catalyst loading level (entry 3-11), incomplete conversion was noted for analogous reactions employing **1** as a catalyst in THF, even after 24 h (entry 3-12). Unlike [**5b**]$^+$PF$_6^-$ and **5c**, which exhibited comparable catalytic abilities, the zwitterionic **6c** proved to be a considerably less effective styrene hydrogenation catalyst than both [**6b**]$^+$PF$_6^-$ and **1**. When employing 0.5 mol % **6c** as a catalyst in CH$_2$Cl$_2$, a maximum conversion of 56% was achieved after 4 h (entry 3-13), and only 76% conversion was realized by use of 5.0 mol % **6c** after a 24 h period (entry 3-14). However, given that reasonable initial styrene hydrogenation rates are observed for **6c** (355 h$^{-1}$; cf. 740 h$^{-1}$ for [**6b**]$^+$PF$_6^-$),[40c] it is feasible that the lower styrene conversions obtained by use of **6c** as a catalyst, as compared to reactions employing [**6b**]$^+$PF$_6^-$, may reflect the instability of **6c** under these experimental conditions, rather than the inherent catalytic activity of this zwitterionic species. In exploring further the effect of solvent on the catalytic performance of **6c**, the production of ethylbenzene in THF (entry 3-15) was found to be similar to that obtained in CH$_2$Cl$_2$ at the same catalyst loading. In addition, while both [**6b**]$^+$PF$_6^-$ and **1** are not soluble in hydrocarbons, complex **6c** exhibited modest catalytic activity in benzene (entry 3-16), as well as in hexanes (entry 3-17). Other differences in the catalytic abilities of [**6b**]$^+$PF$_6^-$ and **6c** were brought to light through the study of more highly substituted alkene substrates (0.5 mol % catalyst, 24 °C, ~1 atm H$_2$). Whereas the cationic Ir(I) complex [**6b**]$^+$PF$_6^-$ in CH$_2$Cl$_2$ proved capable of reducing cyclohexene quantitatively (0.5 h) and 1-methylcyclohexene to a significant extent (4 h, 83%), only 26% reduction of cyclohexene was achieved by use of **6c** as a catalyst after 4 h, and no zwitterion-mediated reduction of the aforementioned trisubstituted alkene was observed in CH$_2$Cl$_2$ or benzene.

**Styrene Hydrosilylation Studies.** In continuing our head-to-head reactivity comparison of the structurally related cationic and zwitterionic Rh(I) and Ir(I) species reported herein, the catalytic addition of triethylsilane to styrene mediated by [**5b**]$^+$PF$_6^-$, [**6b**]$^+$PF$_6^-$, **5c**, or **6c** was chosen as a second test reaction (5.0 mol % catalyst, 60 °C, excess styrene); selected experimental results are provided in Table 4. As well as representing a widely employed chemical transformation that provides access to synthetically useful organosilicon compounds,[41] metal-catalyzed alkene hydrosilylation can serve as a prototype for E−H addition reactions in which product selectivity can be a challenge. In contrast to the relative simplicity of alkene hydrogenation, the metal-mediated addition of silanes to substituted olefins can generate a range of organosilicon species; the predominant products of this reaction in the case of triethylsilane and styrene are depicted in eq 5. Beyond the two possible regioisomers that can arise from simple Si−H addition (**10a** and **10c**), vinylsilanes formed via dehydrogenative silylation (**10b**, **10d**, and **10e**) are also commonly observed. Notably, **10b** is often generated as the major product in such metal-catalyzed reactions where an excess of styrene is employed as a sacrificial H$_2$ acceptor.[41,42]

In keeping with the poor alkene hydrogenation activity noted for [**5b**]$^+$PF$_6^-$ and **5c** in CH$_2$Cl$_2$, no hydrosilylation chemistry was observed for reactions conducted in 1,2-dichloroethane employing either of these Rh(I) catalyst complexes (entries 4-1 and 4-2). However, the ability of Rh(I) species to mediate alkene hydrosilylations under these conditions was confirmed through the use of **2**. Complete consumption of the silane was achieved after 4 h in 1,2-dichloroethane, along with excellent selectivity for the vinylsilane **10b** (entry 4-3); similar results were obtained in benzene. While upon changing the solvent to THF only modest catalytic productivity was exhibited by [**5b**]$^+$PF$_6^-$ (37%, entry 4-4), quantitative consumption of the silane was achieved under similar conditions employing **5c**, affording **10b** along with the anti-Markovnikov addition product **10a** in a 90:10 ratio (entry 4-5). Similarly high conversions and even greater selectivity were achieved by use of **5c** as a catalyst in toluene (entry 4-6), a solvent in which the structurally related cationic complex [**5b**]$^+$PF$_6^-$ is not soluble.



(5)

In contrast to some of the other platinum-group metals, the use of Ir complexes as alkene hydrosilylation catalysts has received relatively little attention.[43] However, evidence for the selectivity advantages that can be brought about by use of Ir catalysts in such transformations is provided in a report by Uemura and co-workers.[44] These workers observed that whereas analogous chiral $\kappa^2$-*P*,*N* Rh and Ir species both proved capable of mediating the asymmetric hydrosilylation of acetophenone in nearly quantitative yield and with high enantioselectivity, the

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[41] For selected reviews, see: (a) Marciniec, B. *Coord. Chem. Rev.* **2005**, *249*, 2374. (b) Ojima, I.; Li, Z.; Zhu, J. In *Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2 p 1687. (c) Marciniec, B.; Guliński, J. *J. Organomet. Chem.* **1993**, *446*, 15. (d) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol 8, p 763. (e) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

[42] For examples featuring Rh(I) catalysts, 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.

[43] 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.

[44] Nishibayashi, Y.; Segawa, K.; Ohe, K.; Uemura, S. *Organometallics* **1995**, *14*, 5486.

chiral alcohol products obtained upon workup from the respective reactions were found to possess different absolute configurations.

The lack of catalytic activity observed for both [**5b**]$^+$PF$_6^-$ and **5c** in 1,2-dichloroethane contrasts the substantial silane conversion (66%) and complete selectivity for **10a** that was achieved by use of catalytic amounts of the Ir(I) cation [**6b**]$^+$PF$_6^-$ in this solvent (entry 4-7). Even more remarkable is the catalytic performance exhibited by the zwitterionic species **6c**, which under analogous conditions afforded **10a** quantitatively, despite the 4-fold excess of styrene employed (entry 4-8). High yields of **10a** were also obtained by use of **6c** as a catalyst in 1,2-dichloroethane on lowering the reaction temperature from 60 °C to 24 °C, with no loss in selectivity (entry 4-9). While hydrosilylation reactions mediated by Crabtree's catalyst (**1**) at 60 °C were also quantitative, very poor selectivity was observed (entry 4-10).

In examining the effect of solvent on the catalytic behavior of [**6b**]$^+$PF$_6^-$ and **6c**, hydrosilylation reactions were conducted in THF. Nearly quantitative silane conversions and good selectivity for **10a** were achieved by use of [**6b**]$^+$PF$_6^-$ or **6c** in this solvent at 60 °C (entries 4-11 and 4-13). While on lowering the temperature to 24 °C both of these Ir(I) catalyst complexes displayed complete selectivity for **10a** in THF, the zwitterionic **6c** outperformed the analogous cation in terms of yield (entries 4-12 and 4-14). In contrast to the excellent catalytic performance that was exhibited by the zwitterionic Rh(I) complex **5c** in toluene (entry 4-6), the Ir(I) analogue **6c** proved much less effective in this solvent relative to the others surveyed (entry 4-15). The catalytic abilities of the discrete salts [**6b**]$^+$PF$_6^-$ and **1** in toluene could not be surveyed, due to the poor solubility of these complexes in hydrocarbon media.

## Summary and Conclusions

The versatility of 1-P$^i$Pr$_2$-2-NMe$_2$-indene (**3a**) has been demonstrated through the use of this ligand in the synthesis of neutral, cationic, and zwitterionic Rh(I) and Ir(I) complexes. Whereas the facile rearrangement of **3a** to 3-P$^i$Pr$_2$-2-NMe$_2$-indene (**3b**) within the coordination sphere of these group 9 metals presented a challenge with regard to the isolation of $\kappa^2$-*P*,*N*-**3a** derivatives ([**5a**]$^+$X$^-$ and [**6a**]$^+$X$^-$) in high yield, such an isomerization process has been exploited successfully in the preparation of $\kappa^2$-*P*,*N*-**3b** complexes ([**5b**]$^+$X$^-$ and [**6b**]$^+$X$^-$). Zwitterionic complexes **5c** and **6c** featuring $\kappa^2$-3-*P*$^i$Pr$_2$-2-*N*Me$_2$-indenide ($\kappa^2$-*P*,*N*-**3c**) ligands were prepared in high isolated yield, either upon extrusion of HX from [**5b**]$^+$X$^-$ or [**6b**]$^+$X$^-$ or by addition of [**3c**]Li to 0.5 equiv of [(COD)MCl]$_2$. We view **5c** and **6c** as constituting an unusual new class of formally charge-separated Rh(I) and Ir(I) species that are distinct from more conventional $\eta^5$-indenyl group 9 complexes.

