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Synthesis, Electrochemistry, and Reactivity of Half-Sandwich Ruthenium Complexes Bearing Metallocene-Based Bisphosphines

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The bimetallic complexes CpRu(P−P)X [Cp = η^5-C_5H_5; X = Cl, H; P−P = dppf (1,1′-bis(diphenylphosphino)ferrocene), dppr (1,1′-bis(diphenylphosphino)ruthenocene), dppo (1,1′-bis(diphenylphosphino)-osmocene), dippf (1,1′-bis(diisopropylphosphino)ferrocene), dcpf (1,1′-bis(dicyclohexylphosphino)ferrocene)], Cp*Ru(P−P)X [Cp* = η^5-C_5Me_5; X = Cl, H; P−P = dppf, dippf, dppomf (1,1′-bis(diphenylphosphino) octamethylferrocene), dppc (1,1′-bis(diphenylphosphino)cobaltocene)], $[Cp^*Ru(P-P)X]^+$ (X = H, CCPh; P−P = $dppc^+$), and $[Cp^*Ru(P-P)L]^{2+}$ (L = CH_3CN, *t*-BuCN; P−P = $dppc^+$) have been synthesized. Most of the chloride and hydride complexes have been studied by cyclic voltammetry. The X-ray structures of $[Cp^*Ru(dppc)CH_3CN][PF_6]_2$ and $[Cp^*Ru(dppc)CCPh][PF_6]$ have been determined. Protonation of $[Cp^*Ru(dppc)CCPh]^+$ gives the vinylidene complex $[Cp^*Ru(dppc)CCHPh]^{2+}$. The Co(III/II) potential of the $dppc^+$ ligand undergoes a cathodic shift upon coordination in $[Cp^*Ru\text{-}(dppc)H]^+$ and an anodic shift upon coordination in $[Cp^*Ru(dppc)CH_3CN]^{2+}$. The ^{1}H NMR spectrum of Cp*Ru(dppc)H is consistent with its formulation as a Co(II)/Ru(II) complex. As gauged by their reactivity toward iminium cations, the hydride complexes are poor hydride donors; proton and electron transfer are dominant. CpRu(dippf)H and CpRu(dcpf)H deprotonate iminium cations with acidic α-hydrogens. Cp*Ru(dppc)H is oxidized by the *N*-(benzylidene)pyrrolidinium cation, giving $[Cp^*Ru\text{-}(dppc)H]^+$ and the vicinal diamine 1,2-bis(*N*-pyrrolidino)-1,2-diphenylethane. Most of the hydride complexes give *trans*-dihydride cations upon protonation; an exception is $[Cp^*Ru(dppc)H]^+$, which forms a dihydrogen complex $[Cp^*Ru(dppc)(H_2)]^{2+}$ with surprising kinetic stability. This dihydrogen complex is more acidic and less thermodynamically stable than its dihydride isomer. The H_2 ligand in $[Cp^*Ru(dppc)\text{-}(H_2)]^{2+}$ is readily replaced by nitriles; the reaction with *t*-BuCN occurs by a dissociative mechanism.

Introduction

Since 1,1′-bis(diphenylphosphino)ferrocene (dppf) was reported in 1971,[1] this metallocene-based bisphosphine has attracted much attention. The dppf ligand is valued for the unique steric and electronic properties it bestows upon its complexes, particularly those of Pd.[2] In many cases, the use of dppf improves the yields of Pd-catalyzed Suzuki, Heck, and Buchwald−Hartwig coupling reactions.[2−4] The use of dppf analogues appears to have a promising future.[5] It has recently been reported that dtbpf (1,1′-bis(di-*tert*-butylphosphino)ferrocene) is superior to dppf for the Pd-catalyzed α-arylation of ketones and for certain Pd-catalyzed Suzuki couplings.[6,7] Similarly, the ligands Fe(η^5-C_5H_4P(*o*-(*i*-Pr)-$C_6H_4)_2)_2$ and Fe(η^5-C_5H_4P(*o*-$MeOC_6H_4)_2)_2$ give higher catalytic activities than dppf in some Pd-catalyzed Suzuki and Buchwald−Hartwig reactions.[8] The chemistry of Ru- and Os-based dppf analogues is just beginning to be explored. The X-ray structures of $Pd(dppr)Cl_2$ and $Pd(dppo)Cl_2$ have recently been reported,[9,10] as has their activity in several Suzuki and Buchwald−Hartwig reactions.[8]

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The 1,1′-bis(diphenylphosphino)cobaltocenium cation ($dppc^+$), isoelectronic with dppf, was first reported in 1978.[11] The neutral paramagnetic compound (dppc) was later isolated and characterized by X-ray crystallography.[12] The dppc ligand is nearly identical in size and shape to dppf[13] but is much more easily oxidized.[9,12,14] For this reason the "redox switch" properties of $dppc^+$/dppc have been investigated: Wrighton and co-workers reported that $[Re\text{-}(CO)_4dppc]^{2+}$ reacts with azide 5400 times faster than the reduced form, $[Re(CO)_4dppc]^+$.[14] Soon after, they reported that $[Rh(dppc)(acetone)_n]^{2+}$ is an active hydrosilylation catalyst, while $[Rh(dppc)(acetone)_n]^+$ is an active hydrogenation catalyst.[15] Given such interesting activity, it is surprising that so few $dppc^+$/dppc complexes have been reported.

Combining our interests in half-sandwich ruthenium complexes (J.R.N.) and metallocene-based ligands (C.N.), we report here the synthesis, properties, and electrochemistry of (Cp/Cp*)Ru complexes bearing several metallocene-based bisphosphines.[16] In view of the interest in one of our laboratories (J.R.N.) in hydride transfer reactions,[17−19] we have tested the ability of the hydride complexes to transfer H^- to iminium cations but have found that they are ineffective in that role. However, electrochemical studies of the hydride and chloride complexes have allowed us to compare the electronic influence of the various bisphosphine ligands.

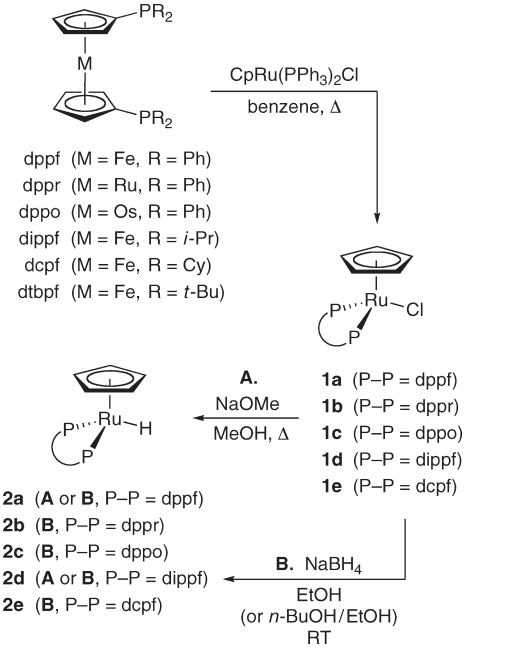
As few $dppc^+$ or dppc complexes have been reported, we have made them with nitrile, phenylacetylide, phenylacetylene, hydride, and dihydrogen ligands. (The only previously reported half-sandwich Ru complex containing $dppc^+$ or dppc is $[Cp^*Ru(dppc)Cl][PF_6]$.[20]) We have examined the redox chemistry of the acetonitrile and hydride complexes. We also report the X-ray structures of the acetonitrile and phenylacetylide complexes.

Results and Discussion

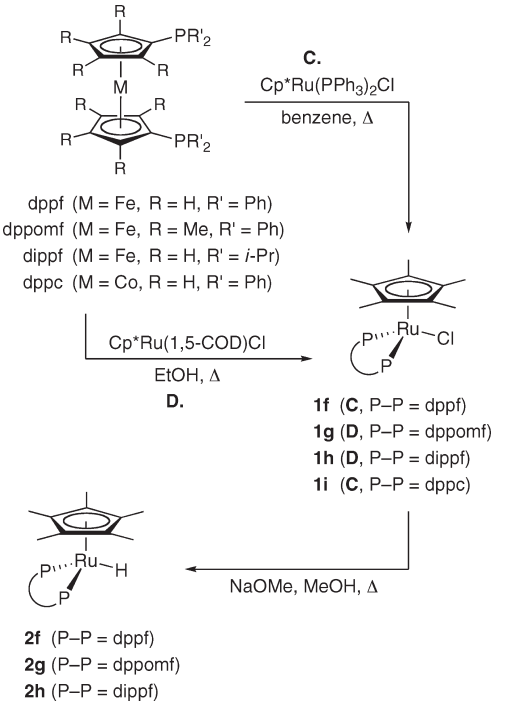
Synthesis of the Complexes. Like many complexes of the type CpRu(P−P)Cl, the Ru chlorides **1a**−**1e** can be prepared by treating $CpRu(PPh_3)_2Cl$ with the corresponding bisphosphine in refluxing benzene (Scheme 1). This method worked well even with the bulky dippf and dcpf ligands, but it failed with the exceptionally hindered dtbpf ligand; in the latter case the retention of PPh_3 was thermodynamically favored.

In general, Ru hydrides can be synthesized by treating the chlorides with NaOMe in refluxing MeOH. After preparing

Scheme 1. Synthesis of CpRu Chlorides and Hydrides



Scheme 2. Synthesis of Cp*Ru Chlorides and Hydrides



2a[21] and **2d** in this way (method **A**), we found that these hydrides are also available in good yield by stirring the respective chlorides with excess $NaBH_4$ in alcohol at room temperature (method **B**). We subsequently prepared **2b**, **2c**, and **2e** by method **B**.

