A Binding Pocket for Coordinated Water Formed by the Metal Center and Two Heterocyclic Nitrogens in Chelating Bis-thioethers of the Complexes $\{Cp^*M[Im'S(CH_2)_2SIm'](H_2O)\}^{2+}$ (M = Rh, Ir; Im′ = 1-alkyl-4-*tert*-butylimidazol-2-yl)

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Two new chelating bis-thioethers of the form $Im'S(CH_2)_2SIm'$ were made, where Im′ = 1-methyl and 1-isopropyl-4-*tert*-butylimidazol-2-yl (**4-Me** and **4-iPr**, respectively). When coordinated to Cp^*Ir^{2+} and Cp^*Rh^{2+} fragments in the presence of water, complexes **2** of the form $\{Cp^*M[Im'S(CH_2)_2SIm'](H_2O)\}^{2+}\{OTf^-\}_2$ were isolated in high yields. In these species, hydrogen-bonding networks were formed between the O−H bonds of the coordinated water molecule and the imidazole nitrogens on each side, as revealed in X-ray diffraction structures of **2-Me-Ir** and **2-Me-Rh**. Proton NMR spectra of the complexes in the presence of varying amounts of D_2O and H_2O led to formation of the three possible isotopomers, of which the H_2O and HOD isotopomers were detected by ^1H NMR. Three of the complexes were evaluated as modestly active catalysts for transfer hydrogenation of acetophenone in the absence of added base. As a control, the Cp^*Rh^{2+} complex from $PhSCH_2CH_2SPh$ was made and shown to be an ineffective catalyst.

Introduction

Secondary interactions between ligands on a single metal center offer the possibility to tune ligand and catalyst reactivity.[1−4] One class of such systems features Lewis-acidic metals such as Al(III), In(III), or Ti(IV), held by ligands containing Brønsted−Lowry bases near enough to act on intermediates but far enough from the metal to prevent coordination. Prominent examples are found in the work of Shibasaki and Kanai,[5−9] Saa,[10,11] Leckta,[12,13] Snapper and Hoveyda,[14] and Kozlowski.[15] In some systems, even a transition metal (e.g., Ru(II)[16,17]) may act simply as a Lewis acid, not forming metal−carbon bonds.

A second class of system showing the benefits of secondary interactions features a central transition metal whose d-electrons along with those of a pendant base or the proton of a pendant acid participate in bonding changes along the path from reactants to products. After early examples,[18,19] perhaps the most widely studied cases are now the transfer hydrogenation catalysts developed extensively by Noyori and co-workers[20,21] and some related Cp*M systems (M = Ru, Rh, Ir).[22,23] These complexes appear to transfer hydrogen by a new, outer-sphere mechanism featuring cooperat-

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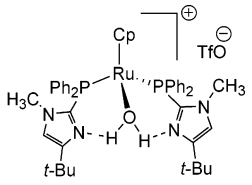
Scheme 1. Comparison of Phosphine and Thioether Complexes



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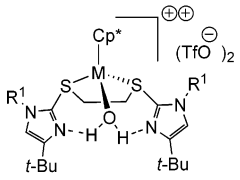

2-Me-Ir $R^1 = CH_3$, M = Ir
2-Me-Rh $R^1 = CH_3$, M = Rh
2-iPr-Ir R^1 = *i*-Pr, M = Ir
2-iPr-Rh R^1 = *i*-Pr, M = Rh

ivity of a metal and the N-H moiety of an amine ligand. In this connection related work by Casey and collaborators on the Shvo catalyst system should also be noted.[24,25] In another set of studies, Drent and collaborators showed[26] that replacing one phenyl group of triphenylphosphine with a 2-pyridyl substituent increased the rate of alkyne alkoxycarbonylation by a factor of at least 1000, and a protonated pyridine substituent may be responsible for this improvement.[27,28] More recently, Grotjahn and co-workers have shown that replacing phenyl groups on phosphines in $[CpRu(PR_3)_2]^+$ fragments with 2-pyridyl[29] or 2-imidazolyl[30] rings can increase rates of anti-Markovnikov alkyne hydration by at least 1000. One key feature of these CpRu systems was the isolation of a discrete complex **1** (Scheme 1) with a hydrogen-bonding network, which was conclusively identified by spectroscopy and X-ray diffraction studies.[30]

Because these ruthenium-phosphine complexes (e.g., **1**) are excellent catalysts for alkyne hydration, it was of interest to see if similar hydrogen-bonding networks could be established in other cases, for example, in thioether-based complexes, or using metal fragments whose complexes would be expected to be air-stable. The lower affinity of thioethers compared with analogous phosphines[31] prompted us to consider new *chelating* bis-thioethers of the form $Im'S(CH_2)_nSIm'$, where $n = 2$ or 3 and Im′ = 1-methyl or 1-isopropyl-4-*tert*-butylimidazol-2-yl (as in structure **2**, Scheme 1). This work was performed with the related dicationic metal fragments Cp^*Ir^{2+} and Cp^*Rh^{2+}, with the expectation that the double positive charge could favor binding of even a water ligand. As a control lacking heterocycles, the known bis-thioether $PhSCH_2CH_2SPh$, which has been shown to function as a chelating ligand,[31−34] would be made and coordinated as well.