Data obtained from X-ray crystallographic experiments revealed that the steric characteristics of the metal coordination environments in these cationic $\kappa^2$-*P*,*N*-**3b** and zwitterionic $\kappa^2$-*P*,*N*-**3c** group 9 complexes are strikingly similar. Despite such apparent similarities, divergent catalytic behavior both within and between the cation/zwitterion pairs [**5b**]$^+$X$^-$/**5c** and [**6b**]$^+$X$^-$/**6c** was observed. Among these four complexes, the Ir(I) cation [**6b**]$^+$PF$_6^-$ proved to be the most effective styrene hydrogenation catalyst in CH$_2$Cl$_2$ or THF, exhibiting catalytic activity rivaling that of Crabtree's catalyst (**1**) under similar conditions. While the catalytic performance of **6c** proved vastly inferior to that of [**6b**]$^+$PF$_6^-$ in these solvents, the initial hydrogenation rates noted for **6c** in CH$_2$Cl$_2$, as well as the modest catalytic activity exhibited by this zwitterionic species in hydrocarbon media, suggest that alterations to the ancillary P,N-ligand architecture in **6c** may provide access to more active and long-lived Ir(I) hydrogenation catalysts that are hydrocarbon-soluble. Although [**6b**]$^+$PF$_6^-$ proved superior to both [**5b**]$^+$PF$_6^-$ and **5c** in terms of styrene hydrogenation activity in CH$_2$Cl$_2$ or THF, high conversion to ethylbenzene was achieved by use of **5c** as a catalyst in benzene, in which [**5b**]$^+$PF$_6^-$ and [**6b**]$^+$PF$_6^-$ are not soluble. The catalytic utility of these zwitterionic Rh(I) and Ir(I) species was also demonstrated in hydrosilylation reactions employing triethylsilane and styrene. Remarkably, while reactions mediated by either **5c** (toluene or THF) or **6c** (1,2-dichloroethane or THF) were observed to occur in nearly quantitative yield and with high selectivity, a different organosilane product was obtained in each case; the use of **5c** as a catalyst afforded *E*-1-triethylsilyl-2-phenylethene (**10b**) selectively, whereas 1-triethylsilyl-2-phenylethane (**10a**) was the only organosilane product detected in reactions employing **6c** as a catalyst in 1,2-dichloroethane. The complete selectivity for **10a** exhibited by this zwitterionic Ir(I) complex in the presence of excess styrene is noteworthy, especially in light of the observation that a nearly equimolar ratio of **10a** and **10b** was generated in reactions employing Crabtree's catalyst (**1**) under similar conditions.

On the basis of the results of this catalytic survey, [**5b**]$^+$PF$_6^-$, [**6b**]$^+$PF$_6^-$, **5c**, **6c**, and their derivatives constitute a complementary family of catalyst complexes for the addition of E−H bonds to alkenes, when issues of catalytic activity/selectivity and solvent compatibility are considered. Notably, these catalytic studies also confirm that zwitterionic species such as **5c** and **6c** represent an effective class of neutral catalyst complexes for the addition of E−H bonds to unsaturated substrates, whose solubility and reactivity properties are in some cases divergent from those of more traditional Rh(I) and Ir(I) [(COD)M($\kappa^2$-*P*,*N*)]$^+$X$^-$ salts. We are presently uncertain as to the specific origins of the differing reactivity properties of structurally related cationic group 9 complexes supported by $\kappa^2$-*P*,*N*-**3b** and their zwitterionic relatives featuring $\kappa^2$-*P*,*N*-**3c**. The observation that [**5b**]$^+$BF$_4^-$ was cleanly transformed into [Rh(PMePh$_2$)$_4$]$^+$BF$_4^-$ upon exposure to excess PMePh$_2$, while under similar conditions only the COD ligand in **5c** was displaced, suggests that tighter binding of the anionic $\kappa^2$-*P*,*N*-**3c** ligand to the [(COD)M]$^+$ fragment in **5c** and **6c** may represent a potential source of such divergent reactivity. In the absence of complete formal charge separation within **5c** and **6c**, the electrophilicity of the associated metal center in each of these complexes should be attenuated relative to [**5b**]$^+$PF$_6^-$ and [**6b**]$^+$PF$_6^-$, which in turn could also influence the catalytic behavior displayed by these species. As well, the participation of the backbone indenide unit in these zwitterionic species during the course of catalytic transformations cannot be discounted, and we are intrigued by the possibility of cooperative metal−ligand bifunctional activation of substrate E−H bonds involving formally zwitterionic derivatives of $\kappa^2$-*P*,*N*-**3c**. Synthetic and mechanistic experiments directed toward addressing these issues are currently underway in our laboratory.[45]

## 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

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[45] Compounds **3a**, [**5b**]$^+$PF$_6^-$, **5c**, [**6b**]$^+$PF$_6^-$, and **6c** are commercially available from Strem Chemicals, Inc.

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, 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, dichloromethane, and diethyl ether were purified over two alumina-packed columns, while toluene, benzene, hexanes, 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. Both $CD_2Cl_2$ (Cambridge Isotopes) and $CDCl_3$ (Aldrich) were degassed by using three repeated freeze−pump−thaw cycles, dried over $CaH_2$ for 7 days, distilled in vacuo, and stored over 3 Å molecular sieves for 24 h prior to use. Purification of $NEt_3$ was achieved by stirring over KOH for 7 days, followed by distillation; the distilled $NEt_3$ was then refluxed over $CaH_2$ for 3 days under dinitrogen, followed by distillation. All silver salts (Aldrich) and anhydrous $K_2CO_3$ (Aldrich) were dried in vacuo for 12 h prior to use. Hydrogen (99.999%, UHP grade) and carbon monoxide gases (99.5%, chemically pure grade) were obtained from Air Liquide and were used as received. All other liquid solvents or reagents (Aldrich) were degassed by using three repeated freeze−pump−thaw cycles and then dried over 3 Å molecular sieves for 24 h prior to use. Compounds **3a**,[18d] [**3c**]Li,[18d] $[(COD)RhCl]_2$,[46a] $[(COD)IrCl]_2$,[46b] $[(CO)_2RhCl]_2$,[47] and $(PPh_3)_3RhCl$ (**2**)[48] were prepared using literature methods and dried in vacuo for 24 h prior to use, while $[(COD)Ir(PCy_3)(Py)]^+PF_6^-$ (**1**) was obtained from Strem (COD = $\eta^4$-1,5-cyclooctadiene). All $^1H$, $^{13}C$, and $^{31}P$ NMR characterization data were collected at 300 K on either a Bruker AC-250 spectrometer operating at 250.1, 62.9, and 101.3 MHz, for $^1H$, $^{13}C$, and $^{31}P$ (respectively) or 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 $^1H$ and $^{13}C$) or 85% $H_3PO_4$ in $D_2O$ (for $^{31}P$). In some cases, $^1H$ and $^{13}C$ NMR chemical shift assignments are made on the basis of data obtained from $^{13}C$-DEPT, $^1H-^1H$ COSY, $^1H-^{13}C$ HSQC, $^1H-^{13}C$ HMBC, and/or 1D $^1H$ NOE NMR experiments. Variable-temperature NMR studies involving **7** were conducted on a Bruker AC-250 spectrometer, with temperature calibrations carried out using an external MeOH/MeOD standard.[49] GC-FID analyses were performed on a Perkin-Elmer autosystem gas chromatograph, while GC-MS analyses were performed on a Varian Saturn-2000 system. All GC analyses were carried out using a 30 m × 0.53 mm J&W DB5 column, with helium as the carrier gas. Elemental analyses were performed either by Desert Analytics, Tucson, AZ, or by Canadian Microanalytical Service Ltd., Delta, British Columbia (Canada).