Hembre reported the synthesis of Cp*Ru(dppf)Cl/H (**1f**/**2f**) by treating dppf with refluxing $Cp^*Ru(PPh_3)_2Cl$/benzene followed by refluxing NaOMe/MeOH.[22] The first part of this sequence (method **C**, Scheme 2) worked for **1i** but not for **1g** or **1h**; the latter two complexes were prepared from

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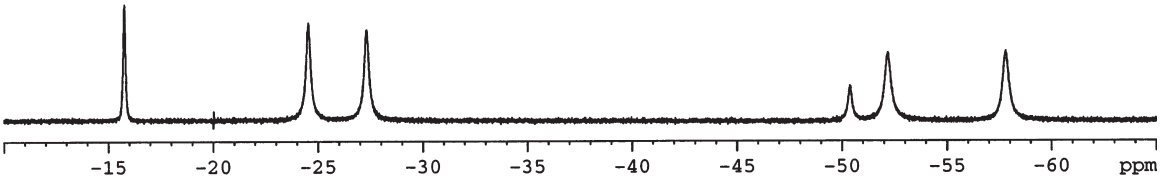
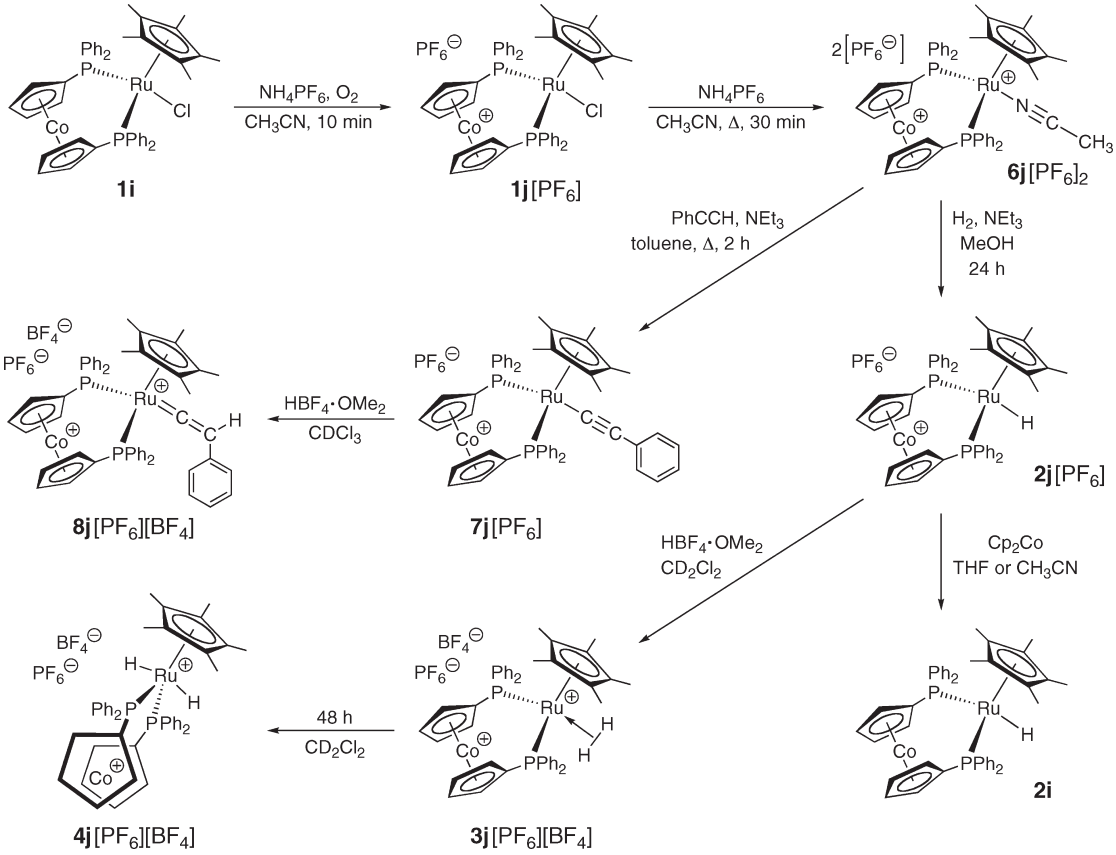


Figure 1. Upfield ^{1}H NMR spectrum of **2i** (400 MHz, toluene-d_8). The small peak at δ −50.4 is due to some residual Cp_2Co.

Scheme 3. Synthesis of the dppc and dppc$^+$ Complexes



Cp*Ru(1,5-COD)Cl (method **D**) since 1,5-cyclooctadiene is easily displaced from Ru(II).[23,24] The Cp*Ru hydrides (except for **2i**, see below) were prepared by the usual treatment of the chlorides with refluxing NaOMe/MeOH.

The dppc and dppc$^+$ complexes synthesized in this work are shown in Scheme 3. The Co(II) in **1i** is readily oxidized to Co(III) in the presence of an acid and atmospheric oxygen. A convenient acid is NH_4PF_6. It is convenient to manipulate these complexes with the ligand in the oxidized state since they are then generally air-stable and amenable to flash chromatography. Heating a CH_3CN solution of **1j**[PF_6][20] with excess NH_4PF_6 gave the characteristically crimson **6j**-[PF_6]$_2$, which, after purification by flash chromatography, was used as a precursor to the other complexes.

After failing to prepare pure samples of **2i** or **2j**[PF_6] in reasonable yield from **1i**, **1j**[PF_6], or **6j**[PF_6]$_2$ by the usual treatment with refluxing NaOMe/MeOH, we found the reaction of **6j**[PF_6]$_2$ with H_2 and NEt_3 in MeOH to be a viable route to **2j**[PF_6]. As with the other hydride complexes in this work, the ^{1}H NMR hydride resonance of **2j**$^+$ is a triplet due to coupling with the two ^{31}P nuclei of the bisphosphine ligand (δ −12.28, J_{P-H} = 34.7 Hz). The reduction of **2j**$^+$ with Cp_2Co gave the paramagnetic hydride complex **2i**; a portion of its ^{1}H NMR spectrum is shown in Figure 1. As expected for a Co(II) complex, the resonances with the greatest isotropic shifts are those of nuclei closest to the Co(II) atom: the cyclopentadienyl hydrogens of the dppc ligand are found at δ −57.8, −52.2, −27.3, and −24.5. The hydride resonance appears at δ −15.76 as a broad (about 50 Hz at half-height) *singlet*. It is noteworthy that no ^{31}P−^{1}H coupling is visible (recall the large ∼35 Hz splitting for the hydride triplet of **2j**$^+$). Such apparent decoupling, known as T_1 spin decoupling, was quantitatively described nearly 35 years ago,[25] but relatively few unambiguous examples have since appeared in the literature. The hydride resonance of **2j**$^+$/**2i** can be described as the A subsystem of an AX_2 system, where X_2 are in close proximity to a metal. When the metal (in this case Co) is paramagnetic, X_2 (the two ^{31}P) relax quickly; this causes additional broadening in the resonance of A (the hydride ligand) as well as a decrease in the apparent X_2−A (^{31}P−^{1}H) coupling constant. The two effects result in a singlet for the hydride resonance of **2i**, although a Ni(II)

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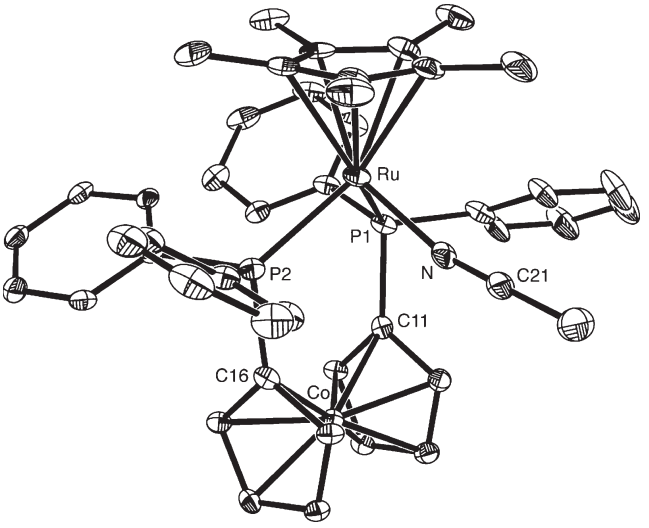

Figure 2. Molecular structure of **6j**$[PF_6]_2 \cdot Et_2O \cdot CH_3CN$ (20% probability level). Counterions, hydrogen atoms, and disordered solvent molecules are omitted for clarity. Selected distances (Å) and angles (deg): Ru−N 2.063(5), Ru−P1 2.3314(13), Ru−P2 2.3198(14), N−C21 1.112(6), Ru−N−C21 166.3(4), P1−Ru−P2 96.87(4), P1−Ru−N 91.15(12), P2−Ru−N 90.42 (12), Ru−P1−C11 120.51(15), Ru−P2−C16 119.92(16).

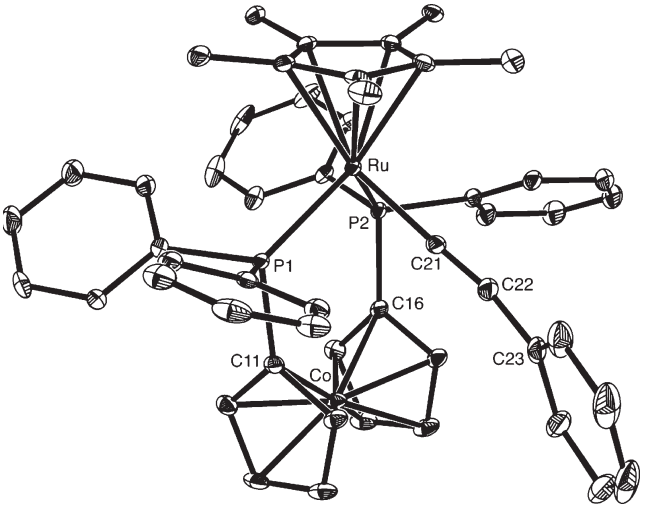

Figure 3. Molecular structure of **7j**$[PF_6] \cdot Et_2O$ (20% probability level). Counterion, hydrogen atoms, and solvent molecule are omitted for clarity. Selected distances (Å) and angles (deg): Ru−C21 2.012(4), Ru−P1 2.2801(9), Ru−P2 2.2737(10), C21−C22 1.212(5), C22−C23 1.434(5), Ru−C21−C22 175.3(3), C21−C22−C23 166.4(4), P1−Ru−P2 98.23(3), P1−Ru−C21 86.34(10), P2−Ru−C21 87.98(11), Ru−P1−C11 121.83(11), Ru−P2−C16 121.70(12).

complex has recently been reported where a reduced X−A coupling constant (in that case $^{19}F-^{13}C$) was observable.[26]

To further study the reactivity of $\mathbf{6j^{2+}}$, we attempted to prepare a vinylidene complex by refluxing a $CHCl_3$ solution of **6j**$[PF_6]_2$ and phenylacetylene. Instead, the green alkynyl complex **7j**$[PF_6]$ was obtained in poor yield. An acceptable yield of **7j**$[PF_6]$ was achieved by heating a slurry of **6j**$[PF_6]_2$ with phenylacetylene and NEt_3 in toluene. Treating **7j**$[PF_6]$ with $HBF_4 \cdot OMe_2$ in $CDCl_3$ gave a yellow solution of the vinylidene $\mathbf{8j^{2+}}$.[27] The Ru-bound ^{13}C resonance is a weak downfield triplet (δ 357.58, $J_{P-C} = 15.7$ Hz) and confirms the vinylidene structure.[28]

X-ray Structures. The structures of **6j**$[PF_6]_2$ and **7j**$[PF_6]$ were determined by single-crystal X-ray diffraction (Figures 2, 3, Table 1). The only $dppc^+$ complex of Ru with a previously published X-ray structure is **1j**$[PF_6]$.[20] Gan and Hor identified several structural parameters specific to dppf and its analogues,[29] some of which are listed for **1j**$[PF_6]$, **6j**$[PF_6]_2$, and **7j**$[PF_6]$ in Table 2. The coordination of the $dppc^+$ ligand is similar in all three cases. In each structure, the Cp rings are nearly eclipsed, as indicated by the low τ values. The P atoms are slightly displaced out of the corresponding Cp planes, away from the Co. The Cp rings are not coplanar, as indicated by the nonzero θ and the small deviations of $Cp_{cent}-Co-Cp_{cent}$ from linearity. The ligand bite angles (P1−Ru−P2) range from 96.7° to 98.2°. These structures are similar to those of related Ru(II) dppf complexes. The dppf bite angles of several (η^5-C_5R_5)Ru(dppf)X