A second major motivation for the work reported here is to develop improved catalysts. Transfer of hydrogen between alcohols and ketones or aldehydes has been studied extensively, leading to impressively efficient and enantioselective systems.[20,35−42] In all cases of which we are aware, unless a preformed metal hydride is used as a catalyst,[43] a base such as hydroxide or isopropoxide must be added to achieve hydrogenation. In the structures proposed here, it was felt that the pendant basic nitrogens could act as a local base, perhaps eliminating the need for a strong external base and making the reaction conditions milder.

Results and Discussion

Ligand and Complex Synthesis. The imidazolethione **3-iPr** was a known compound,[44] and **3-Me** was made in a similar way (Scheme 2). Each thione was readily converted to corresponding bis-thioether **4-Me** or **4-iPr** starting with NaH in DMF, followed by addition of the appropriate amount of 1,2-dibromoethane. As far as we are aware, only a handful of similar bis-thioethers have been made from 1-methylimidazole-2-thione and α,ω-dibromoalkanes,[45−47] and from these only metal complexes of uranium, mercury, and gold have been reported.[46,47] In addition, 1,3-dibromopropane could be used to make homologous ligands. Nonheterocyclic ligand $PhSCH_2CH_2SPh$ was made similarly.

Each ligand was purified either by chromatography over silica and recrystallization or by recrystallization alone. The crystal structure of **4-Me** is reported below. The NMR spectral data for the ligands are very similar.

Assembly of hydrogen-bond networks was accomplished by a two-step procedure, first involving ionization of the two chlorides per metal center in dimer $[Cp^*MCl(\mu\text{-}Cl)]_2$ using silver triflate in acetone,[48] fol-

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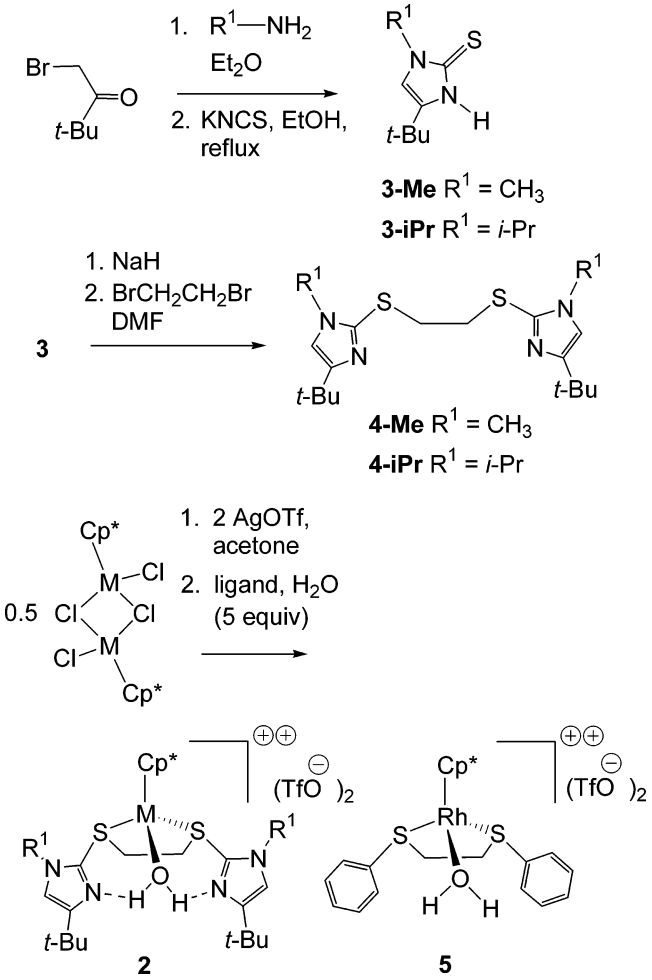
Scheme 2. Ligand and Complex Synthesis



lowed after filtration by addition of the appropriate chelating ligand and 5 equiv of water. After reaction for a day, crystallization afforded complexes of type **2** or **5** in 66 to 89% yields. The composition of the crystalline complexes was confirmed by satisfactory combustion analyses and ultimately, as described below for the heterocyclic species, by X-ray diffraction.

Comparing the NMR spectral data for free and chelating bis-thioether ligands, whereas the CH_2 protons in ligand **4** are all equivalent, giving rise to a four-proton singlet, in the complexes **2** these protons form an AA′BB′ spin system, giving rise to a pair of complex multiplets. The spectral data for **5** were informatively different, as discussed below after an examination of the X-ray crystal structures of **2**.

For the heterocyclic complexes **2**, the proton NMR signal for the aquo protons appeared as a somewhat broad downfield singlet near δ 12 ppm in the case of the Ir complexes and 10 ppm in the case of the Rh congeners.

