ORGANOMETALLICS

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Synthesis, Electrochemistry, and Reactivity of New Iridium(III) and Rhodium(III) Hydrides

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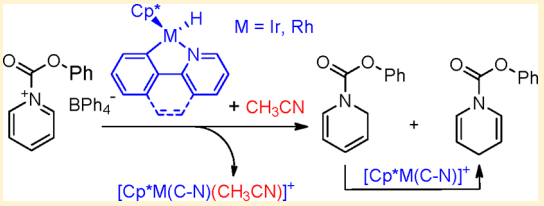
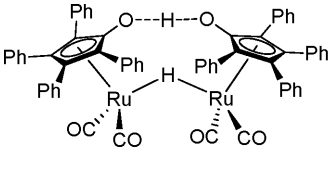
Supporting Information

ABSTRACT: Two new iridium hydride complexes, Cp*Ir(2-phenylpyridine)H (Cp* = pentamethylcyclopentadienyl) and Cp*Ir(benzo[*h*]quinoline)H, and their rhodium analogues Cp*Rh(2-phenylpyridine)H and Cp*Rh(benzo[*h*]quinoline)H have been prepared from the corresponding chlorides. The X-ray structures of Cp*Ir(2-phenylpyridine)H and Cp*Rh(2-phenylpyridine)H have been determined. The electrochemistry of all four hydride complexes and the corresponding chlorides has been studied by cyclic voltammetry; all exhibit irreversible M(III/IV) (M = Ir, Rh) oxidations. The hydride complexes are more easily oxidized than their chloride analogues, and the rhodium hydrides are more easily oxidized than their iridium analogues. The hydride complexes transfer H^- to the *N*-carbophenoxypyridinium cation at room temperature, giving mixtures of the 1,2- and 1,4-dihydropyridine products. In CD_3CN all four hydrides give these products in nearly the same ratio, which results from kinetic control; the thermodynamic ratio of the products has been calculated, and isomerization in that direction has been observed. In weakly coordinating solvents the cations left after H^- transfer catalyze this isomerization. Acetonitrile can trap these cations, slowing isomerization substantially. The X-ray structures of [Cp*Ir(2-phenylpyridine)(CH_3CN)][PF_6] and [Cp*Rh(2-phenylpyridine)(CH_3CN)][PF_6] have also been determined.

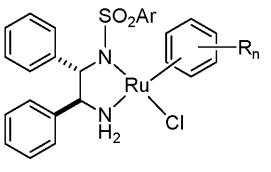


INTRODUCTION

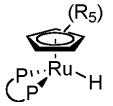
Ruthenium hydride complexes have been extensively used to catalyze "ionic hydrogenations", in which H_2 is transferred to the substrate as H^+ and H^-.[1−5] The fact that the Shvo hydride[2] transfers H_2 to C═N and C═O by an ionic mechanism has been established in detail by the Casey[3] and Bäckvall[4] groups. The Noyori catalyst for the asymmetric hydrogenation of ketones—although its resting state is not a hydride—operates by a similar mechanism.[6] The half-sandwich ruthenium hydride complexes **1**−**4** have been used by the Norton group to effect the ionic hydrogenation of iminium cations, aziridinium cations, and the *N*-acyl pyridinium cation **5** (eq 1).[5] With **5** the ratio of the 1,2- to the 1,4-dihydropyridine product varied as the catalyst was changed from **1** to **2**, **3**, or **4**, which led these authors to suggest competition between two different mechanisms: (a) a single-step H^- transfer, giving principally the 1,2 product, and (b) a two-step (sequential e^- and $H^•$ transfer) process, giving only the 1,4 product.[7]



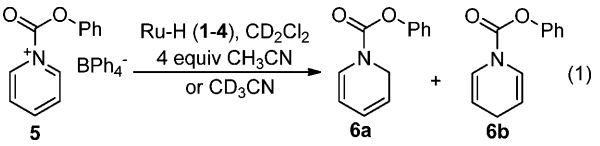
Shvo's catalyst



Noyori's catalyst



1. R = H, P-P = dppe
2. R = H, P-P = dppf
3. R = Me, P-P = dppe
4. R = Me, P-P = dppf



(1)

Relatively few hydrides of the isoelectronic Rh(III) and Ir(III) have been isolated and characterized,[8] although other complexes of these metals have been used to catalyze the hydrogenation of alkenes and imines.[9] Pincer hydride complexes of Ir(III) have attracted recent interest because of their ability to reduce CO_2 to formate complexes[10] and to serve as electrocatalysts for the reduction of CO_2 to formate/formic acid.[11]

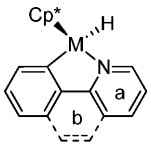
We set out to prepare half-sandwich rhodium(III) and iridium(III) hydrides with simpler C−N chelating ligands, i.e., 2-phenylpyridine, **a**, and benzo[*h*]quinoline, **b**, from the known chloride complexes[12] (chloride complexes of such ligands have also been prepared with Pt[13] and Au[14]). The planarity of these ligands should facilitate electron transfer.