Table 1. Summary of Crystallographic Data

	6j$[PF_6]_2 \cdot Et_2O \cdot CH_3CN$	**7j**$[PF_6] \cdot Et_2O$
empirical formula	$C_{52}H_{59}CoF_{12}N_2OP_4Ru$	$C_{56}H_{58}CoF_6OP_3Ru$
fw	1239.89	1113.93
cryst color/shape	orange/plate	green/plate
cryst size (mm)	0.53 × 0.12 × 0.01	0.43 × 0.31 × 0.01
temp (K)	125(2)	125(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	19.3450(18)	15.8294(19)
b (Å)	13.5915(12)	15.4514(18)
c (Å)	22.247(2)	20.606(2)
α (deg)	90	90
β (deg)	114.8370(10)	92.002(2)
γ (deg)	90	90
V (Å^3)	5308.4(8)	5036.8(10)
Z	4	4
d_{calc} (g/cm^3)	1.551	1.469
λ(Mo Kα) (Å)	0.71073	0.71073
μ (mm^{-1})	0.800	0.786
data collected	53 864	78 581
unique data	13 140	15 606
data/restraints/params	13 140/51/624	15 606/0/614
GOF on F^2	1.015	1.048
R1, wR2 [$I > 2\sigma(I)$]	0.0601, 0.0994	0.0494, 0.1016
R1, wR2 (all data)	0.1521, 0.1094	0.1218, 0.1331

Table 2. Structural Parameters of the $dppc^+$ Ligand

	1j$[PF_6]$[20]	**6j**$[PF_6]_2$	**7j**$[PF_6]$
Ru···Co (Å)	4.438	4.371	4.384
P1···P2 (Å)	3.458	3.480	3.443
δ_{P1} (Å)[a]	−0.083	−0.080	−0.030
δ_{P2} (Å)[a]	−0.081	−0.019	−0.101
τ (deg)[b]	3.63	1.19	2.53
θ (deg)[c]	2.66	4.03	2.37
$Cp_{cent}-Co-Cp_{cent}$ (deg)	177.76	176.76	178.00
P1−Co−P2 (deg)	58.96	59.76	58.87
P1−Ru−P2 (deg)	96.69(3)	96.87(4)	98.23(3)

[a] The distance between the P atom and the Cp plane, negative means away from Co. [b] The torsion angle defined by $C_A-Cp_{cent(A)}-Cp_{cent(B)}-C_B$ where C_A and C_B are the P-bound C atoms of the Cp rings. [c] The angle between the two Cp planes.

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Table 3. Potentials of the Chloride Complexes[a]

complex	E_1[b]	E_2
CpRu(dppf)Cl (**1a**)[c]	+0.06	+0.48[d]
CpRu(dppr)Cl (**1b**)[e]	+0.08	
CpRu(dppo)Cl (**1c**)[e]	+0.09	
CpRu(dippf)Cl (**1d**)[c]	−0.07	+0.46[d]
CpRu(dcpf)Cl (**1e**)[e]	−0.07	+0.45[d]
Cp*Ru(dppf)Cl (**1f**)[c]	−0.13	+0.44[d]
Cp*Ru(dppomf)Cl (**1g**)[c]	−0.35	+0.20[d]
Cp*Ru(dippf)Cl (**1h**)[c]	−0.34	+0.37[d]

[a] $E_{1/2}$ (V vs FcH^+/FcH) for reversible cyclic voltammograms in $[Bu_4N]PF_6/CH_2Cl_2$. [b] Ru(III/II). [c] 50 mV/s. [d] Fe(III/II). [e] 100 mV/s.

and $[(\eta^5\text{-}C_5R_5)Ru(dppf)L]^+$ are in the range 95−99°.[21,22,30] The Cp rings of the dppf ligands in these complexes are usually eclipsed; notable exceptions are CpRu(dppf)H (**2a**) and Cp*Ru(dppf)H (**2f**).[21,22]

Electrochemistry. The anodic electrochemistry of free dppf,[9,12,31] dppomf,[31] dippf,[32] dppr,[9,31] dppo,[10,31] and dppc[12,14] has been reported. There are many reports of the electrochemical oxidation of complexes containing these and other metallocene-based bisphosphines.[9,10,12,14,31−35] The oxidation of (Cp/Cp*)Ru complexes containing such ligands has not been studied extensively; the few chloride and hydride complexes that have been examined include CpRu(dppf)Cl (**1a**),[22,36] Cp*Ru(dppf)Cl (**1f**),[22] CpRu(dppf)H (**2a**),[19,22] Cp*Ru(dppf)H (**2f**),[19,22,35] and the carboxy- and ester-substituted complexes $(CpCO_2H)$Ru(dppf)Cl and $(CpCO_2t\text{-}Bu)$Ru(dppf)Cl.[36]

The Ru chlorides bearing ferrocenyl bisphosphines in Table 3 exhibit two reversible one-electron oxidations. For **1a** and **1f**, Hembre assigned the first oxidation (E_1) to Ru(III/II) and the second (E_2) to Fe(III/II).[22] The E_1 potential decreases by 0.19 V when the Cp ligand in **1a** is exchanged for a Cp* in **1f**, but E_2 decreases only by 0.04 V. The E_2 potentials of **1a**, **1d**−**f**, and **1h** are all within a 0.11 V range, but the E_2 of **1g**, containing the methyl-substituted dppomf ligand, is 0.17 V less than the lowest E_2 of the other complexes. These facts support the aforementioned assignments of E_1 and E_2.

The Ru and Os metallocenes are considerably more difficult to oxidize than their Fe analogues.[10] The dppr and dppo complexes **1b** and **1c** undergo only one oxidation within the potential window; presumably it is the Cp-bearing Ru(III/II). The identity of the metal in the bisphosphine ligand appears to have little influence over the E_1 potentials of **1a**−**1c**.[37] Instead, the E_1 of $(\eta^5\text{-}C_5R_5)Ru(P{-}P)Cl$ is most affected by substituents at the P atoms and the Ru-bound Cp ring.

Ru(III) radical cations result from the oxidation of the hydride complexes (Table 4). A hydride is generally a better donor ligand than chloride,[38,39] so the Ru(III/II) potentials of the hydrides are 0.4 to 0.6 V less positive than those of the corresponding chlorides. Methyl substitution on the Ru-bound Cp ring decreases the potentials substantially (compare **2a**/**2f** and **2d**/**2h**). Hembre initially assigned the first oxidation of Cp*Ru(dppf)H (**2f**) to Ru(III/II), and this was later confirmed by the EPR and spectroelectrochemical studies of Kaim.[22,35]

Table 4. Ru(III/II) Potentials of the Hydride Complexes[a]

complex	potential	parameter
CpRu(dppf)H (**2a**)	−0.35[b]	$E_{1/2}$
CpRu(dppr)H (**2b**)	−0.41[c]	E_{pa}
CpRu(dppo)H (**2c**)	−0.20[c]	E_{pa}
CpRu(dippf)H (**2d**)	−0.61[d]	$E_{1/2}$
CpRu(dcpf)H (**2e**)	−0.65[e]	$E_{1/2}$
Cp*Ru(dppf)H (**2f**)	−0.63[d]	$E_{1/2}$
Cp*Ru(dppomf)H (**2g**)	−0.72[d]	$E_{1/2}$
Cp*Ru(dippf)H (**2h**)	−0.90[d]	$E_{1/2}$
$[Cp^*Ru(dppc)H]^+$ ($\mathbf{2j}^+$)	−0.19[f]	E_{pa}

[a] Potentials (V vs FcH^+/FcH) for reversible cyclic voltammograms in $[Bu_4N]PF_6/CH_2Cl_2$ unless otherwise noted. [b] 50 mV/s, i_a/i_c = 1.17. [c] 100 mV/s, irreversible. [d] 50 mV/s. [e] 100 mV/s. [f] 100 mV/s, $[Bu_4N]PF_6/CH_3CN$, irreversible.

The potentials of the hydride complexes are more sensitive to the nature of the PR_2 groups than those of the chlorides. The dippf and dcpf chlorides **1d** and **1e** are oxidized at potentials only 0.13 V less positive than CpRu(dppf)Cl (**1a**). The analogous hydride complexes **2d** and **2e** are oxidized at potentials 0.26 and 0.30 V less positive than CpRu(dppf)H (**2a**). In contrast, alkyl substitution on the ferrocenyl rings affects the chlorides more than the hydrides. The difference between the Ru(III/II) potentials of the dppf and dppomf chlorides **1f** and **1g** is 0.22 V; the potentials of **2f** and **2g** differ by only 0.09 V.

The oxidations of 18-electron transition metal hydrides are often irreversible because the resulting radical cations are about 20 pK_a units more acidic than the parent hydrides.[40−43] Deprotonation of $MH^{\bullet+}$ is a common (but not the only) follow-up reaction.[44] Ferrocenyl bisphosphines stabilize the Ru(III) hydride radical cations, making most of the oxidations in Table 4 reversible. For example, the oxidation of CpRu(dppe)H (dppe = 1,2-bis(diphenylphosphino)ethane) in $[Bu_4N]PF_6/CH_2Cl_2$ is irreversible,[19] while that of CpRu(dppf)H (**2a**) under the same conditions is chemically reversible. The dppr and dppo ligands apparently do not have the same stabilizing effect and the oxidations of **2b** and **2c** are irreversible.

Steric bulk in the vicinity of the hydride ligand slows the rate of follow-up reactions involving that ligand. Examples include (Cp/Cp*)Ru(dppe)H and (Cp/Cp*)Ru(dppf)H (**2a**/**2f**): in both cases the Cp* complex displays the more reversible oxidation.[19] The complexes in Table 4 exhibit

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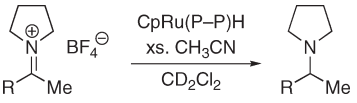
(44) $CpRu(P{-}P)H^{\bullet+}$ are known to disproportionate: Smith, K.-T.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681–8689.

Table 5. Co(III/II) Potentials

complex	electrolyte	potential[a]
Cp_2Co	$[Et_4N]BF_4/CH_3CN$	−1.33[b]
$[Cp^*Ru(dppc)H]^+$ (**2j**$^+$)	$[Bu_4N]PF_6/CH_3CN$	−1.27[c]
dppc	$[Et_4N]BF_4/CH_3CN$	−1.11[b]
$[Cp^*Ru(dppc)CH_3CN]^{2+}$ (**6j**$^{2+}$)	$[Bu_4N]PF_6/CH_3CN$	−1.05[d]
$Mo(CO)_4(dppc)$	$[Bu_4N]BF_4$/THF	−0.98[b]
fac-$[Re(CO)_3(dppc)Br]^+$	$[Bu_4N]PF_6/CH_3CN$	−0.91[e]
$[Re(CO)_4(dppc)]^{2+}$	$[Bu_4N]PF_6/CH_3CN$	−0.71[e]

[a] $E_{1/2}$ (V vs FcH^+/FcH) for reversible cyclic voltammograms unless otherwise noted. [b] Ref 12, 50 mV/s. [c] 200 mV/s. [d] 200 mV/s, i_a/i_c = 0.85. [e] Ref 14.