Interestingly, for the aquo protons of each heterocyclic complex, spectra in deuterated acetone showed two downfield singlets, in varying ratios depending on sample preparation. Eventually, evidence was gathered to indicate that the upper-field resonance was due to the expected complex with an H_2O ligand, whereas the lower-field one was due to its HOD isotopomer. First, the lower-field resonance could be made to disappear by adding H_2O, with concomitant increase of the upper-field one up to the point where its integrated area reached a maximum corresponding to two protons. Second, both resonances could be made to disappear by adding D_2O. Third, during these manipulations, other than changes in the area and chemical shift of the peak ascribed to protons of free water, there was no significant change in the remainder of the proton NMR spectrum. The one exception to this observation constitutes the fourth and final piece of evidence that the downfield peak was due to the HOD isotopomer: in such a species, there is no plane of symmetry bisecting the chelating ligand, and the two imidazoles would be inequivalent. Consistent with this, careful examination of ^{1}H NMR spectra of **2-Me-Ir** and its HOD isotopomer showed in addition to the singlet at 7.37 ppm for the two imidazole aromatic protons of **2-Me-Ir**, two singlets at 7.24 and 7.30 ppm of equal intensity for the inequivalent imidazole aromatic protons in the unsymmetrical HOD complex.

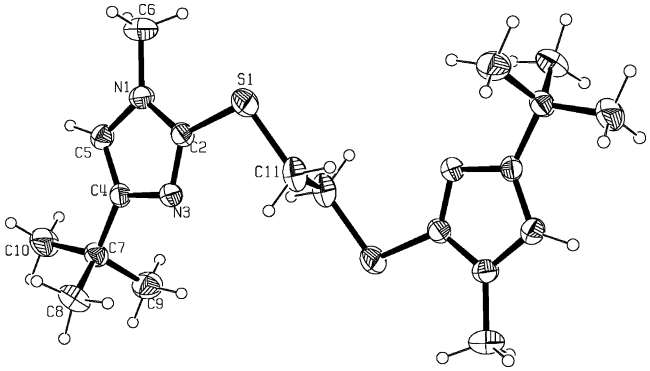


Figure 1. Molecular structure of ligand **4-Me**. Ellipsoids are at 30% probability.

The ^{13}C NMR shifts of the Cp* carbons attached to the metal are upfield in the Ir cases by approximately 6.5 ppm from those in the Rh cases, a general effect for related second- and third-row metals that we ascribed to relativistic effects.[49]

Infrared spectra of complexes **2-Me-Ir** and **2-iPr-Ir** in Nujol mulls show two absorptions at 3554 and 3504 cm^{-1}. These values are in the general region seen for other metal-aquo complexes; however, because of the range of values observed previously,[50,51] determining the degree of hydrogen bonding had to be left to X-ray diffraction results.

X-ray Structures. Figure 1 shows the molecular structure of ligand **4-Me**. The bond lengths and angles will be left without comment.

As expected, significant changes in molecular shape accompany chelation to a metal fragment, as shown by the molecular structures of **2-Me-Ir** and **2-Me-Rh** in Figures 2 and 3. Because the positions of the hydrogens in the coordinated water molecules are of particular interest, in the case of **2-Me-Ir** their positions were

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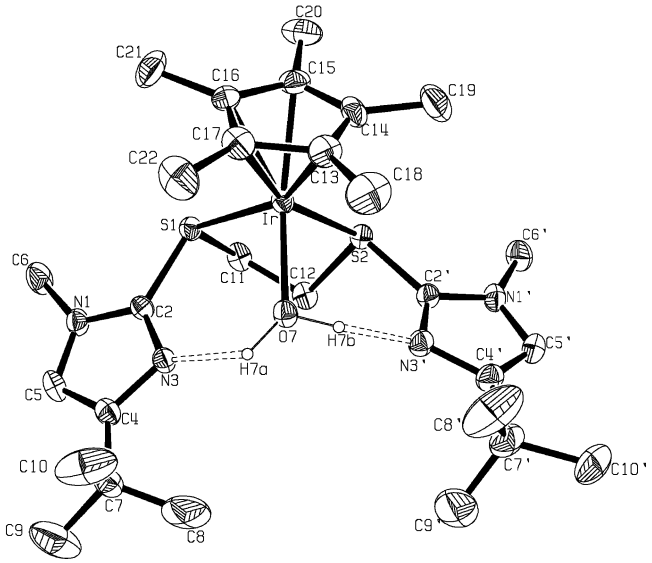

Figure 2. Molecular structure of complex **2-Me-Ir**. Ellipsoids are at 30% probability.