We now report the new Ir and Rh hydride complexes Cp*M(C−N)H (**7a**, **7b**, **7′a**, **7′b**). We have examined them, and their chloride precursors, by cyclic voltammetry. We have investigated the transfer of H^- from **7** and **7′** to the *N*-carbophenoxypyridinium cation **5** in different solvents. We have

Received: May 10, 2012

   dx.doi.org/10.1021/om300398r | *Organometallics* XXXX, XXX, XXX−XXX

determined the structures of **7a**, **7′a**, and the corresponding acetonitrile complexes [Cp*Ir(2-phenylpyridine)(CH_3CN)]-[PF_6] (**9**) and [Cp*Rh(2-phenylpyridine)(CH_3CN)][PF_6] (**9′**) by single-crystal X-ray diffraction.

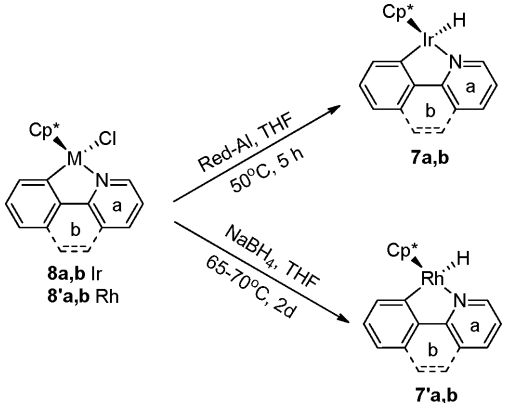


7a,b Ir
7′a,b Rh

RESULTS

Synthesis and Characteristics of the Hydride Complexes. The chloride complexes **8** and **8′** were prepared from [Cp*MCl_2]$_2$ (M = Ir, Rh) and the imine ligands, in the presence of NaOAc, by a method that has been previously reported.[15] Treating **8a,b** and **8′a,b** with the appropriate group-13 hydrides (Scheme 1) gave the hydride complexes **7a,b** and

Scheme 1



7′a,b. Long reaction times (2−3 days) and high temperatures (60−70 °C) were required if the iridium chlorides **8a** and **8b** were treated with $NaBH_4$ in THF, and partial decomposition of the chlorides resulted. However, the use of Red-Al (sodium bis(2-methoxyethoxy)aluminum hydride), which has good solubility in THF, gave the hydrides cleanly at 50 °C in 4−6 h. The opposite results were obtained with the rhodium chlorides **8′a** and **8′b**: the use of Red-Al under the same conditions failed, whereas $NaBH_4$ at 65 °C in THF gave complete conversion to the rhodium hydrides **7′a** and **7′b** after 2 days.

The iridium complex **7a** is bright yellow, with a hydride singlet at δ = −15.21; the iridium complex **7b** is orange, with a hydride singlet at δ = −14.98; the rhodium hydride **7′a** is yellow-brown, with a hydride doublet at δ = −12.64 ($^1J_{H-Rh}$ = 31.6 Hz); the rhodium hydride **7′b** is dark brown, with a hydride doublet at δ = −12.33 ($^1J_{H-Rh}$ = 29.2 Hz). While these complexes are air sensitive in solution, their crystals are stable in air for several hours.

X-ray Structures. Crystals of the hydride complexes were obtained by vapor diffusion of pentane into saturated THF solutions. The structures of **7a** and **7′a** were determined by single-crystal X-ray diffraction (Figures 1 and 2). In both cases the hydride ligand was located. Disorder between the

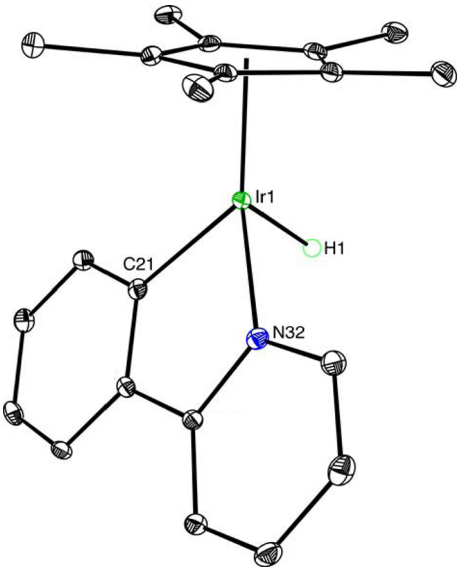


Figure 1. Molecular structure of **7a**. Hydrogen atoms other than the hydride ligand have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−H(1) 1.53(4), N(32)−Ir(1)−C(21) 77.93(13).

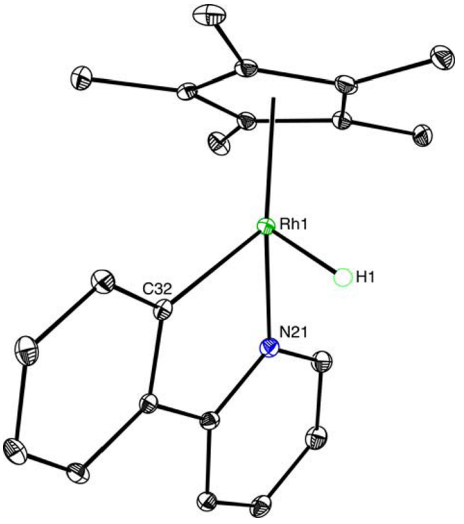


Figure 2. Molecular structure of **7′a**. Hydrogen atoms other than the hydride ligand have been omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−H(1) 1.51(3), N(21)−Rh(1)−C(32) 79.20(8).

coordinated C and N atoms of 2-phenylpyridine was observed in both **7a** and **7′a**. The two structures show similar M−H bond lengths: 1.53(4) Å in the iridium hydride **7a** and 1.51(3) Å in the rhodium hydride **7′a**. Structural parameters are listed in Table 1.