Table 6. Stoichiometric Hydride Transfer Reactions[a]



complex	iminium	reaction (%)[b]
CpRu(dppf)H (**2a**)	R = Ph (**10**)	18
CpRu(dppr)H (**2b**)	R = Ph (**10**)	10
CpRu(dppo)H (**2c**)	R = Ph (**10**)	9
CpRu(dppf)H (**2a**)	R = Me (**9**)	6
CpRu(dppr)H (**2b**)	R = Me (**9**)	< 3
CpRu(dppo)H (**2c**)	R = Me (**9**)	< 3

[a] General reaction conditions: 0.01 mmol of hydride complex, 0.01 mmol of iminium salt, 1 μL of CH_3CN, and 1 mL of CD_2Cl_2. [b] Percent loss of hydride complex after 3 h, determined by ^1H NMR.

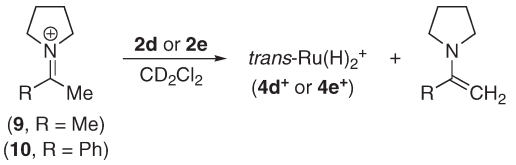
additional anodic waves, typically several hundred mV positive of the initial oxidations. However, these waves are irreversible and we cannot reliably assign them.

Wrighton and DuBois found that coordination of dppc to Re- or Mo-carbonyl fragments causes an anodic shift of 100 to 400 mV in the Co(III/II) potential.[12,14] A similar shift occurs with dppf: the Fe(III/II) potentials of group 6 dppf carbonyls are more positive than that of free dppf.[34] Such anodic shifts are expected upon coordination of dppc or dppf to an electron-poor transition metal, as electron density is removed from the ligand. We studied the reduction of **2j**$^+$ and **6j**$^{2+}$ (Table 5) in CH_3CN, the same solvent used by DuBois and Wrighton for most of their studies. The Co(III/II) potential of the dppc$^+$ ligand undergoes a surprisingly large *cathodic* shift upon coordination in **2j**$^+$. Even in **6j**$^{2+}$, where Ru is cationic, the Co(III/II) potential is only 60 mV more positive than that of free dppc. Clearly, the Cp*Ru(CH$_3$CN)$^+$ and Cp*RuH fragments are quite electron-rich.

Reactivity of the Hydrides with Iminium Cations. We have previously shown that some CpRu(P−P)H can catalyze the ionic hydrogenation of iminium cations.[17] The rate-determining step of such hydrogenations is H^- transfer from the Ru hydride to the iminium cation. The Ru hydrides in this work are generally poor hydride donors (Table 6) and therefore would not be suitable catalysts. The dppf complex **2a** was the most effective hydride donor, although only 18% of this hydride reacted with **10** over the course of 3 h.

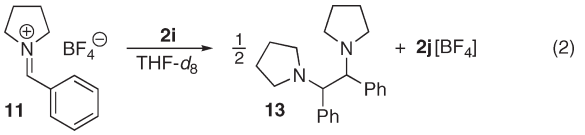
Electron-rich Ru hydride complexes are not necessarily good hydride donors. Guan found an *inverse* correlation between the ease of oxidation of CpRu(P−P)H (P−P = dppm, dppe, dppp) and the rate at which these complexes transfer hydride to **10**.[45,46] However, in that study the rates were greatly affected by the bisphosphine bite angle (with smaller bite angles resulting in faster rates). The accessibility of the hydride ligand is of primary importance. Guan noted that CpRu(dppb)H (P1−Ru−P2 = 94°)[47,46] does not react with **10**, so it is noteworthy that **2a**, with a substantially larger bite angle (P1−Ru−P2 = 99°),[21] does (Table 6). The dppr and dppo ligands in **2b** and **2c** are expected to have even larger bite angles than the dppf in **2a**. In the series Pd(P−P)Cl$_2$ the bite angles of dppf, dppr, and dppo are 97.98(4)°, 100.02(17)°, and 100.82(9)° respectively.[9,10,48] The low reactivities of **2b** and **2c** in Table 6 are likely the result of steric hindrance. Another example demonstrating the importance of steric factors is the reactivity of (Cp/Cp*)Ru(dppf)H (**2a**/**2f**) with *N*-(benzylidene)pyrrolidinium cation (**11**); the Cp complex transfers its hydride, while the more electron-rich (but also more hindered) Cp* complex does not.[19]

Ru hydrides that are easily oxidized are also basic. For example, CpRu(dppe)H (E_{pa} = −0.16 V) transfers H^- to **10**, while Cp*Ru(dppe)H ($E_{1/2}$ = −0.51 V) deprotonates **10**.[17,19] Both CpRu(dippf)H (**2d**) and CpRu(dcpf)H (**2e**) deprotonate **9** and **10** (eq 1).



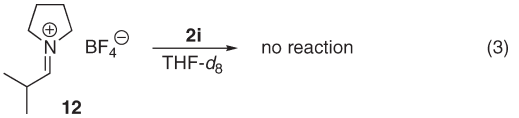
(1)

The *N*-(benzylidene)pyrrolidinium cation (**11**) does not have any acidic protons, so we tested its reactivity toward some of our hydride complexes. Like **2f**, the dppc$^+$ hydride **2j**$^+$ does not react with **11**. More electron-rich hydrides such as **2g** and **2h** are slowly oxidized by **11**, but there is no evidence of H^- transfer.[49] The Co(II) in **2i** is immediately oxidized by one electron in the presence of **11**, cleanly giving **2j**[BF$_4$] and the vicinal diamine **13** (eq 2). Cp_2Co is also oxidized by **11**, giving [Cp_2Co][BF$_4$] and **13** (see Experimental Section). It is known that vicinal diamines are available from the SmI_2-promoted reductive coupling of iminium cations.[50]



(2)

The isopropyl-substituted iminium cation **12** does not oxidize Cp_2Co, so we were confident that it would not oxidize the Co(II) in **2i** (see the potentials in Table 5). While this prediction was correct, **2i** did not transfer H^- to **12** and no reaction was observed (eq 3).



(3)

(45) dppm = 1,1-bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane.

(46) Guan, H.; Iimura, M.; Magee, M. P.; Norton, J. R.; Janak, K. E. *Organometallics* **2003**, *22*, 4084–4089.

(47) dppb = 1,4-bis(diphenylphosphino)butane.

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(49) As expected from their potentials, Cp*Ru(dippf)H reacts more quickly than Cp*Ru(dppomf)H. There is no evidence of hydride transfer. Instead, the dihydride cations (a decomposition product of the hydride radical cations) slowly appear over the course of several hours; see ref 44.

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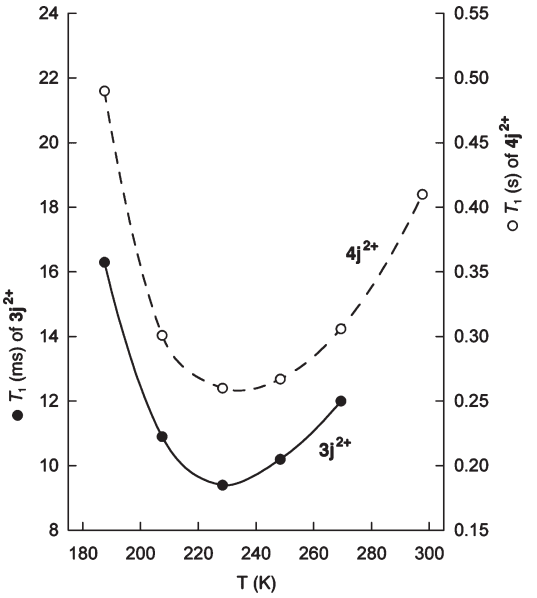
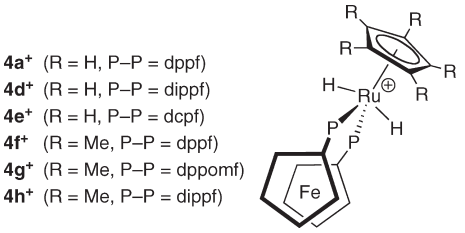


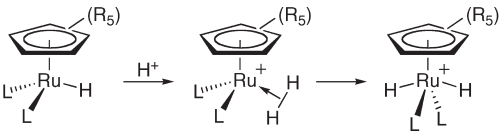
Figure 4. T_1 of the hydride resonances of $\mathbf{3j}^{2+}$ and $\mathbf{4j}^{2+}$ at various temperatures (300 MHz, CD_2Cl_2).

Scheme 4. Ru Dihydride Complexes with Fe-Based Ligands



Protonation of the Hydride Complexes. The protonation of a transition metal hydride generally gives a dihydrogen complex as the kinetic product.[51] In the case of (Cp/Cp*)$Ru(L_2)H$, the resulting cationic dihydrogen complexes usually isomerize, either partially or completely, to the *trans*-dihydride isomers (eq 4).[52−58] For example, the protonation of **2f** gives $Cp^*Ru(dppf)(H_2)^+$, which rapidly isomerizes to *trans*-$Cp^*Ru(dppf)(H)_2^+$ ($\mathbf{4f}^+$) above 0 °C.[19] Treating CD_2Cl_2 solutions of the hydrides with $HBF_4\cdot OMe_2$ (or acidic iminium cations in some cases, eq 1) at room temperature cleanly gives *trans*-dihydride cations (Scheme 4); presumably, these result from the rapid isomerization of intermediate dihydrogen complexes.

The ^{1}H NMR spectra of $\mathbf{4}^+$ establish the *trans* geometry of the two hydride ligands. The high symmetry of this arrangement results in only *two* resonances for the Cp hydrogens of the bisphosphine ligands (and only two resonances for the dppomf methyl groups of $\mathbf{4g}^+$). This argument has previously been made for $\mathbf{4f}^+$ and *trans*-$(CpCO_2H)Ru(dppf)(H)_2^+$.[36,59]



(4)

Surprisingly, the protonation of $[Cp^*Ru(dppc)H][PF_6]$ ($\mathbf{2j}[PF_6]$) gave a dihydrogen complex that was stable for many hours at room temperature (Scheme 3). The $[Cp^*Ru(dppc)(H_2)]^{2+}$ ($\mathbf{3j}^{2+}$) isomerized over the course of 48 h to the *trans*-dihydride $\mathbf{4j}^{2+}$. As with the other dihydride complexes, the ^{1}H NMR spectrum of $\mathbf{4j}^{2+}$ has only two resonances for the Cp hydrogens of the $dppc^+$ ligand. In the ^{1}H NMR spectrum of $\mathbf{3j}^{2+}$ these hydrogens give four resonances, a result of the lower symmetry of this H_2 complex. Generally, isomeric dihydrogen and dihydride complexes may be distinguished by comparing the T_1(min) of their ^{1}H NMR hydride resonances.[60,61] The T_1(min) for $Cp^*Ru(dppf)(H_2)^+$ is 11.5 ms (218.5 K, 300 MHz), while that for $\mathbf{4f}^+$ is much longer, 151 ms (195.2 K, 300 MHz).[19] A similar difference distinguishes $\mathbf{3j}^{2+}$ and $\mathbf{4j}^{2+}$: the T_1(min) for the dihydrogen complex is 9.4 ms, while that for the dihydride is 260 ms (Figure 4).