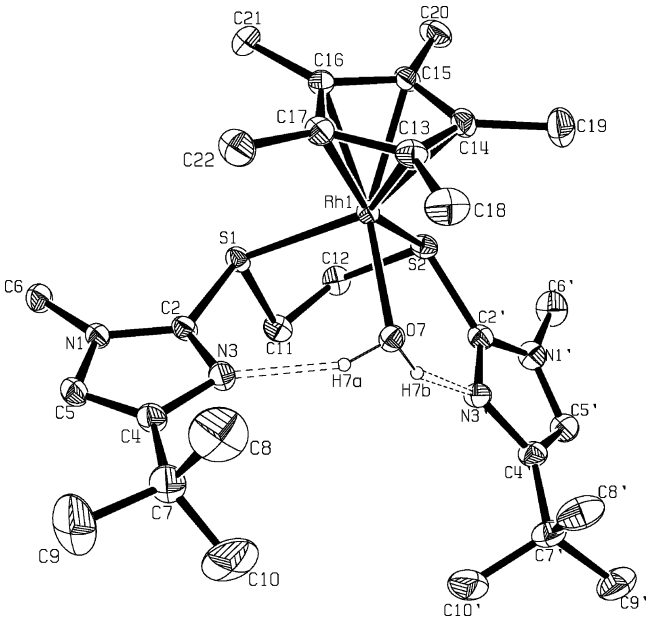

Figure 3. Molecular structure of complex **2-Me-Rh**. Ellipsoids are at 30% probability.

localized and constrained for the refinement process, whereas in the case of **2-Me-Rh** the water protons were both localized and refined. Each structure features an octahedral piano-stool, with the angles S−M−S and S−M−O being somewhat distorted from ideal values of 90°, the angles closest to this ideal value being S−M−O [S−Ir−O = 94.29(10)° and 90.78(9)°, S−Rh−O = 91.33(6)° and 94.98(6)°]. The S−M−S angles are considerably less than 90° [S−Ir−S = 85.17(4)° and S−Rh−S = 84.69(3)°], certainly having to do with the bite angle of the bis-thioether ligand.

The data in Figures 2 and 3 clearly show the presence of hydrogen bonds between the hydrogens of the coordinated water molecules and the two imidazole nitrogens (in the case of **2-Me-Ir**, 1.92 and 1.71 Å, and in **2-Me-Rh**, 1.87(4) and 1.76(4) Å). These distances compare favorably with those seen in **1** (1.802 and 1.638 Å). The metal−oxygen distances are slightly shorter (ca. 0.03 Å) than those reported by Amouri et al. for $[Cp^*M(H_2O)(acetone)_2]^{2+}$.[52]

Comparing NMR Spectra of Heterocyclic and Nonheterocyclic Complexes. The spectral data for **2** and **5** strongly suggest some interesting differences in structure as a function of hydrogen-bonding ability. For Rh complex **2-iPr-Rh** in acetone-d_6, the slightly broad singlet for the aquo protons appeared at δ 10.34 ppm, and in CD_2Cl_2, the same signal appeared at 10.11 ppm. In contrast, for **5** in CD_2Cl_2, the signal for the aquo protons appeared as a much broader singlet near 3.2 ppm at ambient temperature, which at −80 °C moved downfield to 6.0 ppm and sharpened. In short, the presence of hydrogen bond acceptors in the complex shifts the signal for the protons involved in the hydrogen bond downfield.

The appearance of the proton NMR resonance(s) for the ligand methylene protons is also very informative. As already mentioned above, in complexes **2** these protons form an AA′BB′ spin system, giving rise to a pair of complex multiplets. In sharp contrast, in CD_2Cl_2 at ambient probe temperature (30 °C), in complex **5** the four CH_2 protons gave rise to a somewhat broad *singlet* at δ 3.47 ppm. However, on cooling the NMR sample to −20 °C, this signal became considerably broader, at −60 °C turning into several broadened multiplets between 3.1 and 4.2 ppm, which sharpened somewhat at −80 °C to reveal two sets of partially overlapping multiplets whose integrals indicated the presence of two species in a ratio of 3 to 2. In addition, at −80 °C under these conditions two Cp* singlets appeared with intensities in a ratio of 3 to 2. The two sets of resonances may be tentatively assigned to two conformers of the complex, one with both phenyls pointing in opposite directions relative to an imaginary plane through the five-membered chelate ring, the other with both phenyls pointing in the same direction. In the phenyl-substituted complex **5** the absence of hydrogen bonding could allow such conformational flexibility, whereas in the heterocyclic complexes the two imidazol-2-yl substituents are held on the same side of the chelate ring through hydrogen bonding. Finally, in spectra of **5** at temperatures above −20 °C the appearance of all ligand methylene protons as a singlet suggests that site exchange occurs rapidly on the NMR time scale, perhaps through dissociation of the aquo ligand, whereas in the heterocyclic complexes no such broadening is apparent.

Reactivity. Metal complexes have been extremely useful in catalyzing the hydration of nitriles to primary amides. Probably the most active systems yet reported convert unhindered nitriles to amides in 3 h to 1 day at 80 °C using 0.5% catalyst.[53−56] We evaluated two of the Cp*M complexes as catalysts at the 10 mol % level by heating them with propionitrile and water in acetone-d_6. After 6 h at 90 °C, although all of the nitrile remained and none of the desired propanamide was

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detected, most of **2-Me-Rh** and **2-Me-Ir** remained intact, showing that under these conditions the complexes are robust to both heat and an excess of water and nitrile, which could conceivably displace the bis-thioether ligand.