**Synthesis of (COD)RhCl($\kappa^1$-*P*,N-3a) (4a).** A solution of **3a** (0.348 g, 1.26 mmol) in $CH_2Cl_2$ (3 mL) was added via Pasteur pipet over 1 min to a glass vial containing a small magnetic stir bar and a light orange solution of $[(COD)RhCl]_2$ (0.312 g, 0.633 mmol) in $CH_2Cl_2$ (3 mL). The vial was then sealed with a PTFE-lined cap, and the resulting dark orange solution was magnetically stirred for 1 h. $^{31}P$ NMR data collected on an aliquot of this crude reaction solution indicated the quantitative formation of **4a**. The reaction mixture was then filtered through Celite and the $CH_2Cl_2$ solvent and other volatile materials were removed in vacuo, yielding **4a** as an analytically pure, bright yellow powder (0.633 g, 1.21 mmol, 96%). Anal. Calcd for $C_{25}H_{38}N_1P_1Cl_1Rh_1$ (521.91 gmol$^{-1}$): C 57.53, H 7.34, N 2.68. Found: C 57.18, H 7.22, N 2.39. $^1H$ NMR ($CDCl_3$, 250.1 MHz): $\delta$ 8.90 (d, $^3J_{HH}$ = 7.3 Hz, 1H, Ar−H), 7.20−7.04 (m, 3H, Ar−Hs), 5.78 (s, 1H, C3-H), 5.47−5.34 (m, 3H, COD and C1-H), 3.74 (br m, 2H, COD), 3.00 (m, 1H, P(C*H*Me$_2$)), 2.73 (s, 6H, NMe$_2$), 2.38 (m, 5H, COD and P(C*H*Me$_2$)), 1.96 (m, 4H, COD), 1.70 (d of d, $^3J_{PH}$ = 15.8 Hz, $^3J_{HH}$ = 6.8 Hz, 3H, P(CHMe*Me*)), 1.32 (d of d, $^3J_{PH}$ = 14.1 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, P(CHMe*Me*)), 1.02 (d of d, $^3J_{PH}$ = 11.5 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, P(CHMe*Me*)), 0.44 (d of d, $^3J_{PH}$ = 13.7 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, P(CHMe*Me*)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.9 MHz): $\delta$ 161.7 (d, $J$ = 9 Hz, C2), 144.9 (d, $J$ = 4 Hz, C3a or C7a), 139.7 (C7a or C3a), 126.7 (Ar−C), 126.5 (Ar−C), 121.6 (2Ar−Cs), 118.3 (C3), 108.5 (COD), 101.0 (m, COD), 68.6 (m, COD), 43.8 (NMe$_2$), 43.2 (m, C1), 33.2 (COD), 33.1 (COD), 28.3 (COD), 28.2 (COD), 24.0 (m, P*C*HMe$_2$), 23.0 (d, $J$ = 16 Hz, P*C*HMe$_2$), 21.9 (d, $J$ = 15 Hz, PCHMe*Me*), 20.1 (PCHMe*Me*), 19.3 (PCHMe*Me*), 18.0 (m, PCHMe*Me*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 101.3 MHz): $\delta$ 48.2 (d, $^1J_{RhP}$ = 144 Hz). Crystals of **4a·**$CH_2Cl_2$ suitable for use in a single-crystal X-ray diffraction experiment were grown from a concentrated $CH_2Cl_2$ solution stored at −30 °C.

**Synthesis of [(COD)Rh($\kappa^2$-*P*,*N*-3a)]$^+$PF$_6^-$ ([5a]$^+$PF$_6^-$).** To a solution of $[(COD)RhCl]_2$ (0.120 g, 0.244 mmol) in THF (2 mL) was added a solution of $AgPF_6$ (0.123 g, 0.487 mmol) in THF (2 mL) via Pasteur pipet. The vial was sealed with a PTFE-lined cap and the mixture shaken vigorously for ∼30 s; the immediate formation of a white precipitate was observed. After 5 min, a solution of **3a** (0.134 g, 0.487 mmol) in THF (3 mL) was added, producing a yellow-orange solution. The reaction vial was sealed and shaken vigorously for 30 s, after which the precipitate was allowed to settle over 15 min. The reaction mixture was filtered through Celite to remove the precipitated solids, which were discarded. From the initially homogeneous filtrate a yellow microcrystalline precipitate was obtained. This solid was isolated by decanting away the supernatant (which was found to contain a mixture of [**5a**]$^+$PF$_6^-$ and [**5b**]$^+$PF$_6^-$ as identified by $^{31}P$ NMR analysis) and dried in vacuo to leave [**5a**]$^+$PF$_6^-$ as an analytically pure, orange powder (0.041 g, 0.066 mmol, 14%). Anal. Calcd for $C_{25}H_{38}P_2N_1Rh_1F_6$ (631.4 gmol$^{-1}$): C 47.55; H 6.07; N 2.22. Found: C 47.70; H 6.06; N 2.23. $^1H$ NMR ($CD_2Cl_2$, 500.1 MHz): $\delta$ 7.36−7.29 (m, 3H, Ar−Hs), 7.24 (m, 1H, Ar−H), 6.37 (br s, 1H, C3−H), 5.22 (br s, 1H, COD), 4.94 (br s, 1H, COD), 4.42 (d, $^2J_{PH}$ = 12.0 Hz, 1H, C1−H), 4.32 (br s, 1H, COD), 4.15 (br s, 1H, COD), 3.25 (s, 3H, N$Me_a$Me$_b$), 2.79 (s, 3H, NMe$_a$$Me_b$), 2.62−2.37 (m, 4H, COD), 2.32−2.15 (m, 3H, COD and P(C*H*Me$_a$Me$_b$)(CHMe$_c$Me$_d$)), 2.14−2.01 (m, 3H, COD and P(CHMe$_a$Me$_b$)(C*H*Me$_c$Me$_d$)), 1.71 (d of d, $^3J_{PH}$ = 17.8 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, P(CH$Me_a$Me$_b$)(CHMe$_c$Me$_d$)), 1.50 (d of d, $^3J_{PH}$ = 12.5 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CHMe$_a$$Me_b$)(CHMe$_c$Me$_d$)), 1.08 (d of d, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.4 Hz, 3H, P(CHMe$_a$Me$_b$)(CH$Me_c$Me$_d$)), 0.82 (d of d, $^3J_{PH}$ = 17.8 Hz, $^3J_{HH}$ = 6.9 Hz, 3H, P(CHMe$_a$Me$_b$)(CHMe$_c$$Me_d$)). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 125.8 MHz): $\delta$ 165.1 (C2), 143.2 (C3a or C7a), 134.9 (d, $J$ = 6.7 Hz, C7a or C3a), 128.9, 126.4, 125.3, 122.9 (C4, C5, C6, and C7), 116.7 (d, $J$ = 9.4 Hz, C3), 108.4 (COD), 105.1 (COD), 76.0 (d, $J_{RhC}$ = 12.8 Hz, COD), 72.1 (d, $J_{RhC}$ = 12.4 Hz, COD), 51.7 (N$Me_a$Me$_b$), 48.1 (NMe$_a$$Me_b$), 42.9 (d, $^1J_{PC}$ = 10.8 Hz, C1), 33.2 (COD), 32.0 (COD), 28.6 (COD), 28.3 (COD), 25.7 (d, $^1J_{PC}$ = 19.4 Hz, P(CHMe$_a$Me$_b$)(*C*HMe$_c$Me$_d$)), 23.8 (d, $^1J_{PC}$ = 17.0, P(*C*HMe$_a$Me$_b$)(CHMe$_c$Me$_d$)), 20.5 (d, $^2J_{PC}$ = 4.8 Hz, P(CH$Me_a$Me$_b$)(CHMe$_c$Me$_d$)), 19.1 (d, $^2J_{PC}$ = 4.2 Hz, P(CHMe$_a$Me$_b$)(CHMe$_c$$Me_d$)), 18.7 (d, $^2J_{PC}$ = 6.1 Hz, P(CHMe$_a$$Me_b$)(CHMe$_c$Me$_d$)), 18.4 (P(CHMe$_a$Me$_b$)(CH$Me_c$Me$_d$)). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 202.5 MHz): $\delta$ 25.7 (d, $^1J_{RhP}$ = 147.0 Hz, P(CHMe$_2$)$_2$), −143.2 (septet, $^1J_{PF}$ = 709.3 Hz, PF$_6$).