The H_2 in $\mathbf{3j}^{2+}$ is readily replaced by nitriles. The protonation of $\mathbf{2j}^+$ with $HBF_4\cdot OMe_2$ in CD_3CN cleanly gives the solvent complex $[Cp^*Ru(dppc)CD_3CN]^{2+}$ (and presumably H_2, eq 5). The reaction of $\mathbf{3j}^{2+}$ with excess *t*-BuCN in CD_2Cl_2 gives $[Cp^*Ru(dppc)t\text{-BuCN}]^{2+}$. The rate of this reaction does not depend on [*t*-BuCN] and is therefore dissociative; the half-life of $\mathbf{3j}^{2+}$ is about 6 min (eq 6). Even though it is quite labile, H_2 is not lost in the absence of a replacement ligand (recall the slow conversion of $\mathbf{3j}^{2+}$ to $\mathbf{4j}^{2+}$ in Scheme 3).

$$\mathbf{2j}^+ \xrightarrow[CD_3CN]{HBF_4\cdot OMe_2} [Cp^*Ru(dppc)CD_3CN]^{2+} + H_2 \qquad (5)$$

$$\mathbf{3j}^{2+} \xrightarrow[k=2.0(1)\times10^{-3}\ s^{-1}\ at\ 19.5\ °C]{xs.\ t\text{-BuCN},\ CD_2Cl_2} [Cp^*Ru(dppc)t\text{-BuCN}]^{2+} + H_2 \qquad (6)$$

The dihydride complex $\mathbf{4j}^{2+}$ is much less acidic than its dihydrogen isomer $\mathbf{3j}^{2+}$. In CD_2Cl_2, $\mathbf{4j}^{2+}$ is only partially deprotonated by excess NEt_3, while $\mathbf{3j}^{2+}$ is quantitatively deprotonated by 2,6-lutidine, indicating that the pK_a values of the two isomers differ by more than 7 units.[62] Because the deprotonations of isomeric $M(H_2)^+$ and $M(H)_2^+$ cations give the same monohydride complex, their pK_a values are related by the $[M(H)_2^+]/[M(H_2)^+]$ equilibrium constant (eqs 7, 8).[58] The large difference in acidity between $\mathbf{3j}^{2+}$ and $\mathbf{4j}^{2+}$ is in agreement with the fact that the equilibrium between the two lies heavily in favor of $\mathbf{4j}^{2+}$.

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(61) Morris, R. H. *Coord. Chem. Rev.* **2008**, *252*, 2381–2394.
(62) Our estimate for the pK_a of $\mathbf{4j}^{2+}$ is 21. In CH_3CN, the pK_a of Et_3NH^+ is 18.82, while that of 2,6-lutidinium is 14.13: Kaljurand, I.; Kütt, A.; Sooväli, L.; Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70*, 1019–1028.

$$M(H_2)^+ \overset{K_{eq}}{\rightleftharpoons} M(H)_2^+ \quad (7)$$

$$pK_{eq} = pK_a(M(H_2)^+) - pK_a(M(H)_2{}^+) \quad (8)$$

Conclusion

These complexes extend the series (Cp/Cp*)Ru(P−P)L$^+$ and (Cp/Cp*)Ru(P−P)X. As shown by the X-ray structures, the coordination of dppc$^+$ in **6j**$^{2+}$ and **7j**$^+$ is similar to that of dppf in related complexes. Of the complexes examined by CV, all but the dppc ones are initially oxidized at Ru. (This is in contrast to Pd(P−P)Cl$_2$ (P−P = dppf or variants), which undergo initial oxidation at the ligand.[31]) Ferrocenyl bisphosphines stabilize Ru(III) radical cations, and the Ru(III/II) potentials reflect the donor ability of the *neutral* bisphosphine ligands. Steric factors aside, the reactivity of the Ru hydrides toward iminium cations is correlated with the Ru(III/II) potentials. The easily oxidized Ru hydrides in this study are more likely to serve as bases or single-electron reductants than as hydride sources. Upon protonation at room temperature, most of the Ru hydrides give *trans*-dihydride cations, presumably via cationic dihydrogen complexes. The dihydrogen complex [Cp*Ru(dppc)(H$_2$)]$^{2+}$ (**3j**$^{2+}$) has considerably more kinetic stability than its ferrocenyl analogue. The H$_2$ ligand in **3j**$^{2+}$ is readily replaced by nitriles; the reaction with excess *t*-BuCN occurs by a dissociative mechanism. The difference in acidity between **3j**$^{2+}$ and its dihydride isomer **4j**$^{2+}$ reflects the fact that **4j**$^{2+}$ is more stable thermodynamically.

Experimental Section

General Procedures. All air-sensitive compounds were prepared and handled under an N$_2$/Ar atmosphere using standard Schlenk and inert-atmosphere box techniques. CDCl$_3$, CD$_2$Cl$_2$, and CD$_3$CN were degassed and stored over 3 Å molecular sieves. THF-d_8, toluene-d_8, and C$_6$D$_6$ were dried over sodium/benzophenone and purified by vacuum transfer. Hexanes, Et$_2$O, and CH$_2$Cl$_2$ were dried and deoxygenated by two successive columns (activated alumina, Q5 copper catalyst). Anhydrous CH$_3$CN (Sigma-Aldrich) was stored over 3 Å molecular sieves. Benzene and THF were distilled from sodium/benzophenone under an N$_2$ atmosphere. Sodium cyclopentadienide,[63] dppr,[64] dppo,[65] dcpf,[66] CpRu(PPh$_3$)$_2$Cl,[67] Cp*Ru(PPh$_3$)$_2$Cl,[68] CpRu(dppf)Cl (**1a**),[21] CpRu(dppf)H (**2a**),[21] Cp*Ru(dppf)Cl (**1f**),[22] Cp*Ru(dppf)H (**2f**),[22] *trans*-[Cp*Ru(dppf)(H$_2$)]$^+$ (**4f**$^+$),[19] and the iminium salts **9**−**12**[69] were prepared by literature methods.

Electrochemical Procedures. Cyclic voltammetry was performed with a PAR 263A potentiostat/galvanostat (**1b**, **2b**, **1c**, **2c**, **1e**, **2e**) or a BAS CV-50W potentiostat (all other compounds). Experiments on the PAR 263A used a glassy carbon working electrode, an Ag/AgCl reference, and a platinum wire auxiliary electrode. Experiments on the BAS CV-50W used a platinum working electrode, an Ag/Ag$^+$ reference (Ag wire, 0.01 M AgNO$_3$ + 0.10 M [Bu$_4$N]PF$_6$ in CH$_3$CN), and a platinum wire auxiliary electrode. The supporting electrolyte for the sample solutions was 0.10 M [Bu$_4$N]PF$_6$ in CH$_3$CN (**2j**[PF$_6$], **6j**[PF$_6$]$_2$) or CH$_2$Cl$_2$ (all other compounds). All samples were prepared under an N$_2$/Ar atmosphere and further purged with Ar before measurement. Analyte concentrations were 0.001 M. All potentials are reported in volts (V) vs FcH$^+$/FcH.

CpRu(dppf)H (2a). A solution of CpRu(dppf)Cl (**1a**, 0.056 g, 0.074 mmol) and NaBH$_4$ (0.025 g, 0.661 mmol) in 10 mL of EtOH was stirred at room temperature for 4 h. Additional NaBH$_4$ (0.010 g, 0.264 mmol) was added, and the solution was stirred for another 2 h. The yellow product was collected by filtration, washed with EtOH, and dried under vacuum (0.032 g, 0.044 mmol, 60% yield).

***trans*-[CpRu(dppf)(H)$_2$]$^+$ (4a$^+$)** was prepared in situ by the protonation of CpRu(dppf)H (**2a**) with HBF$_4$·OMe$_2$ in CD$_2$Cl$_2$ at room temperature. ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ −7.63 (t, Ru*(H)*$_2$, J_{P-H} = 23.0 Hz, 2H), 4.37 (s, br, dppf Cp, 4H), 4.43 (s, br, dppf Cp, 4H), 4.84 (s, RuCp, 5H), 7.56 (m, Ar, 12H), 7.74 (m, Ar, 8H). ^{31}P{^{1}H} NMR (161.9 MHz, CD$_2$Cl$_2$): δ 59.93. T_1 of the dihydride resonance (400 MHz, CD$_2$Cl$_2$, ambient temperature): 0.721 s.

CpRu(dppr)Cl (1b). A solution of CpRu(PPh$_3$)$_2$Cl (0.116 g, 0.159 mmol) and dppr (0.113 g, 0.189 mmol) in 25 mL of benzene was refluxed for 36 h. Evaporation of the solvent gave an orange powder that was washed with warm hexanes (5 mL × 3) and dried under vacuum (0.107 g, 0.134 mmol, 84% yield). ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.95 (s, RuCp, 5H), 4.43 (m, dppr Cp, 8H), 7.25−7.43 (m, Ar, 20H). ^{31}P{^{1}H} NMR (161.9 MHz, CDCl$_3$): δ 42.7. Anal. Calcd for C$_{39}$H$_{33}$ClP$_2$Ru$_2$: C, 58.46; H, 4.15. Found: C, 58.34; H, 4.35.

CpRu(dppr)H (2b). A solution of **1b** (0.160 g, 0.199 mmol) and NaBH$_4$ (0.076 g, 2.01 mmol) in 25 mL of EtOH was stirred at room temperature for 4 h. Additional NaBH$_4$ (0.040 g, 1.06 mmol) was added and the solution stirred for another 2 h. The yellow product was collected by filtration, washed with EtOH, and dried under vacuum (0.128 g, 0.166 mmol, 84% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ −11.96 (t, Ru*H*, J_{P-H} = 35.2 Hz, 1H), 3.98 (s, RuCp, 5H), 4.45−4.77 (m, dppr Cp, 8H), 7.27−7.40 (m, Ar, 10H), 7.65−7.83 (m, Ar, 10H). ^{31}P{^{1}H} NMR (161.9 MHz, C$_6$D$_6$): δ 63.2. FAB$^+$ MS, *m*-nitrobenzyl alcohol matrix (*m*-NBA): *m*/*z* 766.97 [M − 1]$^+$. The spectrum agreed with the calculated isotopic distribution.

CpRu(dppo)Cl (1c). A solution of CpRu(PPh$_3$)$_2$Cl (0.165 g, 0.227 mmol) and dppo (0.156 g, 0.227 mmol) in 25 mL of benzene was refluxed for 24 h. Evaporation of the solvent gave an orange powder, which was washed with warm hexanes (5 mL × 3) and dried under vacuum (0.128 g, 0.144 mmol, 63%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.95 (s, RuCp, 5H), 4.71 (br, s, dppo Cp, 2H), 4.86 (br, s, dppo Cp, 2H), 5.01 (br, s, dppo Cp, 2H), 5.56 (br, s, dppo Cp, 2H), 7.22−7.39 (m, Ar, 20H). ^{31}P{^{1}H} NMR (161.9 MHz, CDCl$_3$): δ 46.6. Anal. Calcd for C$_{39}$H$_{33}$ClOsP$_2$Ru: C, 52.61; H, 3.74. Found: C, 52.41; H, 3.36.