Greater success was achieved by evaluating three of the complexes for their ability to serve as catalysts for transfer hydrogenation of acetophenone by 2-propanol. After intial screening of various reaction conditions, the complexes were used at the 10 mol % level relative to acetophenone, in mixtures heated at 70 °C. After 4 h, yields of 1-phenylethanol were 6.6%, 13%, and 91% for **2-Me-Ir**, **2-iPr-Ir**, and **2-Me-Rh**, respectively. Thus, **2-Me-Rh** is the fastest catalyst, though further studies would be needed to explain why this is so. Although the catalytic activity is modest compared with existing systems, significantly, transfer hydrogenation was achieved without added hydroxide or alkoxide. Importantly, complex **5**, lacking any heterocyclic groups, was completely ineffective at catalyzing transfer hydrogenation under the same conditions. Further work along these lines may show the generality of this approach.

Conclusions

As designed, two new bis-thioethers with imidazol-2-yl substituents form stable chelates to Cp^*Ir^{2+} and Cp^*Rh^{2+} fragments, forming a binding pocket for coordinated water. Formation of an unsymmetrical HOD isotopomer leads to indicative changes in proton NMR spectral data, both for the coordinated water and for the chelating ligand. X-ray structural data show the geometry of the hydrogen-bonding network in the complexes, which show modest activity in base-free transfer hydrogenation of acetophenone by 2-propanol. Comparing transfer hydrogenation using **2** and **5**, it appears that the heterocycles are necessary to make the title bis-thioether complexes effective catalysts.

Experimental Section

General Procedures. NMR spectra were recorded at 200 or 500 MHz with Varian spectrometers at 30 °C. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane and referenced to residual solvent resonances [^{1}H NMR: 7.27 for C*H*Cl$_3$ in CDCl$_3$, 5.32 for C*H*DCl$_2$ in CD$_2$Cl$_2$, and 2.05 for C*H*D$_2$COCD$_3$ in (CD$_3$)$_2$CO; ^{13}C NMR: 77.23 for *C*DCl$_3$ and 30.60 for *C*D$_3$COCD$_3$], where ^{1}H NMR signals are given followed by multiplicity, coupling constants J in hertz, integration in parentheses. For complex coupling patterns, the first coupling constant listed corresponds to the first splitting listed; for example, for (dt, J = 3.2, 7.9, 1H) the doublet exhibits the 3.2 Hz coupling constant.

IR spectra were obtained on a Perkin-Elmer 1600 series instrument. Elemental analyses were performed at NuMega Resonance Labs (San Diego).

2′-[1,2-Ethanediylbis(thio)]bis[1-methyl-4-*tert*-butyl]-1*H*-imidazole (4-Me). Following a procedure similar to that used for **4-iPr** below, 1-methyl-4-*tert*-butylimidazole-2-thione (1.7568 g, 10.3 mmol), NaH (0.4168 g of 60% in oil, 10.4 mmol), and 1,2-dibromoethane (0.993 g, 5.29 mmol) were allowed to react for 2 h, at which point TLC (EtOAc/CH$_2$Cl$_2$, 1:4) suggested that adding additional portions of thione (53.0 mg, 0.31 mmol) and NaH (85.1 mg of 60% in oil, 2.13 mmol) was advisable. After an additional 3.5 h, the mixture was worked up to give crude product (2.18 g), which began to crystallize. The crude product was redissolved in CH$_2$Cl$_2$ (15 mL) and concentrated to about 1/5 volume. Hexanes (10 mL) was added and the solution boiled until it was reduced to half volume. Addition of hexanes and boiling was repeated, and the mixture left to crystallize. The next day, the mother liquor was removed by pipet and the crystals were dried in air, leaving 1.8961 g (97%). IR (KBr): 2954, 2865, 1559, 1463, 1199, 1138, 742, 715 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 6.63 (s, 2H), 3.59 (s, 6H), 3.13 (s, 4H), 1.29 (s, 18H). ^{1}H NMR (CD$_3$COCD$_3$, 500 MHz): δ 6.80 (s, 2H), 3.57 (s, 6H), 3.29 (s, 4H), 1.21 (s, 18H). ^{13}C{^{1}H} NMR (CD$_3$COCD$_3$, 125.7 MHz): δ 153.0, 139.6, 117.2, 34.6, 33.2, 32.5, 30.6. Anal. Calcd for C$_{18}$H$_{30}$N$_4$S$_2$ (366.60): C, 58.97; H, 8.25; N, 15.28. Found: C, 58.58; H, 8.04; N, 15.09.