Electrochemistry. We chose tetrahydrofuran as the solvent for our CV studies because of reactivity concerns. The rhodium hydrides **7′a** and **7′b** react gradually with CH_2Cl_2 to give the corresponding chlorides, presumably via a radical pathway.[16,17] CH_3CN, while generally a good solvent for organometallic electrochemistry, reacts with the radical cations of many hydride complexes,[18] including those from **7** and **7′**.

The electrochemical peak potentials of the hydrides **7** and **7′**, the chlorides **8** and **8′**, and the *N*-carbophenoxypyridinium salt **5** in THF are listed in Table 2. All of the anodic oxidations are

dx.doi.org/10.1021/om300398r | *Organometallics* XXXX, XXX, XXX−XXX

Table 1. Crystal, Intensity Collection, and Refinement Data for 7a and 7′a

	7a	7′a
lattice	monoclinic	monoclinic
formula	$C_{21}H_{24}IrN$	$C_{21}H_{24}NRh$
fw	482.61	393.22
space group	$P2_1/n$	$P2_1/n$
a, Å	13.3885(11)	13.3812(11)
b, Å	7.5832(6)	7.5998(7)
c, Å	17.8084(14)	17.7777(15)
α, deg	90	90
β, deg	111.5130(10)	111.5040(10)
γ, deg	90	90
V, Å^3	1682.1(2)	1682.0(3)
Z	4	4
temperature, K	150(2)	150(2)
radiation (λ, Å)	0.71073	0.71073
ρ (calcd), g cm^{-3}	1.906	1.553
μ (Mo Kα), mm^{-1}	7.937	1.014
θ_{max}, deg	32.77	32.74
no. of data collected	28 339	28 524
no. of data	5921	5939
no. of params	218	218
R_1 [$I > 2\sigma(I)$]	0.0308	0.0340
wR_2 [$I > 2\sigma(I)$]	0.0555	0.0716
R_1 [all data]	0.0493	0.0529
wR_2 [all data]	0.0612	0.0782
GOF	1.021	1.042

Table 2. Peak Potentials as Determined by Cyclic Voltammetry of the Hydride and the Chloride Complexes[a]

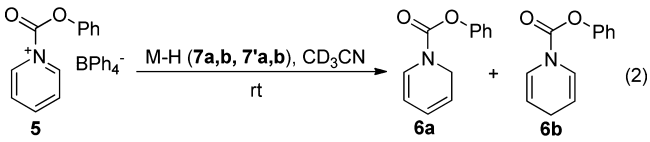
compound	potential (V)	parameter	process
7a	−0.09	E_{pa}[b]	oxidation
7b	−0.06	E_{pa}[b]	oxidation
7′a	−0.38	E_{pa}[b]	oxidation
7′b	−0.39	E_{pa}[b]	oxidation
8a	+0.35	E_{pa}[b]	oxidation
8b	+0.34	E_{pa}[b]	oxidation
8′a	+0.45	E_{pa}[b]	oxidation
8′b	+0.47	E_{pa}[b]	oxidation
5	−0.98	E_{pc}[c]	reduction

[a]From 1 mM THF solutions, containing 0.1 M $[Bu_4N]PF_6$ as the supporting electrolyte, at a scan rate of 100 mV/s. [b]E_{pa}, anodic peak potentials, versus FcH^+/FcH. [c]E_{pc}, cathodic peak potentials, versus FcH^+/FcH.

irreversible, which is expected since hydride cation radicals are quite acidic and undergo rapid deprotonation.[18,19] However, the compounds have similar structures and have been studied under the same conditions, so the kinetic potential shifts should be similar and the E_{pa} values should enable us to make approximate comparisons. The nature of the C−N ligand does not have much influence on the electrochemical properties of the hydride complexes. The E_{pa} of the iridium hydride **7a**, with a 2-phenylpyridine ligand, is only 0.03 V less than that of its benzo[*h*]quinoline analogue **7b**, and the difference is even smaller between the rhodium hydrides **7′a** and **7′b**. The rhodium hydrides **7′a** and **7′b** are more easily oxidized (their E_{pa} values are around 0.3 V more negative) than their iridium analogues **7a** and **7b**. However, all of the hydride complexes have E_{pa} values that are substantially less negative than the E_{pc} of the substrate, suggesting that there is no driving force for electron transfer.