CpRu(dppo)H (2c). A solution of **1c** (0.113 g, 0.127 mmol) and NaBH$_4$ (0.050 g, 1.32 mmol) in 30 mL of 1-butanol/EtOH (1:1) was stirred at room temperature for 6 h. Additional NaBH$_4$ (0.050 g, 1.32 mmol) was added and the solution stirred for another 18 h. The yellow product was collected by filtration, washed with EtOH, and dried under vacuum (0.075 g, 0.088 mmol, 69% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ −12.08 (t, Ru*H*, J_{P-H} = 35.9 Hz, 1H), 3.97 (s, RuCp, 5H), 4.72 (br, s, dppo Cp, 2H), 4.76 (br, s, dppo Cp, 2H), 4.82 (br, s, dppo Cp, 2H), 4.88 (br, s, dppo Cp, 2H), 7.30 (m, Ar, 10H), 7.62 (m, Ar, 5H), 7.78 (m, Ar, 5H). ^{31}P{^{1}H} NMR (161.9 MHz, C$_6$D$_6$): δ 66.9. FAB$^+$ MS (*m*-NBA): *m*/*z* 855.00 [M − 1]$^+$. The spectrum agreed with the calculated isotopic distribution.

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CpRu(dippf)Cl (1d). A solution of $CpRu(PPh_3)_2Cl$ (0.45 g, 0.62 mmol) and dippf (0.27 g, 0.64 mmol) in 30 mL of benzene was refluxed for 5 h. The reaction mixture was concentrated in vacuo, and 20 mL of hexanes was added. Cooling this mixture in an $EtOH/CO_2$ bath gave an orange precipitate, which was filtered cold, washed with hexanes (5 mL × 2) at room temperature, and dried under vacuum (0.26 g, 0.42 mmol, 67% yield). ^1H NMR (300 MHz, CD_2Cl_2): δ 1.07−1.39 (m, dippf CH_3, 24H), 2.42−2.56 (m, dippf C*H*, 2H), 2.64−2.78 (m, dippf C*H*, 2H), 4.09 (s, dippf Cp, 2H), 4.21 (s, dippf Cp, 4H), 4.67 (s, RuCp, 5H), 4.90 (s, dippf Cp, 2H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 52.46. Anal. Calcd for $C_{27}H_{41}ClFeP_2Ru$: C, 52.31; H, 6.67. Found: C, 52.49; H, 6.72.

CpRu(dippf)H (2d). A solution of **1d** (0.23 g, 0.37 mmol) and NaOMe (0.23 g, 4.26 mmol) in 25 mL of MeOH was refluxed for 90 min. The reaction mixture was cooled to room temperature, and the yellow precipitate was filtered, washed with MeOH (10 and 5 mL), and dried under vacuum (0.20 g, 0.33 mmol, 90% yield). The product may also be prepared by stirring **1d** with excess $NaBH_4$ in EtOH. ^1H NMR (300 MHz, CD_2Cl_2): δ −13.44 (t, Ru*H*, J_{P-H} = 37.2 Hz, 1H), 0.92−1.30 (m, dippf CH_3, 24H), 1.80−1.92 (m, dippf C*H*, 2H), 2.03−2.17 (m, dippf C*H*, 2H), 4.16 (m, dippf Cp, 6H), 4.32 (s, dippf Cp, 2H), 4.71 (s, RuCp, 5H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): AB pattern, δ 77.72 ($\Delta\nu$ = 0.20 ppm, J_{P-P} = 9.8 Hz). FAB^+ MS (*m*-NBA): *m*/*z* 584.98 $[M - 1]^+$. The spectrum agreed with the calculated isotopic distribution.

***trans*-[CpRu(dippf)(H)$_2$]$^+$ (4d$^+$)** was prepared in situ by the protonation of **2d** with $HBF_4 \cdot OMe_2$ in CD_2Cl_2 at room temperature. ^1H NMR (300 MHz, CD_2Cl_2): δ −9.12 (t, Ru*(H)*$_2$, J_{P-H} = 22.1 Hz, 2H), 1.15−1.32 (m, dippf CH_3, 24H), 2.16−2.31 (m, dippf C*H*, 4H), 4.31 (s, dippf Cp, 4H), 4.49 (s, dippf Cp, 4H), 5.46 (s, RuCp, 5H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 79.17. T_1 of the dihydride resonance (400 MHz, CD_2Cl_2, ambient temperature): 0.895 s.

CpRu(dcpf)Cl (1e). A solution of $CpRu(PPh_3)_2Cl$ (0.381 g, 0.525 mmol) and dcpf (0.306 g, 0.529 mmol) in 50 mL of benzene was refluxed for 24 h. Evaporation of the solvent gave an orange solid, which was washed with EtOH (5 mL × 3) and dried under vacuum (0.142 g, 0.182 mmol, 35% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 1.08−2.12 (m, Cy, 44H), 4.04 (m, dcpf Cp, 8H), 4.62 (s, RuCp, 5H). $^{31}P\{^1H\}$ NMR (161.9 MHz, $CDCl_3$): δ 47.6. Anal. Calcd for $C_{39}H_{57}ClFeP_2Ru$: C, 60.04; H, 7.36. Found: C, 60.19; H, 7.18.

CpRu(dcpf)H (2e). A solution of **1e** (0.136 g, 0.175 mmol) and $NaBH_4$ (0.066 g, 1.75 mmol) in 25 mL of EtOH was stirred at room temperature for 4 h. Additional $NaBH_4$ (0.01 g, 0.26 mmol) was added and the solution stirred for another 2 h. The yellow product was collected by filtration, washed with EtOH, and dried under vacuum (0.111 g, 0.149 mmol, 85% yield). ^1H NMR (400 MHz, C_6D_6): δ −13.56 (t, Ru*H*, J_{P-H} = 37.4 Hz, 1H), 1.03−1.37 (m, Cy, 22H), 1.60−2.13 (m, Cy, 22H), 4.10 (m, dcpf Cp, 8H), 4.66 (s, RuCp, 5H). $^{31}P\{^1H\}$ NMR (161.9 MHz, C_6D_6): δ 69.6. FAB^+ MS (*m*-NBA): *m*/*z* 745.18 $[M - 1]^+$. The spectrum agreed with the calculated isotopic distribution.

***trans*-[CpRu(dcpf)(H)$_2$]$^+$ (4e$^+$)** was prepared in situ by the protonation of **2e** with $HBF_4 \cdot OMe_2$ in CD_2Cl_2 at room temperature. ^1H NMR (300 MHz, CD_2Cl_2): δ −9.15 (t, Ru*(H)*$_2$, J_{P-H} = 22.5 Hz, 2H), 1.30 (m, Cy, 20H), 1.79 (m, Cy, 24H), 4.24 (s, dcpf Cp, 4H), 4.47 (s, dcpf Cp, 4H), 5.40 (s, RuCp, 5H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): 69.0. T_1 of the dihydride resonance (300 MHz, CD_2Cl_2, ambient temperature): 0.589 s.

1,1′-Bis(diphenylphosphino)octamethylferrocene (dppomf). The following method was adapted from published procedures.[70−72] Lithium tetramethylcyclopentadienide (2.85 g, 22.24 mmol) was dissolved in 80 mL of dry THF and cooled in a water−ice bath. To this solution was added dropwise Ph_2PCl (4.0 mL, 22.24 mmol), the ice bath removed, and the resulting mixture stirred for 70 min. The mixture was cooled again in a water−ice bath, and *n*-BuLi (13.9 mL, 1.6 M in hexanes) was added dropwise. The ice bath was removed, and the mixture was stirred for 45 min. The mixture was cooled again in a water−ice bath, and a slurry of $FeCl_2$ (1.41 g, 11.12 mmol) in 40 mL of THF was added via cannula. The ice bath was removed, and the mixture was stirred for 45 min, then added to a separatory funnel containing 100 mL of Et_2O and 300 mL of water. The fractions were separated, and the aqueous fraction was washed with 50 mL of Et_2O. The organic fractions were combined, washed with 100 mL of water, and dried over $MgSO_4$. Evaporation of two-thirds of the solvent gave an orange precipitate, which was filtered and dried under vacuum (3.30 g, 4.95 mmol, 45% yield based on $FeCl_2$). ^1H NMR (400 MHz, CD_2Cl_2): δ 1.32 (s, CH_3, 12H), 1.77 (s, CH_3, 12H), 7.20−7.30 (m, Ar, 12H), 7.34−7.41 (m, Ar, 8H). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2): δ −20.07. FAB^+ MS (*m*-NBA): *m*/*z* 666.15 $[M]^+$. The spectrum agreed with the calculated isotopic distribution.

Cp*Ru(dppomf)Cl (1g). A solution of Cp*Ru(1,5-COD)Cl (0.38 g, 1.00 mmol) and dppomf (0.67 g, 1.00 mmol) in 60 mL of EtOH was refluxed for 90 min. The reaction mixture was cooled to room temperature, and the orange-red precipitate was filtered, washed with EtOH and hexanes, and dried under vacuum (0.63 g, 0.67 mmol, 67% yield). ^1H NMR (400 MHz, CD_2Cl_2): δ 0.81 (s, dppomf CH_3, 6H), 1.07 (s, dppomf CH_3, 6H), 1.15 (s, RuCp*, 15H), 1.36 (s, dppomf CH_3, 6H), 1.41 (s, dppomf CH_3, 6H), 7.17−7.22 (m, Ar, 2H), 7.35 (br, Ar, 8H), 7.42−7.55 (m, Ar, 4H), 7.82 (br, Ar, 4H), 8.67−8.74 (m, Ar, 2H). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2): δ 49.86. Anal. Calcd for $C_{52}H_{59}ClFeP_2Ru$: C, 66.56; H, 6.34. Found: C, 66.32; H, 6.36.

Cp*Ru(dppomf)H (2g). A solution of **1g** (0.18 g, 0.19 mmol) and NaOMe (0.18 g, 3.33 mmol) in 15 mL of MeOH was refluxed for 45 min. The reaction mixture was cooled to room temperature, and the yellow precipitate was filtered, washed with MeOH (5 mL × 2), and dried under vacuum (0.16 g, 0.17 mmol, 90% yield). ^1H NMR (300 MHz, CD_2Cl_2): δ −13.02 (t, Ru*H*, J_{P-H} = 36.9 Hz, 1H), 0.88 (s, dppomf CH_3, 6H), 1.06 (s, dppomf CH_3, 6H), 1.33 (s, dppomf CH_3, 6H), 1.40 (s, RuCp*, 15H and dppomf CH_3, 6H), 7.25−7.40 (m, Ar, 12H), 8.09 (m, Ar, 4H), 8.29 (m, Ar, 4H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 67.69 (m). FAB^+ MS (*m*-NBA): *m*/*z* 903.9 $[M - 1]^+$. The spectrum agreed with the calculated isotopic distribution.

***trans*-[Cp*Ru(dppomf)(H)$_2$]$^+$ (4g$^+$)** was prepared in situ by the protonation of **2g** with $HBF_4 \cdot OMe_2$ in CD_2Cl_2 at room temperature. ^1H NMR (300 MHz, CD_2Cl_2): δ −7.30 (t, Ru*(H)*$_2$, J_{P-H} = 27.5 Hz, 2H), 1.29 (s, dppomf CH_3, 12H), 1.42 (s, RuCp*, 15H), 1.51 (s, dppomf CH_3, 12H), 7.45−7.56 (m, Ar, 12H), 7.80−7.89 (m, Ar, 8H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 63.00 (m).