**Synthesis of [(COD)Rh($\kappa^2$-*P*,*N*-3b)]$^+$SO$_3$CF$_3^-$ ([5b]$^+$SO$_3$CF$_3^-$).** To a solution of $[(COD)RhCl]_2$ (0.048 g, 0.098 mmol) in THF (1 mL) was added via Pasteur pipet a solution of $AgSO_3CF_3$ (0.050 g, 0.20 mmol) in THF (2 mL). The vial was sealed with a PTFE-lined cap and the mixture shaken vigorously for ∼30 s. A white

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precipitate formed immediately, which was allowed to settle over 15 min and was removed from the reaction mixture by filtration over Celite and discarded. A solution of **3a** (0.054 g, 0.20 mmol) in THF (2 mL) was added to the filtrate, with immediate formation of an orange solution. The reaction vial was sealed, manually shaken for 30 s, and then left to stand for 2.5 h. $^{31}$P NMR data collected on an aliquot of the reaction mixture at this stage revealed a ~ 90:10 isomeric mixture of [**5a**]$^+$$SO_3CF_3^-$ and [**5b**]$^+$$SO_3CF_3^-$. To facilitate the rearrangement of [**5a**]$^+$$SO_3CF_3^-$ to [**5b**]$^+$$SO_3CF_3^-$, $NEt_3$ (0.08 mL) was added to the reaction mixture. The vial was sealed and manually shaken for 10 s. After 5 min, the solvent and other volatile materials were removed in vacuo to leave an orange solid. This solid was dried in vacuo, affording [**5b**]$^+$$SO_3CF_3^-$ as an analytically pure, orange powder (0.11 g, 0.17 mmol, 87%). Anal. Calcd for $C_{26}H_{38}P_1N_1S_1O_3Rh_1F_3$ (619.55 gmol$^{-1}$): C 49.12, H 6.03, N 2.20. Found: C 48.98, H 6.20, N 2.25. $^1$H NMR ($CD_2Cl_2$, 500.1 MHz): $\delta$ 7.53 (m, 1H, Ar−H), 7.49 (m, 1H, Ar−H), 7.39−7.36 (m, 2H, Ar−H), 5.14 (br s, 2H, COD), 4.49 (br s, 2H, COD), 3.72 (s, 2H, C1(H)$_2$), 3.03 (s, 6H, NMe$_2$), 2.83 (m, 2H, P(C*H*Me$_a$Me$_b$)$_2$), 2.54−2.49 (m, 4H, COD), 2.26−2.18 (m, 4H, COD), 1.45 (d of d, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 7.2 Hz, 6H, P(CH*Me$_a$*Me$_b$)$_2$), 1.35 (d of d, $^3J_{PH}$ = 15.9 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe$_a$*Me$_b$*)$_2$). $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 125.8 MHz): $\delta$ 195.9 ($SO_3CF_3$), 177.3 (d, $J$ = 17.9 Hz, C2), 143.5 (C3a or C7a), 137.7 (C7a or C3a), 128.8 (d, $^1J_{PC}$ = 26.3, C3), 127.1, 126.9, 125.3, 123.0 (C4, C5, C6, or C7), 105.9 (m, COD), 73.3 (d, $^1J_{RhC}$ = 12.4 Hz, COD), 51.1 (NMe$_2$), 32.3 (COD), 31.2 (d, $J$ = 10.1 Hz, C1), 28.1 (COD), 24.9 (d, $^1J_{PC}$ = 24.5 Hz, P(*C*HMe$_a$Me$_b$)$_2$), 19.4 (P(CHMe$_a$*Me$_b$*)$_2$), 18.5 (d, $J$ = 3.8 Hz, P(CH*Me$_a$*Me$_b$)$_2$). $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 202.5 MHz): $\delta$ 43.1 (d, $^1J_{RhP}$ = 150.6 Hz).

**Synthesis of [(COD)Rh($\kappa^2$-*P*,*N*-3b)]$^+$$BF_4^-$ ([5b]$^+$$BF_4^-$).** A solution of **3a** (0.20 g, 0.72 mmol) in THF (2 mL) was added via Pasteur pipet to a glass vial containing a small magnetic stir bar and a light orange solution of [(COD)RhCl]$_2$ (0.18 g, 0.36 mmol) in THF (2 mL), thereby producing a dark orange solution. The vial was then sealed with a PTFE-lined cap, and the solution was magnetically stirred for 5 min. The cap was then removed and a solution of $AgBF_4$ (0.14 g, 0.72 mmol) in THF (2 mL) was added to the reaction mixture over 1 min by use of a Pasteur pipet; a precipitate formed immediately. The vial was again sealed with the PTFE-lined cap and the reaction mixture magnetically stirred for 1 h. $^{31}$P NMR data collected on an aliquot of this crude reaction mixture indicated the quantitative formation of [**5b**]$^+$$BF_4^-$. The reaction mixture was filtered through Celite and the THF solvent and other volatile materials were removed in vacuo, yielding analytically pure [**5b**]$^+$$BF_4^-$ as a bright orange powder (0.39 g, 0.68 mmol, 94%). Anal. Calcd for $C_{25}H_{38}N_1P_1B_1F_4Rh_1$ (573.27 gmol$^{-1}$): C 52.38, H 6.68, N 2.44. Found: C 52.12, H 6.84, N 2.32. All $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR data for the cation were identical to those reported for [**5b**]$^+$$SO_3CF_3^-$. Crystals suitable for single-crystal X-ray diffraction analysis were obtained from a concentrated THF solution of [**5b**]$^+$$BF_4^-$ at room temperature.

**Synthesis of [(COD)Rh($\kappa^2$-*P*,*N*-3b)]$^+$$PF_6^-$ ([5b]$^+$$PF_6^-$).** To a solution of [(COD)RhCl]$_2$ (0.120 g, 0.244 mmol) in THF (2 mL) was added a solution of $AgPF_6$ (0.123 g, 0.487 mmol) in THF (2 mL) via Pasteur pipet. The vial was sealed with a PTFE-lined cap and the mixture shaken vigorously for ~30 s; the immediate formation of a white precipitate was observed. After 5 min, a solution of **3a** (0.134 g, 0.487 mmol) in THF (3 mL) was added, which resulted in the formation of a yellow-orange solution. The reaction vial was sealed and shaken vigorously for 30 s, after which the precipitate was allowed to settle over 15 min. The reaction mixture was filtered through Celite to remove the precipitated solids, which were discarded. From the initially homogeneous filtrate some amount of yellow microcrystalline material precipitated ([**5a**]$^+$$PF_6^-$), which was separated from the supernatant. At this stage, $^{31}$P NMR data collected on an aliquot of the supernatant solution indicated the presence of an isomeric mixture of [**5a**]$^+$$PF_6^-$ and [**5b**]$^+$$PF_6^-$. To the isolated supernatant was added $NEt_3$ (0.070 mL) to facilitate the rearrangement of [**5a**]$^+$$PF_6^-$ to [**5b**]$^+$$PF_6^-$. The vial was sealed and manually shaken for 10 s, and after standing for an additional 5 min, the solvent and other volatile materials were removed in vacuo to leave a sticky dark yellow-orange solid. The solid was washed with toluene (2 × 1 mL) and subsequently dried in vacuo to leave [**5b**]$^+$$PF_6^-$ as an analytically pure, orange powder (0.189 g, 0.300 mmol, 62%). Anal. Calcd for $C_{25}H_{38}P_2N_1Rh_1F_6$ (631.4 gmol$^{-1}$): C 47.55; H 6.07; N 2.22. Found: C 47.49; H 6.02; N 2.40. All $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR data for the cation were identical to those reported for [**5b**]$^+$$SO_3CF_3^-$. NB: If precipitated [**5a**]$^+$$PF_6^-$ is not separated from the supernatant in the aforementioned procedure, analytically pure [**5b**]$^+$$PF_6^-$ is obtained in 73% isolated yield.

**Synthesis of (COD)Rh($\kappa^2$-*P*,*N*-3c) (5c).** A solution of [(COD)RhCl]$_2$ (0.044 g, 0.090 mmol) in toluene (3 mL) was transferred dropwise via Pasteur pipet to a glass vial containing a magnetically stirred slurry of [**3c**]Li (0.050 g, 0.18 mmol) suspended in toluene (3 mL). The reaction mixture immediately turned deep orange-red, accompanied by the formation of a fine precipitate. The vial was then sealed with a PTFE-lined cap and the solution was magnetically stirred for 45 min, after which time $^{31}$P NMR data collected on an aliquot of the crude reaction mixture indicated the quantitative formation of **5c**. The reaction mixture was then filtered through Celite, the supernatant was concentrated in vacuo, and the product was crystallized from the supernatant by storing at −30 °C. After 24 h, crystals of **5c** were isolated by transferring the supernatant solution to a new glass vial by using a Pasteur pipet; this solution was then concentrated in vacuo and stored at −30 °C to induce further crystallization. After repeating this procedure, the isolated crops of crystals were combined and dried in vacuo, yielding **5c** as an analytically pure, orange-red microcrystalline solid (0.079 g, 0.16 mmol, 89%). Anal. Calcd for $C_{25}H_{37}N_1P_1Rh_1$ (485.45 gmol$^{-1}$): C 61.85, H 7.68, N 2.89. Found: C 61.68, H 7.62, N 2.76. $^1$H NMR ($C_6D_6$, 250.1 MHz): $\delta$ 7.97 (m, 1H, Ar−H), 7.75 (m, 1H, Ar−H), 7.32 (m, 2H, Ar−Hs), 6.31 (d, $J$ = 3.7 Hz, 1H, C1−H), 4.23 (m, 2H, COD), 3.95 (m, 2H, COD), 2.66 (s, 6H, NMe$_2$), 2.48 (m, 2H, P(C*H*Me$_2$)$_2$), 2.09−1.45 (m, 8H, COD), 1.17 (d of d, $^3J_{PH}$ = 14.6 Hz, $^3J_{HH}$ = 7.3 Hz, 6H, P(CH*Me$_a$*Me$_b$)$_2$), 1.05 (d of d, $^3J_{PH}$ = 15.9 Hz, $^3J_{HH}$ = 7.3 Hz, 6H, P(CHMe$_a$*Me$_b$*)$_2$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 62.9 MHz): $\delta$ 181.1 (d, $J$ = 10 Hz, C2), 163.1 (m, C3, C3a, or C7a), 138.8 (m, C3, C3a, or C7a), 121.1, 120.0, 116.9, 116.6 (C4, C5, C6, C7), 99.8 (m, COD), 87.4 (d, $J$ = 12 Hz, C1), 69.1 (d, $J$ = 13 Hz, COD), 54.2 (NMe$_2$), 32.6 (m, COD), 28.3 (COD), 26.4 (d, $J$ = 26 Hz, P(*C*HMe$_2$)$_2$), 19.7 (P(CH*Me$_a$*Me$_b$)$_2$), 19.5 (d, $J$ = 4 Hz, P(CHMe$_a$*Me$_b$*)$_2$). $^{31}$P{$^1$H} NMR ($C_6D_6$, 101.3 MHz): $\delta$ 33.2 (d, $^1J_{RhP}$ = 145 Hz). Slow evaporation of a benzene solution of **5c** within the glovebox produced crystals suitable for single-crystal X-ray diffraction analysis.