The iridium chlorides **8a,b** appear to be more easily oxidized than the rhodium chlorides **8′a,b**. The E_{pa} values of the iridium hydrides **7** are 0.4 V more negative than those of the corresponding chlorides **8**; the difference between the rhodium hydrides **7′** and the corresponding chlorides is even larger, around 0.8 V. We have reported similar differences between the potentials of Ru hydrides and chlorides.[20] These results reflect the fact that hydride ligands are generally better donors than chloride ligands.[21]

Reactivity of the Hydrides with an *N*-Acyl Pyridinium Cation. When we treated the *N*-carbophenoxypyridinium cation **5** with the new hydride complexes **7** and **7′**, we expected (given the E_{pa} values of **7** and **7′**) mixtures of the 1,2- and 1,4-dihydropyridine products **6a** and **6b**. This prediction proved correct. In CD_3CN (eq 2) the reactions were complete within



(2)

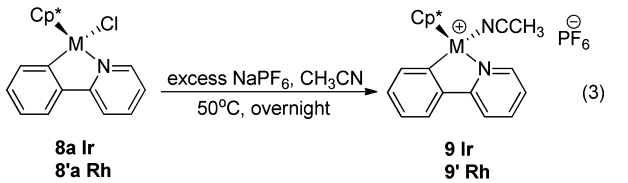
Table 3. Product Ratios from the Reaction of 5 with Different Hydride Complexes in CD_3CN[a]

	product ratio (**6a**:**6b**)[b]		
	10 min	9 h	24 h
7a	40:60	40:60	38:62
7b	37:63	37:63	34:66
7′a	44:56	40:60	37:63
7′b	37:63	34:66[c]	33:67

[a]Conditions: 0.01 mmol of **5**, 0.01 mmol of hydride complex, 700 μL of CD_3CN, room temperature. [b]Product ratio determined by ^1H NMR integration. [c]12 h.

10 min, giving only **6a** and **6b** in the ratios shown in Table 3. The product ratios remained nearly constant over time. The product ratios from the iridium hydride complexes **7a** and **7b** proved similar to those from the rhodium hydrides **7′a** and **7′b**, even though the E_{pa} values of **7** differ from those of **7′** by 0.3 V. Apparently the mechanism of hydride transfer is *not merely* a function of the redox potential of the hydride complex.

From the related reactions with Ru hydrides[7] we presumed that the organometallic products of eq 2 were acetonitrile complexes. We prepared the expected complexes independently by heating CH_3CN solutions of the chlorides with $NaPF_6$ (eq 3). The complex $[Cp^*Ir(2\text{-phenylpyridine})(CH_3CN)][PF_6]$



(3)

(**9**) was crystallized by vapor diffusion of pentane into a saturated THF solution, while the complex $[Cp^*Rh(2\text{-phenylpyridine})(CH_3CN)][PF_6]$ (**9′**) was crystallized by vapor diffusion of diethyl ether into a saturated acetonitrile solution. While other CH_3CN complexes of Ir and Rh had been

dx.doi.org/10.1021/om300398r | *Organometallics* XXXX, XXX, XXX−XXX

reported,[22] our complexes **9** and **9′** were previously unknown, so we determined their X-ray structures (Figures 3 and 4).

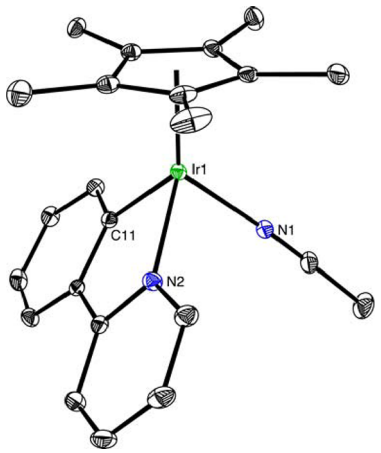


Figure 3. Molecular structure of **9**. The counteranion and the hydrogens have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ir(1)−N(1) 2.068(4), C(11)−Ir(1)−N(2) 86.85(12).

Disorder between the coordinated C and N atoms of 2-phenylpyridine was observed in both **9** and **9′**. The structural parameters of **9** and **9′** are given in the Supporting Information.

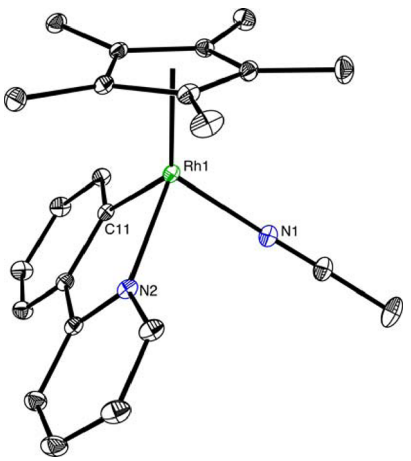


Figure 4. Molecular structure of **9′**. The counteranion and the hydrogens have been omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−N(1) 2.064(2), C(11)−Rh(1)−N(2) 78.51(8).

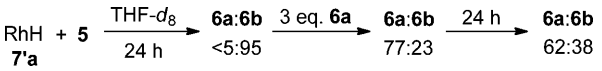
In the *absence* of CH_3CN the Ir or Rh complex remaining after hydride transfer catalyzed the isomerization of the 1,2-dihydropyridine **6a** to the 1,4-dihydropyridine **6b**. The effect was most obvious with Rh hydride **7′a**: in THF-d_8 or C_6D_6 the **6a**:**6b** ratio was 1:3 after 10 min, but decreased substantially over 24 h (Table 4). The hydride peak of **7′a** disappeared completely within 10 min, so isomerization was slower than hydride transfer. Isomerization was also observed when excess 1,2-dihydropyridine **6a** (about 3 equiv) was added—24 h *after* hydride transfer was complete—to an NMR tube in which **5** had been treated with **7′a** in THF-d_8 (the experiment is summarized in Scheme 2). After 24 h at room temperature the **6a**:**6b** ratio in the tube decreased from 77:23 to 62:38, again