Cp*Ru(dippf)Cl (1h). A solution of Cp*Ru(1,5-COD)Cl (0.31 g, 0.82 mmol) and dippf (0.34 g, 0.82 mmol) in 40 mL of EtOH was refluxed for 1 h. The reaction mixture was concentrated in vacuo until a red precipitate formed. The precipitate was filtered, washed with EtOH (10 mL) and hexanes (5 mL), and dried under vacuum (0.28 g, 0.41 mmol, 50% yield). ^1H NMR (400 MHz, CD_2Cl_2): δ 0.88 (br, dippf CH_3, 6H), 1.16−1.26 (m, dippf CH_3, 12H), 1.34 (br, dippf CH_3, 6H), 1.62 (s, RuCp*, 15H), 2.32−2.53 (br, dippf C*H*, 4H), 4.02−4.20 (br, dippf Cp, 6H), 4.91 (s, dippf Cp, 2H). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2): δ 44.77. Anal. Calcd for $C_{32}H_{51}ClFeP_2Ru$: C, 55.70; H, 7.45. Found: C, 55.90; H, 7.57.

Cp*Ru(dippf)H (2h). A solution of **1h** (0.20 g, 0.29 mmol) and NaOMe (0.20 g, 3.70 mmol) in 20 mL of MeOH was refluxed for 30 min. The reaction mixture was cooled to room temperature, and the yellow precipitate was filtered, washed with MeOH (3 mL × 2), and dried under vacuum (0.18 g, 0.28 mmol, 96% yield). ^1H NMR (300 MHz, CD_2Cl_2): δ −14.37

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(t, Ru*H*, J_{P-H} = 36.8 Hz, 1H), 0.91−1.19 (m, dippf CH_3, 18H), 1.23−1.37 (m, dippf CH_3, 6H), 1.87 (br, RuCp*, 15H and dippf C*H*, 2H), 2.08 (br, dippf C*H*, 2H), 4.12 (s, dippf Cp, 6H), 4.23 (s, dippf Cp, 2H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 70.31. FAB$^+$ MS (*m*-NBA): *m*/*z* 655.95 $[M - 1]^+$. The spectrum agreed with the calculated isotopic distribution.

***trans*-[Cp*Ru(dippf)(H)$_2$]$^+$ (4h$^+$)** was prepared in situ by the protonation of **2h** with $HBF_4 \cdot OMe_2$ in CD_2Cl_2 at room temperature. ^1H NMR (300 MHz, CD_2Cl_2): δ −8.84 (t, Ru*(H)*$_2$, J_{P-H} = 26.7 Hz, 2H), 1.09−1.33 (m, dippf CH_3, 24H), 1.97 (s, RuCp*, 15H), 2.15−2.29 (m, dippf C*H*, 4H), 4.21 (s, dippf Cp, 4H), 4.44 (s, dippf Cp, 4H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2): δ 69.86.

1,1′-Bis(diphenylphosphino)cobaltocene (dppc). The following method was adapted from published procedures.[12,73] Sodium cyclopentadienide (1.96 g, 22.24 mmol) was dissolved in 80 mL of dry THF and cooled in an EtOH/CO_2 bath. To this solution was added dropwise Ph_2PCl (4.0 mL, 22.24 mmol), the cold bath was removed, and the resulting mixture was stirred for 70 min. The mixture was cooled again in an EtOH/CO_2 bath, and *n*-BuLi (13.9 mL, 1.6 M in hexanes) was added dropwise. The cold bath was removed, and the mixture was stirred for 45 min. The mixture was cooled again in an EtOH/CO_2 bath, and a slurry of $CoCl_2$ (1.44 g, 11.12 mmol) in 20 mL of THF was added via cannula. The cold bath was removed, and the mixture was stirred for 15 h, after which the solvent was evaporated to give a brown residue. The residue was extracted with Et_2O (150 mL and 3 × 100 mL), and the resulting brown solution was concentrated in vacuo to a volume of 20 mL. Addition of 50 mL of hexanes and evaporation of the solvent gave the product, a dark brown powder (4.39 g, 7.87 mmol, 71% yield based on $CoCl_2$). ^1H NMR (300 MHz, THF-d_8): δ −54.8 (br, Cp, 4H), −22.7 (br, Cp, 4H), 6.38 (br, Ar, 8H), 7.38 (t, Ar, 4H), 8.09 (br, Ar, 8H). $^{31}P\{^1H\}$ NMR (121.5 MHz, THF-d_8): δ −158 (br). FAB$^+$ MS (*m*-NBA): *m*/*z* 556.86 $[M]^+$. The spectrum agreed with the calculated isotopic distribution.

Cp*Ru(dppc)Cl (1i). A solution of Cp*Ru(PPh_3)$_2$Cl (0.50 g, 0.63 mmol) and dppc (0.35 g, 0.63 mmol) in 20 mL of benzene was refluxed for 1 h. The solvent was evaporated, and the resulting brown solid was washed with hexanes twice and dried under vacuum (0.39 g, 0.47 mmol, 75% yield). FAB$^+$MS (*m*-NBA): *m*/*z* 829.21 $[M]^+$, 794.20 $[Cp^*Ru(dppc)]^+$. The spectrum agreed with the calculated isotopic distribution.

[Cp*Ru(dppc)CH$_3$CN][PF$_6$]$_2$ (6j[PF$_6$]$_2$). A solution of **1i** (0.25 g, 0.30 mmol) and NH_4PF_6 (0.49 g, 3.0 mmol) in 40 mL of CH_3CN, stirred rapidly under air, became dark green over the course of 10 min. This solution was refluxed under air for 30 min and became red. The red solution was passed through a short silica column (230−400 mesh, 10 cm × 2 cm diameter), and then the solvent was removed under vacuum. Extraction of the resulting residue with CH_2Cl_2 (20 and 5 mL) gave a translucent red solution. Concentration in vacuo and addition of hexanes gave a brick red precipitate, which was filtered, washed with a 2:1 mixture of hexanes/CH_2Cl_2 (2 × 15 mL) and hexanes (5 mL), and dried under vacuum (0.15 g, 0.13 mmol, 44% yield). On a larger scale, starting with 4.58 mmol of Cp*Ru(PPh_3)$_2$Cl, the title compound was prepared in 43% overall yield. ^1H NMR (400 MHz, CD_3CN): δ 1.08 (s, RuCp*, 15H), 2.89 (s, CH_3CN), 5.53 (s, dppc$^+$ Cp, 2H), 5.63 (s, dppc$^+$ Cp, 2H), 5.66 (s, dppc$^+$ Cp, 2H), 5.70 (s, dppc$^+$ Cp, 2H), 7.40−7.50 (br, Ar, 4H), 7.50−7.66 (m, Ar, 14H), 7.71−7.79 (m, Ar, 2H). The coordinated CH_3CN exchanges with CD_3CN over the course of several hours at room temperature. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN): δ −144.46 (septet, PF_6^-, J_{F-P} = 706 Hz), 40.67 (s, dppc$^+$). Anal. Calcd for $C_{46}H_{46}NCoF_{12}P_4Ru$: C, 49.12; H, 4.12; N, 1.25. Found: C, 48.86; H, 4.20; N, 1.32. The product is readily crystallized by the addition of Et_2O to concentrated CH_3CN solutions. However, the resulting crystals contain uncoordinated Et_2O and CH_3CN and must be dried under vacuum for an extended period to remove these solvents.

[Cp*Ru(dppc)H][PF$_6$] (2j[PF$_6$]). A solution of **6j**[PF_6]$_2$ (0.112 g, 0.10 mmol) and NEt_3 (0.28 mL, 2.0 mmol) was stirred in 10 mL of MeOH under 80 psi of H_2 for 24 h. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 and loaded on a silica column (230−400 mesh, 6 cm × 2 cm diameter). The product was eluted with a 1:1 mixture of Et_2O/CH_2Cl_2. The solvent was evaporated, and the residue was dissolved in a small amount of CH_3CN. The addition of Et_2O gave a brown precipitate that was filtered, washed with 5 mL of Et_2O, and dried under vacuum (0.040 g, 0.043 mmol, 43%). On a larger scale, **6j**[PF_6]$_2$ (0.90 g, 0.80 mmol) and NEt_3 (2.3 mL, 16.5 mmol) were stirred in 15 mL of MeOH under 80 psi of H_2 for 16 h. The solvent was evaporated, and the residue was dissolved in CH_2Cl_2 and passed through two successive silica columns (230−400 mesh, 12 cm × 2 cm diameter, 1:1 Et_2O/CH_2Cl_2). Precipitation, washing, and drying of the product (as described above) gave a brown solid (0.33 g, 0.35 mmol, 44%). ^1H NMR (300 MHz, CD_3CN): δ −12.28 (t, Ru*H*, J_{P-H} = 34.7 Hz, 1H), 1.21 (s, RuCp*, 15H), 5.18 (s, dppc$^+$ Cp, 2H), 5.28 (s, dppc$^+$ Cp, 2H), 5.44 (s, dppc$^+$ Cp, 2H), 5.91 (s, dppc$^+$ Cp, 2H), 7.43 (m, Ar, 6H), 7.58 (m, Ar, 6H), 7.73 (br, Ar, 4H), 7.88 (br, Ar, 4H). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN): δ −144.46 (septet, PF_6^-, J_{F-P} = 706 Hz), 61.78 (s, dppc$^+$). FAB$^+$MS (*m*-NBA): *m*/*z* 795.32 [Cp*Ru(dppc)H]$^+$. The spectrum agreed with the calculated isotopic distribution.

[Cp*Ru(dppc)(H$_2$)]$^{2+}$ (3j^{2+}). The title dihydrogen complex was prepared in situ by the protonation of **2j**[PF_6] with $HBF_4 \cdot OMe_2$ in CD_2Cl_2 at room temperature. ^1H NMR (300 MHz, RT, CD_2Cl_2): δ −7.32 (s, br, Ru*(H*$_2$), 2H), 1.36 (s, RuCp*, 15H), 5.63 (s, dppc$^+$ Cp, 2H), 5.67 (s, dppc$^+$ Cp, 2H), 5.81 (s, dppc$^+$ Cp, 2H), 6.48 (s, dppc$^+$ Cp, 2H), 7.35−7.44 (m, Ar, 4H), 7.54 (m, Ar, 10H), 7.68−7.85 (m, Ar, 6H). $^{31}P\{^1H\}$ NMR (121.5 MHz, RT, CD_2Cl_2): δ 51.98 (s, dppc$^+$). T_1 of the dihydrogen resonance (300 MHz in CD_2Cl_2): 16.3(4) ms, 187.5 K; 10.9(2) ms, 207.5 K; 9.4(2) ms, 228.4 K; 10.2(1) ms, 248.4 K; 12.0(1) ms, 269.4 K.