**Synthesis of [(COD)Ir($\kappa^2$-*P*,*N*-3a)]$^+$$SO_3CF_3^-$ ([6a]$^+$$SO_3CF_3^-$).** To a solution of [(COD)IrCl]$_2$ (0.080 g, 0.12 mmol) in THF (5 mL) was added a solution of $AgSO_3CF_3$ (0.061 g, 0.24 mmol) in THF (2 mL) via Pasteur pipet. Immediate formation of a white precipitate was observed. After 1 h, the reaction mixture was filtered through Celite and the filtered solids were discarded. To the clear, bright yellow filtrate solution was added a solution of **3a** (0.065 g, 0.24 mmol) in THF (1.5 mL); the solution turned dark red immediately. The reaction vial was sealed with a PTFE-lined cap, shaken vigorously for 30 s, and allowed to sit undisturbed for 1 h. Over this time, an orange crystalline solid had formed in the reaction vial. The supernatant (which was found to contain a mixture of [**6a**]$^+$$SO_3CF_3^-$ and [**6b**]$^+$$SO_3CF_3^-$ as identified by $^{31}$P NMR analysis) was decanted away from the solid product. In turn, this solid was dried in vacuo to afford [**6a**]$^+$$SO_3CF_3^-$ as an analytically pure, bright orange solid (0.071 g, 0.098 mmol, 41%). Anal. Calcd for $C_{26}H_{38}P_1N_1Ir_1O_3S_1F_3$ (724.8 gmol$^{-1}$): C 43.08; H 5.28; N 1.93.

Found: C 43.08; H 5.55; N 1.95. $^1$H NMR ($\mathrm{CD_2Cl_2}$, 500.1 MHz): $\delta$ 7.43−7.32 (m, 4H, Ar−Hs), 6.57 (s, 1H, C3-H), 4.98 (m, 1H, COD), 4.78 (m, 1H, COD), 4.62 (d, $^2J_{\mathrm{PH}} = 13.0$ Hz, 1H, C1-H), 4.20 (m, 1H, COD), 3.94 (m, 1H, COD), 3.27 (s, 3H, $\mathrm{N\mathit{Me_a}Me_b}$), 3.16 (s, 3H, $\mathrm{NMe_a\mathit{Me_b}}$), 2.56−2.41 (m, 3H, COD and $\mathrm{P(C\mathit{H}Me_aMe_b)(CHMe_cMe_d)}$ and $\mathrm{P(CHMe_aMe_b)(C\mathit{H}Me_cMe_d)}$), 2.38−2.21 (m, 3H, COD), 2.13−2.03 (m, 2H, COD), 1.89−1.86 (m, 2H, COD), 1.73 (d of d, $^3J_{\mathrm{PH}} = 13.1$ Hz, $^3J_{\mathrm{HH}} = 7.2$ Hz, 3H, $\mathrm{P(CH\mathit{Me_a}Me_b)(CHMe_cMe_d)}$), 1.59 (d of d, $^3J_{\mathrm{PH}} = 13.1$ Hz, $^3J_{\mathrm{HH}} = 6.9$ Hz, 3H, $\mathrm{P(CHMe_a\mathit{Me_b})(CHMe_cMe_d)}$), 1.16 (d of d, $^3J_{\mathrm{PH}} = 15.3$ Hz, $^3J_{\mathrm{HH}} = 7.3$ Hz, 3H, $\mathrm{P(CHMe_aMe_b)(CH\mathit{Me_c}Me_d)}$), 0.79 (d of d, $^3J_{\mathrm{PH}} = 17.9$ Hz, $^3J_{\mathrm{HH}} = 7.0$ Hz, 3H, $\mathrm{P(CHMe_aMe_b)(CHMe_c\mathit{Me_d})}$). $^{13}$C{$^1$H} NMR ($\mathrm{CD_2Cl_2}$, 125.8 MHz): $\delta$ 166.9 (C2), 143.5 (C3a or C7a), 134.7 (C7a or C3a), 129.1, 126.9, 125.6, 123.6 (C4, C5, C6, and C7), 118.1 (d, $^3J_{\mathrm{PC}} = 8.7$ Hz, C3), 96.8 (d, $^2J_{\mathrm{PC}} = 11.5$ Hz, COD), 93.6 (d, $^2J_{\mathrm{PC}} = 11.1$ Hz, COD), 61.4 (COD), 58.2 (COD), 53.0 ($\mathrm{N\mathit{Me_a}Me_b}$), 49.1 ($\mathrm{NMe_a\mathit{Me_b}}$), 42.9 (d, $^1J_{\mathrm{PC}} = 17.3$ Hz, C1), 34.3 (br s, COD), 32.3 (br s, COD), 29.7 (COD), 28.7 (COD), 26.2 (d, $^1J_{\mathrm{PC}} = 25.6$ Hz, $\mathrm{P(\mathit{C}HMe_aMe_b)(CHMe_cMe_d)}$), 24.3 (d, $^1J_{\mathrm{PC}} = 23.4$, $\mathrm{P(CHMe_aMe_b)(\mathit{C}HMe_cMe_d)}$), 20.7 (d, $^2J_{\mathrm{PC}} = 3.1$ Hz, $\mathrm{P(CH\mathit{Me_a}Me_b)(CHMe_cMe_d)}$), 19.3 (d, $^2J_{\mathrm{PC}} = 2.5$ Hz, $\mathrm{P(CHMe_aMe_b)(CHMe_c\mathit{Me_d})}$), 19.1 (d, $^2J_{\mathrm{PC}} = 5.6$ Hz, $\mathrm{P(CHMe_a\mathit{Me_b})(CHMe_cMe_d)}$), 18.5 ($\mathrm{P(CHMe_aMe_b)(CH\mathit{Me_c}Me_d)}$). $^{31}$P{$^1$H} NMR ($\mathrm{CD_2Cl_2}$, 202.5 MHz): $\delta$ 15.0.