Table 4. Product Ratios from the Stoichiometric Reduction of 5 with Hydride 7′a in Different Solvents[a]

	product ratio (**6a**:**6b**)[b]		
solvent	10 min	9 h	24 h
CD_3CN	44:56	40:60	37:63
THF-d_8	25:75	10:90	<5:95
C_6D_6	24:76	13:87	10:90

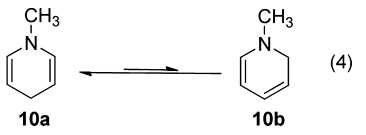
[a]Conditions: 0.01 mmol of **5**, 0.01 mmol of **7′a**, 700 μL of solvent, room temperature. [b]Product ratio determined by ^{1}H NMR integration.

Scheme 2



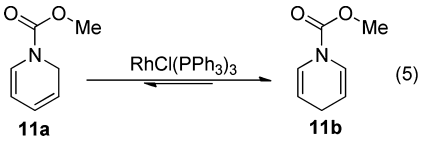
demonstrating the ability of "$[Cp^*M(C{-}N)]^+$" to catalyze the **6a** → **6b** isomerization.

Both the literature and other experiments are consistent with the implication that the 1,4-dihydropyridine **6b** is more stable than its 1,2 isomer **6a**.[23] Fowler measured in 1972 a positive ΔG, 2.3 kcal/mol, for the equilibrium (established by base in DMSO at 91.6 °C) between the *N*-methyl dihydropyridines **10a** and **10b** in eq 4.[24] Eisner and Sadeghi reported catalysis by



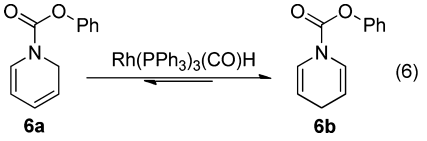
(4)

some rhodium complexes of the isomerization of the 1,2-dihydropyridine **11a** to its 1,4 analogue **11b** (eq 5).[25] We have



(5)

treated the 1,2-dihydropyridine **6a** with $Rh(PPh_3)_3(CO)H$ in THF-d_8 at room temperature and obtained a **6a**:**6b** ratio of 13:87 after three weeks (eq 6). Calculations using Spartan′10[26] imply that the gas-phase equilibrium ratio of **6a** to **6b** is 7:93 at room temperature.



(6)

Even 4 equiv of CH_3CN proved enough to slow (but not stop) the isomerization of **6a** → **6b** during a hydride transfer experiment in THF-d_8, CD_2Cl_2, or C_6D_6 (Table 5). It is clear that the product ratios in CD_3CN (Table 3) are the result of *kinetic control*. It is also clear that under other conditions (no CH_3CN, Table 4, or a small amount of CH_3CN, Table 5) the product ratios reflect the slow isomerization of **6a** → **6b**.

DISCUSSION

Table 3 shows that the kinetic product ratios from these hydride transfer reactions are not much affected by the nature of the C−N ligand (2-phenylpyridine, **a**, or benzo[*h*]quinoline,

dx.doi.org/10.1021/om300398r | *Organometallics* XXXX, XXX, XXX−XXX

Table 5. Product Ratios from the Stoichiometric Reduction of 5 with Hydrides 7 and 7′ in the Presence of 4 equiv of CH_3CN in Different Solvents[a]

		product ratio (6a:6b)[b]		
complex	solvent	10 min	9 h	24 h
7a	THF-d_8	21:79	16:84	15:85
	CD_2Cl_2	19:81	18:82	17:83
	C_6D_6	20:80	15:85	14:86
7b	THF-d_8	27:73	19:81	15:85
	CD_2Cl_2	20:80	17:83	15:85
	C_6D_6	25:75	24:76	20:80
7′a[c]	THF-d_8	40:60	19:81	13:87
	C_6D_6	43:57	39:61	35:65
7′b[c]	THF-d_8	28:72	16:84	11:89
	C_6D_6	35:65	28:72	24:76

[a]Conditions: 0.01 mmol of 5, 0.01 mmol of hydride complex, 0.04 mmol of CH_3CN, 700 μL of solvent, room temperature. [b]Product ratio determined by ^1H NMR integration. [c]The hydride complexes 7′a and 7′b are converted back to the corresponding chloride complexes in CD_2Cl_2.

b), a result that is consistent with the "outer-sphere" mechanism proposed previously: hydride transfer to an *uncoordinated* substrate. Table 3 also shows little difference in kinetic product ratio between the iridium hydrides 7 and the rhodium hydrides 7′. Although the potentials of 7 and 7′ differ significantly in Table 2, *all* of the hydride complexes have E_{pa} values that are substantially less negative than the E_{pc} of the substrate, implying that there is little driving force for electron transfer. The $e^-/H^•$ mechanism may not be important for either the Ir hydrides 7 or the Rh hydrides 7′.

Finally, the left-hand column of Table 5 shows that the kinetic product ratios are little affected by the nature of the solvent. The isomerization of 6a to 6b must be catalyzed by coordinatively unsaturated species in equilibrium with acetonitrile complexes. ([Cp*Rh(2-phenylpridine)]$^+$ from 9′ is a particularly effective catalyst.) Large amounts of acetonitrile inhibit isomerization by trapping the catalytically active metal complex cation "[Cp*M(C−N)]$^+$".