***trans*-[Cp*Ru(dppc)(H)$_2$]$^{2+}$ (4j^{2+})** was prepared by leaving a solution of **3j**$^{2+}$ at room temperature for 48 h; ^1H and $^{31}P\{^1H\}$ NMR indicated nearly complete conversion to **4j**$^{2+}$. ^1H NMR (300 MHz, RT, CD_2Cl_2): δ −7.52 (t, Ru*(H)*$_2$, J_{P-H} = 26.2 Hz, 2H), 1.31 (s, RuCp*, 15H), 5.73 (s, dppc$^+$ Cp, 4H), 5.75 (s, dppc$^+$ Cp, 4H), 7.67−7.79 (m, Ar, 12H), 7.87−7.97 (m, Ar, 8H). $^{31}P\{^1H\}$ NMR (121.5 MHz, RT, CD_2Cl_2): δ 56.81 (s, dppc$^+$). T_1 of the dihydride resonance (300 MHz in CD_2Cl_2): 0.49(2) s, 187.5 K; 0.301(3) s, 207.5 K; 0.260(1) s, 228.4 K; 0.267(4) s, 248.4 K; 0.306(4) s, 269.4 K; 0.410(6) s, 297.6 K.

Cp*Ru(dppc)H (2i). Cp_2Co (0.02−0.03 mmol) and **2j**[PF_6] (ca. 0.01 mmol) were added to 500 μL of CH_3CN; vigorous shaking gave a dark precipitate. The solvent was carefully decanted from the product, which was then washed with CH_3CN (2 × 300 μL) and dried under Ar. This dark solid, the paramagnetic **2i**, readily dissolves in toluene to give a red solution. ^1H NMR (400 MHz, toluene-d_8): δ −57.8 (br, dppc Cp, 2H), −52.2 (br, dppc Cp, 2H), −27.3 (br, dppc Cp, 2H), −24.5 (br, dppc Cp, 2H), −15.76 (br, Ru*H*, 1H), 2.63 (s, RuCp*, 15H), 6.16 (m, Ar, 2H), 6.76 (br, Ar, 4H), 6.84 (m, Ar, 2H), 7.56 (br, Ar, 4H), 7.70 (br, Ar, 4H), 7.95 (br, Ar, 4H); a small amount of residual Cp_2Co (δ −50.4) was present. Solutions of **2i** are conveniently generated by reducing **2j**[PF_6] with Cp_2Co in THF-d_8; [Cp_2Co][PF_6] (yellow) precipitates, while **2i** (red) is soluble. ^1H NMR (300 MHz, THF-d_8): δ −54.9 (br, dppc Cp), −45.4 (br, dppc Cp), −28.0 (br, dppc Cp), −23.0 (br, dppc Cp), −15.56 (br, Ru*H*, 1H), 2.29 (s, RuCp*, 15H), 6.47 (m, Ar, 2H), 6.66 (br, Ar, 4H), 7.01 (m, Ar, 2H), 7.75 (m, Ar, 12H).

[Cp*Ru(dppc)CCPh][PF$_6$] (7j[PF$_6$]). A rapidly stirred slurry of **6j**[PF_6]$_2$ (0.113 g, 0.100 mmol), NEt_3 (3.5 mL), phenylacetylene (0.5 mL), and toluene (5.0 mL) was heated to 105 °C for 2 h. The volatiles were evaporated and the residue, dissolved in a

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small amount of CH_2Cl_2, was loaded on a silica column (230−400 mesh, 4 cm × 1 cm diameter). A green band was spread to the bottom with CH_2Cl_2 and then eluted with 99:1 CH_2Cl_2/CH_3CN. Evaporation of the solvent gave a green residue. The addition of Et_2O to a concentrated CH_2Cl_2 solution gave a blue precipitate that became green once dried under vacuum (0.077 g, 0.074 mmol, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (s, RuCp*, 15H), 5.45 (s, dppc$^+$ Cp, 2H), 5.56 (s, dppc$^+$ Cp, 4H), 6.55 (s, dppc$^+$ Cp, 2H), 7.20 (m, Ar, 1H), 7.32−7.63 (m, Ar, 18H), 7.59 (m, Ar, 2H), 8.02 (m, Ar, 4H). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ −144.33 (septet, PF_6^-, J_{F-P} = 713 Hz), 46.39 (s, dppc$^+$). Anal. Calcd for $C_{52}H_{48}CoF_6P_3Ru$: C, 60.06; H, 4.65. Found: C, 60.35; H, 4.72.

[Cp*Ru(dppc)CCHPh]$^{2+}$ (8j^{2+}). Treating **7j**[PF_6] with $HBF_4\cdot OMe_2$ in $CDCl_3$ gave a yellow solution. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (s, RuCp*, 15H), 5.65 (s, dppc$^+$ Cp, 2H), 5.87 (s, RuCC*H*Ph, 1H), 6.08 (s, dppc$^+$ Cp, 4H), 6.14 (s, dppc$^+$ Cp, 2H), 7.22 (m, Ar, 4H), 7.31−7.55 (m, Ar, 15H), 7.65 (m, Ar, 4H), 7.78 (m, Ar, 2H). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 47.80 (s, dppc$^+$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) distinctive resonance: δ 357.58 (t, Ru*C*CHPh, J_{P-C} = 15.7 Hz).

***N*-(Isopropylidene)pyrrolidinium Tetrafluoroborate (9).** ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.22 (m, β-CH_2, 4H), 2.51 (s, CH_3, 6H), 3.95 (m, α-CH_2, 4H). FAB$^+$MS (*m*-NBA): *m*/*z* for $C_7H_{14}N^+$ calcd 112.1126; found 112.1120.

***N*-(1-Methylbenzylidene)pyrrolidinium Tetrafluoroborate (10).** ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.09 (m, β-CH_2, 2H), 2.31 (m, β-CH_2, 2H), 2.78 (s, CH_3, 3H), 3.89 (m, α-CH_2, 2H), 4.21 (m, α-CH_2, 2H), 7.46−7.62 (m, Ar, 5H). FAB$^+$MS (*m*-NBA): *m*/*z* for $C_{12}H_{16}N^+$ calcd 174.1283; found 174.1276.

***N*-(Benzylidene)pyrrolidinium Tetrafluoroborate (11).** ^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.13−2.42 (m, β-CH_2, 4H), 4.23 (m, α-CH_2, 2H), 4.43 (m, α-CH_2, 2H), 7.68 (t, *m*-Ar, J = 7.7 Hz, 2H), 7.82 (t, *p*-Ar, J = 7.4 Hz, 1H), 7.95 (d, *o*-Ar, J = 7.7 Hz, 2H), 9.06 (s, C*H*, 1H). FAB$^+$MS (*m*-NBA): *m*/*z* for $C_{11}H_{14}N^+$ calcd 160.1126; found 160.1130.

***N*-(Isobutylidene)pyrrolidinium Tetrafluoroborate (12).** ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.32 (d, CH_3, J = 6.7 Hz, 6H), 2.23 (m, β-CH_2, 4H), 2.89 (m, C*H*, 1H), 3.98 (m, α-CH_2, 2H), 4.26 (m, α-CH_2, 2H), 8.35 (d, C*H*, J = 9.4 Hz, 1H). FAB$^+$MS (*m*-NBA): *m*/*z* for $C_8H_{16}N^+$ calcd 126.1283; found 126.1279.

1,2-Bis(*N*-pyrrolidino)-1,2-diphenylethane (13). The two diastereomers of **13** may be distinguished by ^{1}H NMR in $CDCl_3$ but not in THF-d_8. In $CDCl_3$, the methine proton resonances of the diastereomers appear at δ 3.93 and 3.87, while in THF-d_8 these resonances overlap at δ 3.95. The ^{1}H NMR spectrum of (*S,S*)-**13** in $CDCl_3$ has been reported.[74] Mixing **11** with **2i** in THF-d_8 gave a solution of **13** and **2j**[BF_4]. In another experiment, mixing **11** with Cp_2Co in THF-d_8 gave [Cp_2Co][BF_4] as a yellow precipitate and **13** in solution. An aliquot of the solution was used for FAB$^+$MS (*m*-NBA): *m*/*z* for **13**(H)$^+$ calcd 321.2331; found 321.2318. The remainder of the solution was decanted and evaporated, and the residue was dissolved in $CDCl_3$. The ^{1}H NMR spectrum showed a 4:5 ratio of the δ 3.93 to 3.87 peaks, indicating a 4:5 diastereomer ratio.

Kinetics of the Reaction between 3j^{2+} and *t*-BuCN. A stock solution of **3j**$^{2+}$ was prepared by treating 0.06 mmol of **2j**[PF_6] with an equimolar amount of $HBF_4\cdot OMe_2$ in 2.4 mL of CD_2Cl_2. The stock solution was stored at −20 °C when not in use. For each experiment, an NMR tube was loaded with 400 μL of stock solution, additional CD_2Cl_2, and *t*-BuCN. The additional CD_2Cl_2 was such that the total volume of the solution was always 600 μL. After the addition of *t*-BuCN, the NMR tube was shaken and kept in an EtOH/CO_2 bath until being inserted into the NMR probe. The ratio of the **3j**$^{2+}$ peak at δ 6.48 to the solvent peak at δ 5.32 was monitored at 19.5 °C. The rate did not depend on [*t*-BuCN]. The average of five experiments (ranging from 13.6 to 31.7 equiv of *t*-BuCN) gave a first-order rate constant of 2.0(1) × 10^{-3} s^{-1} for the disappearance of **3j**$^{2+}$. The product of the reaction is [Cp*Ru(dppc)*t*-BuCN]$^{2+}$. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.09 (s, RuCp*, 15H), 1.72 (s, *t*-BuCN, 9H), 5.63 (s, br, dppc$^+$ Cp, 4H), 5.69 (s, dppc$^+$ Cp, 2H), 5.98 (s, dppc$^+$ Cp, 2H), 7.43−7.79 (m, Ar, 20H). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2): δ 40.45 (s, dppc$^+$).

X-ray Structure Determination. Data were collected on a Bruker Apex II diffractometer. The structures were solved using direct methods and standard difference map techniques and refined by full-matrix least-squares procedures using SHELXTL version 5.10 software. Hydrogen atoms on carbon were included in calculated positions. Vapor diffusion of Et_2O into a concentrated CH_3CN solution of **6j**[PF_6]$_2$ gave crystals of **6j**[PF_6]$_2\cdot Et_2O\cdot CH_3CN$ suitable for X-ray analysis; the disordered solvent molecules were treated with SQUEEZE in PLATON.[75] A ^{1}H NMR spectrum in CD_2Cl_2 confirmed that the crystals contained Et_2O, CH_3CN, and **6j**[PF_6]$_2$ in a 1:1:1 ratio. Layering Et_2O onto a concentrated CH_2Cl_2 solution of **7j**[PF_6] gave crystals of **7j**[PF_6]$\cdot Et_2O$ suitable for X-ray analysis; the uncoordinated Et_2O was not disordered. CCDC 709698 and 709699 contain the supplementary crystallographic data for **6j**[PF_6]$_2\cdot Et_2O\cdot CH_3CN$ and **7j**[PF_6]$\cdot Et_2O$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: Crystallographic data (CIF files) for **6j**[PF_6]$_2\cdot Et_2O\cdot CH_3CN$ and **7j**[PF_6]$\cdot Et_2O$. This material is available free of charge via the Internet at http://pubs.acs.org.

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