2′-[1,2-Ethanediylbis(thio)]bis[1-isopropyl-4-*tert*-butyl]-1*H*-imidazole (4-iPr). Under argon a solution was made from 1-isopropyl-4-*tert*-butylimidazole-2-thione (1.32 g, 6.66 mmol) and dry DMF (12 mL). The flask was cooled in an ice bath, and NaH (0.279 g, 6.9 mmol) was added. After 5 min, the ice bath was removed. After an additional 1 h, the flask was cooled in an ice bath once more, and 1,2-dibromoethane (0.591 g, 3.15 mmol) was added. After 22 h, a solution of Na$_2$CO$_3$ (50 mL) of pH 12 was added, and the resulting mixture was extracted with EtOAc (4 × 25 mL). The aqueous phases were combined and washed with water (2 × 50 mL), dried over MgSO$_4$, and filtered, and the filtrate was concentrated by rotary evaporation. The oily residue was purified using radial chromatography over a 4 mm SiO$_2$ plate and eluted with mixtures of ethyl acetate in dichloromethane, to give a white crystalline solid (0.449 g, 1.06 mmol, 33%). IR (KBr): 2966, 2864, 1552, 1435, 1362, 1224, 1196, 750 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 6.68 (s, 2H), 4.62 (septet, J = 6.6 Hz, 2H), 3.13 (s, 4H), 1.36 (d, J = 6.6 Hz, 12H), 1.23 (s, 18H). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 153.2, 136.9, 110.8, 48.0, 35.2, 32.0, 30.1, 23.6. Anal. Calcd for C$_{22}$H$_{38}$N$_4$S$_2$ (422.69): C, 62.51; H, 9.06; N, 13.26. Found: C, 61.94; H, 8.20; N, 13.29.

1,2-Bis(phenylthio)ethane. Following a procedure similar to that used for **4-iPr**, benzenethiol (2.20 g, 20 mmol), NaH (0.842 g of 60% in oil, 21 mmol), and 1,2-dibromoethane (1.878 g, 10 mmol) were allowed to react for 24 h. The reaction mixture was worked up to give a white crude product, which was purified by crystallization from a concentrated solution in diethyl ether/hexane. The obtained white crystals were washed with cold pentane (3 × 25 mL) and vacuum-dried (2.219 g, 90%). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.10−7.40 (br m, 10H), 3.07 (s, 4H). ^{13}C{^{1}H} NMR (CDCl$_3$, 50.2 MHz): δ 134.6, 129.6, 128.7, 126.2, 33.2.

Representative Procedure for the Synthesis of Complexes. Synthesis of 2-Me-Ir. Under argon, deoxygenated acetone (7 mL) was added to the dimer [Cp*IrCl(μ-Cl)]$_2$ (0.1629 g, 0.2044 mmol) and AgOTf (0.2102 g, 0.8182 mmol), leading to the formation of a white precipitate and a yellow solution. The mixture was stirred 3 h at ambient temperature before being filtered using a cannula. (In some cases the filtrate was passed through a Pasteur pipet containing a bit of cotton to eliminate traces of solid.) The filtrate solution was delivered to a Schlenk flask containing bis(1-methyl-4-*tert*-butylimidazol-2-yl)ethane (**4-Me**, 0.1498 g, 0.4086 mmol). Degassed water (36.7 μL, 2.04 mmol) was added, and the solution was stirred at ambient temperature for 22 h. The solution was concentrated to a volume of approximately 4 mL, deoxygenated ether (2 mL, approximately) was added, and the flask was placed in the refrigerator for 9 days to produce small yellow crystals of **2-Me-Ir**, which were dried under vacuum (0.3679 g, 0.3642 mmol, 89%). Mp: 119−122 °C. ^{1}H NMR (acetone-d_6, 200 MHz): δ 12.03 (br s, 1H), 11.83 (br s, 2H), 7.37 (s, 2H), 4.11 (s, 6H), 3.83 (m, 2H), 3.48 (m, 2H), 1.90 (s, 15H), 1.27 (s, 18H). ^{13}C NMR (acetone-d_6, 125.71 MHz): δ 153.9, 134.7, 122.0, 99.0, 43.7, 35.1, 32.6, 30.2, 9.0. Anal. Calcd for C$_{30}$H$_{47}$F$_6$IrN$_4$O$_7$S$_4$ (1010.20): C, 35.67; H, 4.69; N, 5.55. Found: C, 35.31; H, 4.69; N, 5.57.

Synthesis of Complex 2-iPr-Ir. Following the general procedure, [Cp*IrCl(μ-Cl)]$_2$ (0.3769 g, 0.4731 mmol), AgOTf (0.4861 g, 1.892 mmol), and ligand **4-iPr** (0.40 g, 0.946 mmol)