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. CD_2Cl_2 and CD_3CN were deoxygenated and stored over 3 Å molecular sieves. THF-d_8 and C_6D_6 were dried over CaH_2 and purified by vacuum transfer. *n*-Hexane, Et_2O, and CH_2Cl_2 were deoxygenated and dried by two successive columns (Q-5, activated alumina). THF and pentane were distilled from sodium/benzophenone under an N_2 atmosphere. *N*-Carbophenoxypyridinium tetraphenylborate (5) was prepared by the method of King[27] and recrystallized from CH_2Cl_2−Et_2O. Cp*Ir(2-phenylpyridine)Cl (8a),[15a] Cp*Ir(benzo[*h*]quinoline)Cl (8b),[15a] Cp*Rh(2-phenylpyridine)Cl (8′a),[15a] Cp*Rh(benzo[*h*]quinoline) (8′b),[15a] $Rh(PPh_3)_3(CO)H$,[28] and *N*-carbophenoxy-1,2-dihydropyridine (6a)[29] were prepared by literature methods.

Electrochemical Procedures. Cyclic voltammetry was performed with a BAS CV-50W potentiostat. The supporting electrolyte for all solutions except the reference electrode was 0.10 M $[Bu_4N]PF_6$ in THF. The cell consisted of a 1.6 mm diameter platinum disk working electrode, a platinum wire auxiliary electrode, and a silver wire reference electrode (0.01 M $AgNO_3$ + 0.10 M $[Bu_4N]PF_6$ in CH_3CN). The reference electrode was separated from the sample solutions with a porous Vycor tip (Bioanalytical Systems, MF-2042). Ferrocene (FcH^+/FcH) was used as an external reference and was found to be +0.24 V with respect to our reference electrode. All samples were prepared under an N_2/Ar atmosphere and further purged with N_2 before measurement. Analyte concentrations were 0.001 M. The scan rate was 100 mV/s. All potentials are reported in volts (V) vs FcH^+/FcH.

Cp*Ir(2-phenylpyridine)H (7a). Under a nitrogen atmosphere, 110 μL of Red-Al (3.5 M toluene solution, 0.39 mmol) was added dropwise to a suspension of 200 mg of Cp*Ir(2-phenylpyridine)Cl (8a) (0.39 mmol) in 40 mL of THF. Heating the resulting mixture at 50 °C for 5 h gave a bright yellow solution and a white precipitate, which was removed by filtration after the mixture was cooled to room temperature. The solvent was removed under vacuum, and the yellow solid was washed with *n*-hexane three times, then dried under vacuum to give the bright yellow powder 7a (121 mg, 64% yield). IR (KBr): 2053 cm^{-1} (Ir−H). ^1H NMR (400 MHz, THF-d_8): δ −15.21 (s, 1H, IrH), 1.89 (s, 15H, Cp*), 6.85 (dd, *J* = 7.2, 5.6 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 8.77 (d, *J* = 5.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 9.67 (Cp*), 89.72 (Cp*), 118.53, 119.34, 120.79, 124.25, 129.11, 134.49, 136.14, 143.97, 152.77 (HC═N), 163.71, 168.61 (Ir−C). The LRMS (FAB$^+$) showed peaks for ^{191}Ir (*m*/*e* = 480.2, [M − 1]$^+$) and ^{193}Ir (*m*/*e* = 482.2, [M − 1]$^+$) with the appropriate isotopic distribution; calculated ^{191}Ir (*m*/*e* = 480.14, [M − 1]$^+$) and ^{193}Ir (*m*/*e* = 482.15, [M − 1]$^+$).

Cp*Ir(benzo[*h*]quinoline)H (7b). The synthesis was analogous to that of 7a, using Red-Al (3.5 M toluene solution, 106 μL, 0.37 mmol) and Cp*Ir(benzo[*h*]quinoline)Cl (8b) (200 mg, 0.37 mmol) in 60 mL of THF at 50 °C for 5 h. The hydride complex 7b was isolated as an orange solid (143 mg, 76% yield). IR (KBr): 2043 cm^{-1} (Ir−H). ^1H NMR (400 MHz, THF-d_8): δ −14.98 (s, 1H, IrH), 1.94 (s, 15H, Cp*), 7.27 (br, 1H), 7.38 (br, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.92 (br, 1H), 8.03 (d, *J* = 5.6 Hz, 1H), 9.02 (br, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 10.04 (Cp*), 89.83 (Cp*), 117.62, 120.73, 123.63, 127.23, 129.43, 130.17, 132.95, 133.67, 135.04, 142.36, 151.09 (HC═N), 159.15, 161.08 (Ir−C). The LRMS (FAB$^+$) showed peaks for ^{191}Ir (*m*/*e* = 504.2, [M − 1]$^+$) and ^{193}Ir (*m*/*e* = 506.2, [M − 1]$^+$) with the appropriate isotopic distribution; calculated ^{191}Ir (*m*/*e* = 504.14, [M − 1]$^+$) and ^{193}Ir (*m*/*e* = 506.15, [M − 1]$^+$).