**Synthesis of [(COD)Ir($\kappa^2$-*P,N*-3b)]$^+$SO$_3$CF$_3^-$ ([6b]$^+$SO$_3$CF$_3^-$).** To a solution of [(COD)IrCl]$_2$ (0.10 g, 0.15 mmol) in THF (3 mL) was added a solution of $\mathrm{AgSO_3CF_3}$ (0.076 g, 0.30 mmol) in THF (2 mL) via Pasteur pipet. Immediate formation of a white precipitate was observed. After 1 h, the reaction mixture was filtered through Celite and the filtered solids were discarded. To the clear, bright yellow filtrate solution was added a solution of **3a** (0.082 g, 0.30 mmol) in THF (1.5 mL); a dark red solution immediately formed. After magnetically stirring the mixture for 1 h, the supernatant was decanted away from any precipitate that had formed (identified as [**6a**]$^+$SO$_3$CF$_3^-$ based on $^{31}$P NMR analysis) and $\mathrm{NEt_3}$ (0.4 mL) was added to the solution to facilitate the rearrangement of [**6a**]$^+$SO$_3$CF$_3^-$ to [**6b**]$^+$SO$_3$CF$_3^-$. After 30 min, the solvent and other volatile materials were removed in vacuo to leave a dark brown, sticky solid. This solid was washed with toluene (2 × 2 mL) and pentane (2 mL) to leave [**6b**]$^+$SO$_3$CF$_3^-$ as an analytically pure, orange solid (0.10 g, 0.14 mmol, 47%). Anal. Calcd for $\mathrm{C_{26}H_{38}P_1N_1Ir_1O_3S_1F_3}$ (724.8 gmol$^{-1}$): C 43.08; H 5.28; N 1.93. Found: C 42.96; H 5.09; N 1.78. $^1$H NMR ($\mathrm{CD_2Cl_2}$, 500.1 MHz): $\delta$ 7.52−7.48 (m, 2H, Ar−Hs), 7.38−7.34 (m, 2H, Ar−Hs), 4.81−4.76 (m, 2H, COD), 4.26−4.20 (m, 2H, COD), 3.80 (s, 2H, C1(H)$_2$), 3.13 (s, 6H, $\mathrm{NMe_2}$), 3.06−2.99 (m, 2H, $\mathrm{P(C\mathit{H}Me_2)_2}$), 2.32−2.26 (m, 4H, COD), 1.94−1.90 (m, 4H, COD), 1.38 (d of d, $^3J_{\mathrm{PH}} = 17.5$ Hz, $^3J_{\mathrm{HH}} = 7.5$ Hz, 6H, $\mathrm{P(CH\mathit{Me_a}Me_b)_2}$), 1.30 (d of d, $^3J_{\mathrm{PH}} = 15.5$ Hz, $^3J_{\mathrm{HH}} = 7.0$ Hz, 6H, $\mathrm{P(CHMe_a\mathit{Me_b})_2}$). $^{13}$C{$^1$H} NMR ($\mathrm{CD_2Cl_2}$, 125.8 MHz): $\delta$ 195.9 ($\mathrm{SO_3CF_3}$), 179.5 (d, $^2J_{\mathrm{PC}} = 16.0$ Hz, C2), 144.2 (d, $^2J_{\mathrm{PC}} = 6.0$ Hz, C3a), 136.9 (C7a), 130.7 (d, $^1J_{\mathrm{PC}} = 34.8$ Hz, C3), 127.4, 127.2, 125.9, 122.6 (C4, C5, C6, C7), 93.4 (d, $^2J_{\mathrm{PC}} = 11.3$ Hz, COD), 59.8 (COD), 52.2 ($\mathrm{NMe_2}$), 33.0 (d, $^3J_{\mathrm{PC}} = 2.6$ Hz, COD), 31.6 (d, $^3J_{\mathrm{PC}} = 9.5$ Hz, C1), 28.8 (COD), 25.4 (d, $^1J_{\mathrm{PC}} = 30.4$ Hz, $\mathrm{P(\mathit{C}HMe_2)_2}$), 19.7 ($\mathrm{P(CH\mathit{Me_a}Me_b)_2}$), 18.5 ($\mathrm{P(CHMe_a\mathit{Me_b})_2}$). $^{31}$P{$^1$H} NMR ($\mathrm{CD_2Cl_2}$, 202.5 MHz): $\delta$ 35.9. Crystals suitable for single-crystal X-ray diffraction analysis were obtained from a concentrated THF solution of [**6b**]$^+$SO$_3$CF$_3^-$ at room temperature. NB: If in using the procedure above the precipitated [**6a**]$^+$SO$_3$CF$_3^-$ is not separated from the supernatant containing a mixture of [**6a**]$^+$SO$_3$CF$_3^-$ and [**6b**]$^+$SO$_3$CF$_3^-$, then $\mathrm{NEt_3}$ can be added to the mixture to afford analytically pure [**6b**]$^+$SO$_3$CF$_3^-$ in 89% isolated yield.

**Synthesis of [(COD)Ir($\kappa^2$-*P,N*-3b)]$^+$BF$_4^-$ ([6b]$^+$BF$_4^-$).** To a solution of [(COD)IrCl]$_2$ (0.050 g, 0.075 mmol) in THF (3 mL) was added a solution of $\mathrm{AgBF_4}$ (0.032 g, 0.16 mmol) in THF (2 mL) via Pasteur pipet. Immediate formation of a white precipitate was observed. After 1 h, the reaction mixture was filtered through Celite and the filtered solids were discarded. To the clear, bright yellow filtrate solution was added **3a** (0.041 g, 0.15 mmol) in THF (1.5 mL), with formation of an orange solution. After 1.5 h, the solvent and other volatile materials were removed in vacuo to leave a sticky, brown solid. The solid was washed with toluene (2 mL) and subsequently with pentane (2 mL) to leave [**6b**]$^+$BF$_4^-$ as an analytically pure, orange powder (0.037 g, 0.056 mmol, 37%). Anal. Calcd for $\mathrm{C_{25}H_{38}P_1N_1Ir_1B_1F_4}$ (662.6 gmol$^{-1}$): C 45.32; H 5.78; N 2.11. Found: C 45.39; H 5.70; N 2.15. All $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR data for the cation were identical to those reported for [**6b**]$^+$SO$_3$CF$_3^-$. Whereas a much higher apparent isolated yield of [**6b**]$^+$BF$_4^-$ is obtained by use of less toluene and pentane in the washing procedure, the resulting solids thereby obtained did not reliably provide satisfactory combustion analysis.

**Synthesis of [(COD)Ir($\kappa^2$-*P,N*-3b)]$^+$PF$_6^-$ ([6b]$^+$PF$_6^-$).** To a solution of [(COD)IrCl]$_2$ (0.060 g, 0.090 mmol) in THF (3 mL) was added a solution of $\mathrm{AgPF_6}$ (0.045 g, 0.18 mmol) in THF (2 mL) via Pasteur pipet. A white precipitate formed immediately. After 5 min a solution of **3a** (0.049 g, 0.18 mmol) in THF (3 mL) was added to the reaction mixture, with immediate darkening of the solution to deep red. The reaction vial was then sealed and shaken vigorously for 30 s, after which the precipitate was allowed to settle over 15 min. The reaction mixture was filtered through Celite and the filtered solids were discarded. To the filtrate was added $\mathrm{NEt_3}$ (0.075 mL), after which the reaction vial was sealed, manually shaken for 10 s, and left to sit for 5 min. The solvent and other volatile materials were then removed in vacuo to leave a sticky, orange-brown solid. The product was extracted into $\mathrm{CH_2Cl_2}$ (5 mL) and the mixture filtered over Celite in order to remove any insoluble materials. The filtrate was dried in vacuo to leave an orange solid, which was washed once with pentane (2 mL) and subsequently dried in vacuo to leave [**6b**]$^+$PF$_6^-$ as an analytically pure, orange powder (0.10 g, 0.14 mmol, 78%). Anal. Calcd for $\mathrm{C_{25}H_{38}P_2N_1Ir_1F_6}$ (720.7 gmol$^{-1}$): C 41.66; H 5.31; N 1.94. Found: C 41.44; H 5.41; N 2.11. All $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR data for the cation were identical to those reported for [**6b**]$^+$SO$_3$CF$_3^-$. Crystals suitable for single-crystal X-ray diffraction analysis were obtained from a concentrated THF solution of [**6b**]$^+$PF$_6^-$ at room temperature.

**Synthesis of (COD)Ir($\kappa^2$-*P,N*-3c) (6c).** A solution of [(COD)IrCl]$_2$ (0.099 g, 0.15 mmol) in toluene (3 mL) was added to a slurry of [**3c**]Li (0.081 g, 0.29 mmol) in toluene (3 mL) via Pasteur pipet; the solution instantly darkened to ruby red. After 40 min, the reaction mixture was filtered through Celite to remove any precipitate. At this stage, $^{31}$P NMR data collected on an aliquot of the crude reaction mixture indicated the quantitative formation of **6c**. The solvent and any other volatile materials were then removed in vacuo to yield **6c** as an analytically pure, dark orange solid (0.16 g, 0.27 mmol, 93%). Anal. Calcd for $\mathrm{C_{25}H_{37}P_1N_1Ir_1}$ (574.8 gmol$^{-1}$): C 52.24; H 6.49; N 2.44. Found: C 52.53; H 6.44; N 2.68. $^1$H NMR ($\mathrm{C_6D_6}$, 500.1 MHz): $\delta$ 7.98 (d, $^3J_{\mathrm{HH}} = 11.0$, 1H, C7-H), 7.80 (d, $^3J_{\mathrm{HH}} = 8.0$, 1H, C4-H), 7.39−7.32 (m, 2H, C6-H and C5-H), 6.30 (d, $J = 3.7$ Hz, 1H, C1-H), 3.88−3.84 (m, 4H, COD), 2.75 (s, 6H, $\mathrm{NMe_2}$), 2.71 (m, 2H, $\mathrm{P(C\mathit{H}Me_2)_2}$), 1.95−1.79 (m, 4H, COD), 1.39 (m, 2H, COD), 1.29 (m, 2H, COD), 1.18 (d of d, $^3J_{\mathrm{PH}} = 15.1$ Hz, $^3J_{\mathrm{HH}} = 7.0$ Hz, 6H, $\mathrm{P(CH\mathit{Me_a}Me_b)_2}$), 1.05 (d of d, $^3J_{\mathrm{PH}} = 15.9$ Hz, $^3J_{\mathrm{HH}} = 7.2$ Hz, 6H, $\mathrm{P(CHMe_a\mathit{Me_b})_2}$). $^{13}$C{$^1$H} NMR ($\mathrm{C_6D_6}$, 125.8 MHz): $\delta$ 164.5 (d, $^2J_{\mathrm{PC}} = 22.8$ Hz, C2), 139.3 (d, $J = 10.2$ Hz, C3, C3a, or C7a), 130.6 (C3, C3a, or C7a), 121.5, 119.8, 116.9, 116.7 (C4, C5, C6, and C7), 87.3 (d, $^3J_{\mathrm{PC}} = 11.2$ Hz, C1), 84.7 (d, $J_{\mathrm{PC}} = 11.8$ Hz, COD), 54.8 ($\mathrm{NMe_2}$), 54.6 (COD), 32.8 (d, $J_{\mathrm{PC}} = 2.3$ Hz, COD), 28.7 (COD), 26.4 (d, $^1J_{\mathrm{PC}} = 33.8$ Hz, $\mathrm{P(\mathit{C}HMe_2)_2}$), 19.6 ($\mathrm{P(CH\mathit{Me_a}Me_b)_2}$), 19.1 ($\mathrm{P(CHMe_a\mathit{Me_b})_2}$). $^{31}$P{$^1$H} NMR ($\mathrm{C_6D_6}$, 202.5 MHz): $\delta$ 25.0. Crystals suitable for single-crystal X-ray diffraction analysis were grown from a concentrated toluene solution of **6c** at room temperature.