Table 1. Collection Data for Crystal Structures of 4-Me, 2-Me-Ir, and 2-Me-Rh

	4-Me	2-Me-Ir	2-Me-Rh
formula	$C_{18}H_{30}N_4S_2$	$C_{36}H_{59}F_6IrN_4O_9S_4$	$C_{31}H_{49}Cl_2F_6N_4O_7RhS_4$
M_w	366.58	1126.31	1005.79
cryst dimens (mm)	0.346 × 0.282 × 0.254	0.292 × 0.188 × 0.156	0.462 × 0.196 × 0.114
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	6.430(1)	11.892(1)	12.578(1)
b (Å)	9.321(1)	14.532(1)	13.659(1)
c (Å)	9.463(1)	15.385(1)	13.886(1)
α (deg)	83.124(2)	101.934(1)	68.913(1)
β (deg)	73.692(2)	95.489(1)	80.391(1)
γ (deg)	75.836(2)	103.635(1)	84.195(1)
V (Å^3)	527.0(1)	2498.6(3)	2192.5(3)
Z	1	2	2
diffractometer	Bruker Smart Apex CCD	Bruker Smart Apex CCD	Bruker Smart Apex CCD
D_{calcd} (g cm^{-3})	1.155	1.497	1.524
λ (Å)	0.71073	0.71073	0.71073
T (K)	293(2) K	293(2) K	293(2) K
$2\theta_{max}$ (deg)	30.52	30.55	30.57
no. of measd reflns	9242	44 138	38 696
no. of indep reflns	3191 [R(Int) = 0.031]	15 164 [R(Int) = 0.1239]	13 331 [R(Int) = 0.0569]
no. of reflns with $I > 2\sigma(I)$	2276	9302	9042
no. of params	113	559	515
$R(F)$ ($I > 2\sigma(I)$), %	6.27 wR_2 = 16.92	5.53 wR_2 = 10.43	5.22 wR_2 = 9.30
$R(wF^2)$ ($I > 2\sigma(I)$), %	8.42 wR_2 = 18.47	9.45 wR_2 = 11.50	8.49 wR_2 = 10.19
GOF	1.031	0.977	0.980

were used to make **2-iPr-Ir** (0.7595 g, 0.7122 mmol, 75%). Mp: 137−139 °C. ^{1}H NMR (acetone-d_6, 200 MHz): δ 12.09 (br s, 1H), 11.88 (br s, 2H), 7.60 (s, 2H), 5.31 (septet, J = 6.6 Hz, 2H), 3.87 (m, 2H), 3.45 (m, 2H), 1.89 (s, 15H), 1.63 (d, J = 6.6 Hz, 6H), 1.29 (s, 18H). ^{13}C NMR (acetone-d_6, 50 MHz): δ 154.4, 132.9, 116.8, 98.6, 51.3, 44.6, 32.7, 24.0, 23.3, 8.9. Anal. Calcd for $C_{34}H_{55}F_6N_4IrO_7S_2 + CH_2Cl_2$ (1087.11): C, 38.67; H, 5.28; N, 5.15. Found: C, 38.18; H, 5.01; N, 5.65.

Synthesis of 2-Me-Rh. Following the general procedure, [Cp*RhCl(μ-Cl)]$_2$ (0.126 g, 0.204 mmol), AgOTf (0.210 g, 0.818 mmol), and **4-Me** (0.149 g, 0.409 mmol) were used to make **2-Me-Rh** (0.2722 g, 0.2955 mmol, 72%). Crystals for X-ray diffraction were obtained by diffusing pentane into a concentrated solution of the complex in dichloromethane. ^{1}H NMR (acetone-d_6, 200 MHz): δ 10.44 (br s, 1H), 10.25 (br s, 2H), 7.41 (s, 2H), 4.09 (s, 6H), 3.90 (m, 2H), 3.50 (m, 2H), 1.88 (s, 15H), 1.28 (s, 18H). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 10.14 (br s, 2H), 7.03 (s, 2H), 3.99 (s, 6H), 3.76−3.70 (m, 2H), 3.22−3.18 (m, 2H), 1.77 (s, 15H), 1.24 (s, 18H). ^{13}C NMR (acetone-d_6, 50 MHz): δ 153.6, 133.0, 122.2, 105.5, 42.6, 35.0, 32.7, 30.2, 9.6. ^{13}C NMR (CD_2Cl_2, 75.4 MHz): δ 154.7, 131.8, 121.9, 105.2 (d, J_{C-Rh} = 7.3 Hz), 42.4, 35.1, 32.4, 29.9, 9.7. Anal. Calcd for $C_{30}H_{47}F_6N_4O_7RhS_4$ (920.89): C, 39.13; H, 5.14; N, 6.08. Found: C, 38.73; H, 5.03; N, 5.90.