Cp*Rh(2-phenylpyridine)H (7′a). Under a nitrogen atmosphere, 80 mL of THF was added to a mixture of Cp*Rh(2-phenylpyridine)Cl (8′a) (400 mg, 0.94 mmol) and $NaBH_4$ (80 mg, 2.16 mmol), giving a yellow-orange suspension. Heating the mixture at 65 °C for 2 d resulted in a brownish mixture. The precipitate was removed by filtration after the mixture was cooled to room temperature. The volume of the brownish filtrate was reduced to around 3 mL; then pentane was added to cause precipitation. The solvent was removed by cannula, and the solid was washed with pentane three times, then dried under vacuum to give 162.5 mg of the yellow-brown solid 7′a (42% yield). IR (KBr): 1935 cm^{-1} (Rh−H). ^1H NMR (400 MHz, THF-d_8): δ −12.64 (d, *J* = 31.6 Hz, 1H, RhH), 1.85 (s, 15H, Cp*), 6.88 (t, *J* = 7.2 Hz, 1H), 7.00 (m, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 8.61 (d, *J* = 5.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 10.03 (s, Cp*), 95.61 (d, *J* = 17.6 Hz, Cp*), 118.71, 120.62, 120.71, 123.67, 128.38, 135.24, 137.52, 143.24, 152.45 (HC═N), 165.75, 179.54 (d, *J* = 141.2 Hz, Rh−C). The LRMS (FAB$^+$) showed a peak for ^{103}Rh (*m*/*e* = 392.1, [M − 1]$^+$) with the appropriate isotopic distribution; calculated ^{103}Rh (*m*/*e* = 392.09, [M − 1]$^+$).

Cp*Rh(benzo[*h*]quinoline)H (7′b). The synthesis was analogous to that of 7′a, using Cp*Rh(benzo[*h*]quinoline)Cl (8′b) (400 mg, 0.89 mmol) and $NaBH_4$ (80 mg, 2.16 mmol) in 80 mL of THF at 65 °C for 2 d. The hydride complex 7′b was isolated as a dark brown solid (252.3 mg, 68% yield). IR (KBr): 1923 cm^{-1} (Rh−H). ^1H NMR (400 MHz, THF-d_8): δ −12.33 (d, *J* = 29.2 Hz, 1H, RhH), 1.87 (s, 15H, Cp*), 7.34−7.70 (m, 5H), 7.88 (d, *J* = 5.2 Hz, 1H), 8.11 (d, *J* = 7.2 Hz, 1H), 8.86 (br, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, THF-d_8): δ 9.85 (s, Cp*), 95.22 (s, Cp*), 118.62, 120.16, 122.90, 126.74, 128.07, 129.50, 133.53, 133.81, 134.22, 140.04, 150.46 (HC═N), 155.52, 176.51 (d, *J* = 142.0 Hz, Rh−C). The LRMS (FAB$^+$) showed a peak

dx.doi.org/10.1021/om300398r | *Organometallics* XXXX, XXX, XXX−XXX

for ^{103}Rh (m/e = 416.1, [M − 1]$^+$) with the appropriate isotopic distribution; calculated ^{103}Rh (m/e = 416.09, [M − 1]$^+$).

[Cp*Ir(2-phenylpyridine)(CH$_3$CN)][PF$_6$] (9). Under a nitrogen atmosphere, 30 mL of CH$_3$CN was added to a mixture of Cp*Ir(2-phenylpyridine)Cl (**8a**) (200 mg, 0.39 mmol) and NaPF$_6$ (100 mg, 0.60 mmol), giving an orange solution. The solution was heated at 50 °C overnight, a white precipitate formed, and the solution became light yellow. The precipitate (NaCl) was removed by filtration after the mixture was cooled to room temperature. The solvent was pumped off, leaving a sticky material. *n*-Hexane was added, and the resulting mixture was stirred for several hours to give a light orange solid. The solid was washed with *n*-hexane three times and then dried under vacuum. Excess NaPF$_6$ was not removed from the product. IR (KBr): 2345, 2322 cm^{-1} (N≡C); two peaks for one coordinated CH$_3$CN were also observed in some Zr complexes.[30] ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 1.71 (s, 15H, Cp*), 2.31 (s, 3H, CH$_3$CN), 7.20 (m, 1H), 7.30 (m, 2H), 7.77 (m, 2H), 7.93 (m, 2H), 8.73 (d, J = 4.8 Hz, 1H). The LRMS (FAB$^+$) showed peaks for ^{191}Ir (m/e = 480.2, [M − CH$_3$CN]$^+$) and ^{193}Ir (m/e = 482.2, [M − CH$_3$CN]$^+$) with the appropriate isotopic distribution; calculated ^{191}Ir (m/e = 480.14, [M − CH$_3$CN]$^+$) and ^{193}Ir (m/e = 482.15, [M − CH$_3$CN]$^+$). The analogous CD$_3$CN complex, **9-*d*$_3$**, is prepared by heating 0.01 mmol of **8a** and 0.02 mmol of NaPF$_6$ in 700 μL of CD$_3$CN at 50 °C. The reaction was monitored over time by ^{1}H NMR. After 2 h, the reaction was finished and the NMR data of the product were recorded. IR (KBr): 2254, 2110 cm^{-1} (N≡C). ^{1}H NMR (400 MHz, CD$_3$CN): δ 1.69 (s, 15H, Cp*), 7.18 (t, J = 7.6 Hz, 1H), 7.27 (dd, J = 7.2, 7.6 Hz, 1H), 7.35 (ddd, J = 1.2, 6.0, 7.4 Hz, 1H), 7.82 (d, J = 7.6 Hz, 2H), 7.95 (ddd, J = 1.6, 8.0, 8.4 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 8.74 (d, J = 5.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ 8.73 (Cp*), 92.03 (Cp*), 120.48, 124.50, 124.66, 125.19, 131.94, 136.65, 140.14, 145.98, 153.26 (HC═N), 157.45, 167.92 (Ir−C).