**Synthesis of (CO)(Cl)Rh($\kappa^2$-*P*,*N*-3b) (7).** To a solution of **3a** (0.050 g, 0.18 mmol) in THF (2 mL) was added via Pasteur pipet a solution of $[(CO)_2RhCl]_2$ (0.016 g, 0.091 mmol) in THF (1 mL). The resulting clear yellow solution was magnetically stirred for 10 min, upon which $K_2CO_3$ (0.050 g, 0.36 mmol) was added. After magnetically stirring the heterogeneous mixture for 30 min, the slurry was filtered through Celite and the filtered solid discarded, to leave a clear orange filtrate solution. The solvent was removed in vacuo to leave an oily residue, from which some product (**7**) was extracted into $Et_2O$ (2 × 2 mL); yellow-orange crystalline plates of **7** suitable for X-ray crystallographic analysis were obtained from this fraction. Additional product was obtained by dissolution of the remaining oily residue in benzene (2 mL), from which brown impurities were precipitated out by addition of pentane (1 mL), to leave a yellow solution. The solution was filtered through Celite and the product isolated by removal of the solvent in vacuo. The combined crops of analytically pure **7** were dried in vacuo for 18 h (0.034 g, 0.077 mmol, 43%). Anal. Calcd for $C_{18}H_{26}PNOClRh$: C 48.94, H 5.93, N 3.17. Found: C 49.07, H 6.26, N 3.29. $^1H$ NMR ($C_6D_6$, 500.1 MHz): $\delta$ 7.11−7.06 (m, 2H, C5-H and C6-H), 7.03 (d, $^3J_{HH} = 6.8$ Hz, 1H, C4-H), 7.00 (d, $^3J_{HH} = 6.8$ Hz, 1H, C7-H), 2.59 (s, 6H, $NMe_2$), 2.46 (s, 2H, $C1(H)_2$), 2.06−1.97 (m, 2H, $P(C\mathit{H}Me_aMe_b)_2$), 1.06 (d of d, $^3J_{PH} = 17.8$ Hz, $^3J_{HH} = 6.9$ Hz, 6H, $P(CH\mathit{Me_a}Me_b)_2$), 0.81 (d of d, $^3J_{PH} = 16.7$ Hz, $^3J_{HH} = 6.9$ Hz, 6H, $P(CHMe_a\mathit{Me_b})_2$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 125.8 MHz): $\delta$ 189.7 (d of d, $^1J_{RhC} = 73.2$ Hz, $^2J_{PC} = 18.5$ Hz, CO), 175.3 (d, $J = 18.9$ Hz, C2), 143.4 (C3a or C7a), 138.3 (C7a or C3a), 132.4 (d, $^1J_{PC} = 29.2$ Hz, C3), 126.8 (C5 or C6), 125.8 (C6 or C5), 124.9 (C7), 121.6 (C4), 48.8 ($NMe_2$), 29.8 (d, $J = 10.2$ Hz, C1), 26.5 (d, $J = 30.8$ Hz, $P(\mathit{C}HMe_aMe_b)_2$), 19.7 (d, $^2J_{PC} = 5.3$ Hz, $P(CH\mathit{Me_a}Me_b)_2$), 19.5 ($P(CHMe_a\mathit{Me_b})_2$). $^{31}P\{^1H\}$ NMR ($C_6D_6$, 202.5 MHz): $\delta$ 72.2 (d, $^1J_{RhP} = 161.5$ Hz). FTIR ($C_6H_6$/CsI; $cm^{-1}$) $\nu$(CO): 1977.

**Synthesis of $[(CO)_2Rh(\kappa^2$-*P*,*N*-3b)$]^+PF_6^-$ (8).** Compound **[5b]**$^+PF_6^-$ (0.054 g, 0.085 mmol) was dissolved in $CH_2Cl_2$ (4 mL) in a Schlenk flask equipped with a magnetic stir bar. The flask was transferred to a Schlenk line, and the orange solution was degassed by use of three successive freeze−pump−thaw cycles. Magnetic stirring of the solution was initiated, and the flask was backfilled with CO (~1 atm). Within 30 s, the solution turned bright yellow in color. After 90 min, the flask was purged with $N_2$ for 20 min. The reaction vessel was then transferred into the glovebox, whereupon pentane (2 mL) was added to the reaction mixture in order to induce precipitation of the product (**8**) as a fluffy, yellow solid. The solid product **8** was isolated by filtration through a Büchner funnel equipped with a fine-porosity filter paper. Additional product was isolated in a similar manner by concentrating the filtrate to approximately half the original volume in vacuo, followed by adding an additional amount of pentane (2 mL) to induce further precipitation. This process was repeated until the filtrate was essentially colorless. All isolated crops of **8** were combined and dried in vacuo for 5 h (0.033 g, 0.056 mmol, 66%). Anal. Calcd for $C_{19}H_{26}P_2NO_2F_6Rh$: C 39.39, H 4.52, N 2.42. Found: C 39.23, H 4.88, N 2.38. $^1H$ NMR ($CD_2Cl_2$, 500.1 MHz): 7.62 (m, 1H, C7−H), 7.46−7.44 (m, 3H, C4−H, C5−H, and C6−H), 3.79 (s, 2H, $C1(H)_2$), 3.30 (s, 6H, $NMe_2$), 2.89−2.82 (m, 2H, $P(C\mathit{H}Me_aMe_b)_2$), 1.51 (d of d, $^3J_{PH} = 19.4$ Hz, $^2J_{HH} = 7.0$ Hz, 6H, $P(CH\mathit{Me_a}Me_b)_2$), 1.32 (d of d, $^3J_{PH} = 18.1$ Hz, $^2J_{HH} = 7.0$ Hz, 6H, $P(CHMe_a\mathit{Me_b})_2$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$, 125.8 MHz): $\delta$ 175.7 (d, $J = 16.5$ Hz, C2), 144.2 (d, $J = 6.4$ Hz, C3a or C7a), 136.2 (C7a or C3a), 130.0 (d, $^1J_{PC} = 34.0$ Hz, C3), 127.9, 127.7, 122.2 (C4, C5, and C6), 125.8 (C7), 54.8 ($NMe_2$), 30.9 (d, $J = 10.8$ Hz, C1), 26.1 (d, $^1J_{PC} = 29.6$ Hz, $P(\mathit{C}H(Me_aMe_b)_2)$, 19.9 ($P(CH\mathit{Me_a}Me_b)_2$ or $P(CHMe_a\mathit{Me_b})_2$), 19.8 (d, $^2J_{PC} = 3.7$ Hz, $P(CHMe_a\mathit{Me_b})_2$ or $P(CH\mathit{Me_a}Me_b)_2$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 202.3 MHz): $\delta$ 62.7 (d, $^1J_{RhP} = 123.5$ Hz, $P(CHMe_2)_2$), −144.5 (septet, $^1J_{PF} = 710.7$ Hz, $PF_6^-$). FTIR ($CH_2Cl_2$/CsI; $cm^{-1}$) $\nu$(CO): 2100, 2030, 1990.