Synthesis of 2-iPr-Rh. Following the general procedure, [Cp*RhCl(μ-Cl)]$_2$ (0.0967 g, 0.1566 mmol) and AgOTf (0.1609 g, 0.6264 mmol) were allowed to react for 40 min in acetone before filtration into a flask containing ligand **4-iPr** (0.1324 g, 0.3132 mmol). Water (28 μL, 1.56 mmol) was added. After 22 h, the solution was concentrated to about 3 mL and ether (about 3 mL) was added until two phases were produced. The flask was stored in the refrigerator 5 days to give small orange crystals after washing with ether and storing under vacuum (0.2023 g, 0.207 mmol, 66%). Mp: 200−201 °C. ^{1}H NMR (acetone-d_6, 200 MHz): δ 10.40 (br s, 1H), 10.34 (br s, 2H), 7.63 (s, 2H), 5.28 (septet, J = 6.6 Hz, 2H), 3.93−3.82 (m, 2H), 3.48−3.34 (m, 2H), 1.86 (s, 15H), 1.61 (d, J = 6.6 Hz, 12H), 1.29 (s, 18H). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 10.11 (br s, 2H), 7.08 (s, 2H), 5.08 (septet, J = 6.8 Hz, 2H), 3.87−3.78 (m, 2H), 3.17−3.10 (m, 2H), 1.77 (s, 15H), 1.58 (d, J = 6.8 Hz, 12H), 1.27 (s, 18H). ^{13}C NMR (acetone-d_6, 50 MHz): δ 154.3, 131.1, 125.0, 118.7, 117.1, 105.1, 105.0, 51.0, 43.4, 32.6, 23.9, 23.4, 9.4. For a sample recrystallized using CH_2Cl_2 and ether, Anal. Calcd for $C_{34}H_{55}F_6N_4RhO_7S_2 + CH_2Cl_2$ (997.80): C, 42.13; H, 5.75; N, 5.62. Found: C, 41.55; H, 5.55; N, 6.07.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2-Me-Ir and 2-Me-Rh

	2-Me-Ir	2-Me-Rh
M−S(1)	2.3580(13)	2.4005(7)
M−S(2)	2.3560(13)	2.4277(8)
M−O(7)	2.137(3)	2.132(2)
M−C(13)	2.173(6)	2.166(3)
M−C(14)	2.155(6)	2.156(3)
M−C(15)	2.139(6)	2.162(3)
M−C(16)	2.172(5)	2.160(3)
M−C(17)	2.177(5)	2.137(3)
O(7)−M−C(13)	90.9(2)	87.71(10)
O(7)−M−C(14)	120.4(2)	107.28(10)
O(7)−M−C(15)	155.4(2)	145.84(10)
O(7)−M−C(16)	130.4(2)	144.43(10)
O(7)−M−C(17)	95.9(2)	105.32(10)
S(1)−M−S(2)	85.17(4)	84.69(3)
S(1)−M−O(7)	94.29(10)	91.33(6)
S(2)−M−O(7)	90.78(9)	94.98(6)
C(11)−S(1)−M	104.74(18)	101.30(10)
C(12)−S(2)−M	101.70(17)	102.83(10)
N(3)···H(7A)	1.92	1.87(4)
N(3′)···H(7B)	1.71	1.76(4)

Synthesis of 5. Under argon, to the dimer [Cp*RhCl(μ-Cl)]$_2$ (0.243 g, 0.393 mmol) and AgOTf (0.404 g, 1.573 mmol) was added deoxygenated acetone (7 mL), leading to the formation of a white precipitate and an orange solution. The mixture was stirred 1 h at ambient temperature before being filtered using a cannula. The filtrate solution was delivered to a Schlenk flask containing a solution of 1,2-bis(phenylthio)ethane (0.193 g, 0.786 mmol) in acetone (2 mL). Degassed water (70.8 μL, 3.93 mmol) was added, and the solution was stirred at ambient temperature for 24 h. Evaporation of the solvent to dryness gave the product as an orange solid, which was washed with cold diethyl ether (2 × 4 mL) and vacuum-dried (0.539 g, 0.673 mmol, 85%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 7.65−7.75 (br m, 4H), 7.50−7.56 (br m, 6H), 3.47 (sl br s, 4H), 3.20 (br s, 2H), 1.30 (s, 15H). Partial data at −80 °C: 4.14 (dd, J = 3.5, 12.8 Hz, 0.6 H), 3.98 (sl br d, J = 12.1 Hz, 0.4H), 3.90 and 3.86 (two overlapping sl br d, J = ca 12 Hz, total 1H), 3.54 (sl br dt, J = ca. 3, ca. 12 Hz, 0.4H), 3.40 (dt, J = 4.6, 12.8 Hz, 0.6H), 3.12−3.22 (m, 1H), 1.45 and 1.42 ppm (two s, intensity ratio 2 to 3, total 15H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 50.2 MHz): δ

132.7, 132.5, 130.9, 127.5, 103.5, 39.1, 9.61. Anal. Calcd for $C_{26}H_{31}F_6O_7S_4Rh$ (800.68): C, 39.00; H, 3.90. Found: C, 39.20; H, 3.78.

General Procedure for Acetophenone Reduction. Under argon atmosphere, catalyst **2-Me-Rh** (0.0136 g, 0.0147 mmol) was dissolved in anhydrous 2-propanol (2.5 mL). After stirring the mixture for 5 min at room temperature, acetophenone (0.0117 g, 0.147 mmol) followed by dodecane (0.0125 g, 0.0738 mmol) were added. The mixture was stirred and heated at 70 °C for 4 h, after which the solvent was removed with a stream of argon and the residue was passed through silica (1 g) to remove the catalyst, eluting with dichloromethane (150 mL). The resulting solution was concentrated to a volume of about 4 mL using a rotary evaporator and the solution analyzed by GC.

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Supporting Information Available: CIF files for **4-Me**, **2-Me-Ir**, and **2-Me-Rh**. This information is available free of charge via the Internet at http://pubs.acs.org.

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