[Cp*Rh(2-phenylpyridine)(CH$_3$CN)][PF$_6$] (9′). The synthesis was analogous to that of **9**, except using Cp*Rh(2-phenylpyridine)Cl (**8′a**) (200 mg, 0.47 mmol) and NaPF$_6$ (110 mg, 0.66 mmol) in 30 mL of CH$_3$CN at 50 °C overnight. The complex **9′** is a light orange solid. The excess NaPF$_6$ was not removed from the product. IR (KBr): 2318, 2289 cm^{-1} (N≡C); two peaks for one coordinated CH$_3$CN were also observed in some Zr complexes.[30] When the title complex was dissolved in CD$_3$CN, the coordinated CH$_3$CN exchanged with solvent to give the CD$_3$CN complex and free CH$_3$CN. ^{1}H NMR (400 MHz, CD$_3$CN): δ 1.61 (s, 15H, Cp*), 7.18 (dd, J = 7.2, 7.6 Hz, 1H), 7.30 (dd, J = 7.2, 7.6 Hz, 1H), 7.39 (td, J = 2.4, 6.0 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.97 (m, 2H), 8.77 (d, J = 5.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$CN): δ 8.96 (s, Cp*), 98.96 (d, J = 25.2 Hz, Cp*), 120.54, 124.29, 124.84, 125.00, 131.44, 137.29, 139.86, 145.38, 152.79 (HC═N), 165.83, 174.50 (d, J = 119.2 Hz, Rh−C). The LRMS (FAB$^+$) showed a peak for ^{103}Rh (m/e = 392.1, [M − CH$_3$CN]$^+$) with the appropriate isotopic distribution; calculated ^{103}Rh (m/e = 392.09, [M − CH$_3$CN]$^+$).

Stoichiometric Hydride Transfer from Metal Hydrides to 5 in CD$_3$CN. The Ir or Rh hydride (0.01 mmol) and **5** (0.01 mmol) were dissolved in 700 μL of CD$_3$CN at room temperature, and the product ratio was measured by ^{1}H NMR integration.

Stoichiometric Hydride Transfer from Metal Hydrides to 5 in Other Solvents without the Addition of CH$_3$CN. The Ir or Rh hydride (0.01 mmol) and **5** (0.01 mmol) were dissolved in 700 μL of solvent (for Ir hydrides, THF-d_8, CD$_2$Cl$_2$, C$_6$D$_6$; for Rh hydrides, THF-d_8, C$_6$D$_6$) at room temperature. The product ratio was measured by ^{1}H NMR integration. The hydrides are sparingly soluble in C$_6$D$_6$, so in this solvent the solutions were saturated.

Stoichiometric Hydride Transfer from Metal Hydrides to 5 in Other Solvents with the Addition of CH$_3$CN. The Ir or Rh hydride (0.01 mmol), **5** (0.01 mmol), and CH$_3$CN (0.04 mmol, 2.1 μL) were combined in 700 μL of solvent (for Ir hydrides, THF-d_8, CD$_2$Cl$_2$, C$_6$D$_6$; for Rh hydrides, THF-d_8, C$_6$D$_6$) at room temperature. The product ratio was measured by ^{1}H NMR integration. The hydrides are sparingly soluble in C$_6$D$_6$, so in this solvent the solutions were saturated.

X-ray Structure Determinations. X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection, and refinement parameters are summarized in Table 1 and in the Supporting Information. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (version 6.10).

Computational Methods. Calculations were done with Spartan'10. The structures were minimized using the B3LYP functional in conjunction with the 6-311++G** basis set. For the N-methylated 1,2 to 1,4 ratio, single-point energy calculations were performed with a variety of basis sets, and the results compared to those in ref 24. (Calculated entropies were negligible.) The best results were obtained with the triple-ζ (cc-PVTZ) basis set, and this method was used for single-point calculations on compounds **6a** and **6b**, which were used to determine the equilibrium ratio. For computational details see ref 31.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Lists of ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **7a,b**, **7′a,b**, **9**, and **9′**, cyclic voltammograms of **7a,b**, **7′a,b**, **8a,b**, **8′a,b**, and **5**, and complete details of the crystallographic study (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by NSF grant CHE-0749537 and by Boulder Scientific and OFS Fitel. The National Science Foundation is thanked for acquisition of an X-ray diffractometer (CHE-0619638) and a 400 MHz NMR spectrometer (CHE-0840451). We thank Prof. G. Parkin for assistance with the X-ray structure determinations, and Jim Yang for synthesizing compound **5**. We thank Deven P. Estes for the calculations.

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