**Synthesis of $(PPh_2Me)_2Rh(\kappa^2$-*P*,*N*-3c) (9).** A dark red solution of **5c** (0.096 g, 0.20 mmol) in toluene (5 mL) was cooled to −35 °C, after which $PPh_2Me$ (0.19 mL, 0.99 mmol) was added via Eppendorf pipet. The solution immediately darkened to brown-red. The vial was sealed with a PTFE-lined cap, and the mixture was left to magnetically stir for 36 h. $^{31}P$ NMR analysis of the reaction at this stage confirmed the quantitative conversion of **5c** to **9**. The solvent was removed in vacuo and the dark brown solid was washed with pentane (3 × 2 mL). The resulting solid was dried in vacuo for 16 h to leave **9** as an analytically pure, light brown powder (0.11 g, 0.14 mmol, 66%). Anal. Calcd for $C_{43}H_{51}P_3N_1Rh_1$ (777.7 $gmol^{-1}$): C 66.41; H 6.61; N 1.80. Found: C 66.21; H 6.49; N 1.60. NB: Signals in the $^1H$ NMR spectrum of **9** are broadened at 300 K, in keeping with the observed dynamic behavior of this complex (see text). Some $^{13}C$ NMR resonances are also broadened, and we were unable to observe the $NMe_2$ resonances in the $^{13}C\{^1H\}$ NMR spectrum of this complex. Data reported here were obtained at 300 K, unless otherwise indicated. $^1H$ NMR ($C_6D_6$, 500.1 MHz): $\delta$ 7.84 (d, $^3J_{HH} = 7.6$ Hz, 1H, C4-H), 7.73 (m, 1H, C5-H or C6-H), 7.59 (m, 1H, C6-H or C5-H), 7.51 (d, $^3J_{HH} = 7.5$ Hz, C7−H), 7.39−7.26 (m, 5H, Ar−Hs), 7.16−6.92 (m, some resonances obscured by reference solvent, Ar−Hs), 6.18 (s, 1H, C1-H), 3.50−2.10 (very broad resonance at 300 K; upon cooling to 240 K, this resolved into two singlets at 3.34 ppm (3H, $NMe_a$) and 2.52 ppm (3H, $NMe_b$)), 3.00 (m, 1H, $P\mathit{c}(C\mathit{H}Me_2)(CHMe_2)$), 2.79 (m, 1H, $P\mathit{c}(CHMe_2)(C\mathit{H}Me_2)$), 1.58 (d, $^2J_{PH} = 6.2$ Hz, 3H, $P\mathit{a}(C_6H_5)_2\mathit{Me}$), 1.29−1.12 (m, 6H, $P\mathit{c}(CH\mathit{Me_a}Me_b)_2$), 1.10 (d, $^2J_{PH} = 6.8$ Hz, 3H, $P\mathit{b}(C_6H_5)_2\mathit{Me}$), 0.95−0.83 (m, 6H, $P\mathit{c}(CHMe_a\mathit{Me_b})_2$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 125.8 MHz): $\delta$ 167.3 (C2), 147.6 (C3a or C7a), 144.1, 143.4 ($P\mathit{a}(\mathit{C}(CH)_5)_2Me$), 142.3 (C7a or C3a), 140.4, 139.4 ($P\mathit{b}(\mathit{C}(CH)_5)_2Me$), 133.8, 133.6, 132.9, 132.7, 132.1, 131.9, 131.8 ($P(C(\mathit{CH})_5)_2Me$), 123.7 (C4), 121.5 (C5 or C6), 118.2, 118.1 (C7 and C6 or C7 and C5), 103.2 (C1), 37.3 (d, $^1J_{PC} = 112.3$ Hz, C3), 27.7 (br s, $P\mathit{c}(\mathit{C}HMe_2)(CHMe_2)$), 26.9 (br s, $P\mathit{c}(CHMe_2)(\mathit{C}HMe_2)$), 22.3 ($P\mathit{c}(CH\mathit{Me_a}Me_b)_2$), 21.5 (d, $^1J_{PC} = 20.9$ Hz, $P\mathit{a}(C_6H_5)_2\mathit{Me}$), 20.1, 20.0 ($P\mathit{c}(CHMe_a\mathit{Me_b})_2$), 14.5 (d, $^1J_{PC} = 23.1$ Hz, $P\mathit{b}(C_6H_5)_2\mathit{Me}$). $^{31}P\{^1H\}$ NMR ($C_6D_6$, 202.5 MHz): $\delta$ 35.8 (d of d of d, $^1J_{PaRh} = 113.8$ Hz, $^2J_{PaPb} = 31.6$ Hz, $^2J_{PaPc} = 237.4$ Hz, $P\mathit{a}(C_6H_5)_2Me$, *cis* to N), 24.2 (d of d of d, $^1J_{PbRh} = 189.8$ Hz, $^2J_{PbPa} = 31.1$ Hz, $^2J_{PbPc} = 26.6$ Hz, $P\mathit{b}(C_6H_5)_2Me$, *trans* to N), 15.6 (d of d of d, $^1J_{PcRh} = 177.0$ Hz, $^2J_{PcPb} = 26.0$ Hz, $^2J_{PcPa} = 237.2$ Hz, $P\mathit{c}(CHMe_2)_2$).

**General Protocol for Hydrogenation Experiments.** The protocol used for hydrogenation reactions employing 0.5 mol % catalyst loading in $CH_2Cl_2$ is provided as a representative procedure. A solution of catalyst compound in $CH_2Cl_2$ (0.014 mmol in 7 mL to give a 0.002 M solution) was allowed to equilibrate for 5 min, at which point the alkene (2.8 mmol) was added by use of an Eppendorf pipet. The vial was then sealed and shaken vigorously. Subsequently, 1 mL aliquots of the mixture were placed in glass reactor cells, which were each equipped with a magnetic stir bar and sealed under nitrogen with a PTFE valve. The cells were transferred immediately to a Schlenk line and degassed by use of three freeze−pump−thaw cycles employing liquid nitrogen. Magnetic stirring of the solutions was initiated, and the evacuated cells were backfilled with hydrogen gas (~1atm, UHP grade). With the exception of the noted experiments in which the catalyst was not fully soluble, clear yellow homogeneous solutions were observed throughout. At the desired sampling time, the reactor cell was opened to air and 2 mL of hexanes (or pentane in the case of the hydrogenation of cyclohexene) was added via Pasteur pipet. The resultant slurries were then filtered through a short $Al_2O_3$ column (2 cm), from which clear, colorless solutions eluted. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC-MS, and quantitative data were obtained from GC-FID analysis; tabulated data represent the average of at least two runs.

**General Protocol for Hydrosilylation Experiments.** The protocol used for these reactions employing 5.0 mol % catalyst loading (relative to $Et_3SiH$) in benzene with a styrene to silane ratio of 5:1 run at 60 °C is provided as a representative procedure. A solution of catalyst compound in benzene (0.0225 mmol in 4.5 mL to give a 0.005 M solution) was allowed to equilibrate for 5 min, at which point the alkene (2.25 mmol) was added by use of an Eppendorf pipet. The vial was then sealed and shaken vigorously. Subsequently, $Et_3SiH$ (0.45 mmol) was added by use of an Eppendorf pipet to the reaction mixture, and the vial was then sealed and shaken as before. Aliquots (1 mL) of the mixture were placed in glass reactor cells, which were each equipped with a magnetic stir bar and sealed under nitrogen with a PTFE valve. The cells were transferred immediately to a Schlenk line, and magnetic stirring of the solutions was initiated. At the desired sampling time, the reactor cell was opened to air and ~1 mL of pentane was added via Pasteur pipet. The resultant mixtures were then filtered through a short $Al_2O_3$ column (2 cm), from which clear, colorless solutions eluted. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC-MS, while quantitative data were obtained from GC-FID analysis; tabulated data represent the average of at least two runs.

**Crystallographic Solution and Refinement Details.** With the exception of **7**, crystallographic data were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation, employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, data reduction, and absorption correction (including SAINT and SADABS) were supplied by Bruker. The structures were solved by use of direct methods (except for **4a**·$CH_2Cl_2$ and **5c**, where in each case a Patterson search/structure expansion was employed) 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-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. Structural disorder was noted during the refinement of [**6b**]$^+PF_6^-$, which was treated in a satisfactory manner by employing a model featuring two half-occupied formula units of the complex within the asymmetric unit. Data and experimental details related to the crystallographic characterization of **7** (including an ORTEP diagram) are provided in the Supporting Information.

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**Supporting Information Available:** Single-crystal X-ray diffraction data in CIF format for **4a**·$CH_2Cl_2$, [**5b**]$^+BF_4^-$, **5c**, [**6b**]$^+SO_3CF_3^-$, [**6b**]$^+PF_6^-$, **6c**, and **7**, as well as crystallographic details and an ORTEP diagram of **7**, are available free of charge via the Internet at http://pubs.acs.org.

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