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Amide Complexes of Zirconium, Rhodium, and Iridium: Synthesis and Reactivity. X-ray Crystal Structures of $(\eta^5\text{-}C_5H_5)_2Zr(NHC_6H_4\text{-}o\text{-}SMe)_2$ and $[Rh(\mu\text{-}SC_6H_4\text{-}o\text{-}NHMe)(COD)]_2$[†]

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The reaction of Cp_2ZrCl_2 (Cp = η^5-C_5H_5) with 2 equiv of the lithium amide derivative $LiNHC_6H_4$-*o*-SMe affords the new zirconium complex $Cp_2Zr(NHC_6H_4$-*o*-$SMe)_2$ (**2**). The structure of **2** has been determined by X-ray diffraction. When the reaction is carried out in an 1:1 ratio, the complex $Cp_2ZrCl(NHC_6H_4$-*o*-SMe) (**3**) is generated as the major product. Reaction of "$Cp*_2Zr$" (Cp* = η^5-C_5Me_5) with 2-(methylmercapto)aniline yields a hydride−amide complex $Cp*_2ZrH(NHC_6H_4)$ (**4**). Reaction of complex **2** with $[RhCl(COD)]_2$ generates complex **3** and the new rhodium amide complex $Rh(NHC_6H_4$-*o*-SMe)(COD), which has been also directly synthesized by reacting $[RhCl(COD)]_2$ with $LiNHC_6H_4$-*o*-SMe. Thermolysis of complex **6**, at 100 °C, produces to a new rhodium thiolate complex $[Rh(\mu$-SC_6H_4-*o*-NHMe)-$(COD)]_2$ (**5**). Its structure has been determined by X-ray diffraction methods. Reaction of $[IrCl(COD)]_2$ with $LiNHC_6H_4$-*o*-SMe gives the iridium(III) complex $Ir(Me)(SC_6H_4NH)(COD)$ (**7**) by oxidative addition of the S−Me bond.

Introduction

In the past few years, there has been a growing interest in the chemistry of transition metal amide complexes studied mainly for early transition metals in a high oxidation state.[1] Only a limited number of complexes of late transition metals in high oxidation states have been reported and even fewer in their lower one.[2] Some of these derivatives can act as catalysts in hydroammination processes,[3] furthermore, they can be used as precursors in the synthesis of imide[4] complexes, which are the focus of much attention because of their reactivity and applications to organic transformations[5] and to the synthesis of heterometallic complexes.[6]

Moreover, in recent years, transition metal complexes with ligands containing dissimilar donor atoms such as sulfur and nitrogen have been widely investigated, primarily for their applications in the synthesis of early−late transition metal heterometallic complexes.[7] Such ligands would be capable of forming strong bonds with early transition metals in their higher oxidation state through the nitrogen atom, while the sulfur atom would assist the formation of the heterometallic complex by forming a stable bond to the late transition metal center.

We have undertaken the synthesis of zirconium complexes with 2-(methylmercapto)anilide as the amide

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ligand containing dissimilar donor atoms with the aim of bonding the sulfur atom to a rhodium or iridium center and forming heterometallic complexes. Such complexes are particularly interesting because of their relevance in understanding and modeling the key processes involved in metal-catalyzed hydrodesulfurization.[8]

Herein, we report the synthesis and characterization of some amide complexes of zirconium and their reactivity toward $[Rh(\mu\text{-}Cl)(COD)]_2$ as well as the synthesis of an amide complex of rhodium and its thermolysis reaction through a sulfur−carbon bond cleavage process.

Results and Discussion

Synthesis of the Zirconium Complexes. Lithium amides have been shown to react with early transition metal chlorides to provide metal amides in high yield.[9] This methodology is useful in the synthesis of bis-amide complexes, such as $Cp_2Zr(NHR)_2$ ($Cp = \eta^5\text{-}C_5H_5$). In this way, reaction of Cp_2ZrCl_2 (**1**) with 2 equiv of lithium 2-(methylmercapto)phenylamide in THF at room temperature afforded the zirconium bis-amide complex **2** in 76% yield (eq 1).

$$\underset{\mathbf{1}}{Cp_2ZrCl_2} + 2LiNH(C_6H_4\text{-}o\text{-}SMe) \rightarrow \underset{\mathbf{2}}{Cp_2Zr(NHC_6H_4\text{-}o\text{-}SMe)_2} + 2LiCl \quad (1)$$

The yellow complex **2** is air sensitive, soluble in THF and toluene, and partially soluble in pentane. It has been characterized by ^1H and ^{13}C NMR and IR spectroscopy (see Experimental Section), and its structure has been determined by X-ray diffraction. The ^1H and ^{13}C NMR spectra show that both amide groups are equivalent, pointing to the nonexistence, in solution, of bonding between the sulfur atoms and the zirconium center. In the same way, both cyclopentadienyl groups are equivalent.

The bonding mode in complex **2** is confirmed by its structure in the solid state, which has been determined by X-ray diffraction. X-ray-quality crystals were grown by slow diffusion of pentane on a THF-saturated solution. An ORTEP drawing of the structure is shown in Figure 1. Selected bond distances and angles are given in Table 1.

Complex **2** exhibits the typical bent metallocene structure. The cyclopentadienyl rings are bonded to the zirconium atom in a nearly symmetric η^5-fashion. The Zr(1)−CE(1) and Zr(1)−CE(2) (CE = ring centroid) distances of 2.2338(4) and 2.2324(4) Å compare well with those of other $Cp_2Zr(IV)$ complexes.[10]

The zirconium atom is also bonded to both amide ligands through N(4) and N(5) with bond distances of 2.122(3) and 2.110(4) Å, respectively, which are in the range expected for Zr(IV) amide complexes.[11] Angles Zr(1)−N(4)−C(1) and Zr(1)−N(5)−C(8) are 134.7(3)° and 133.6(3)°, respectively, and could indicate a π-bonding contribution between the N and the zirconium atom.

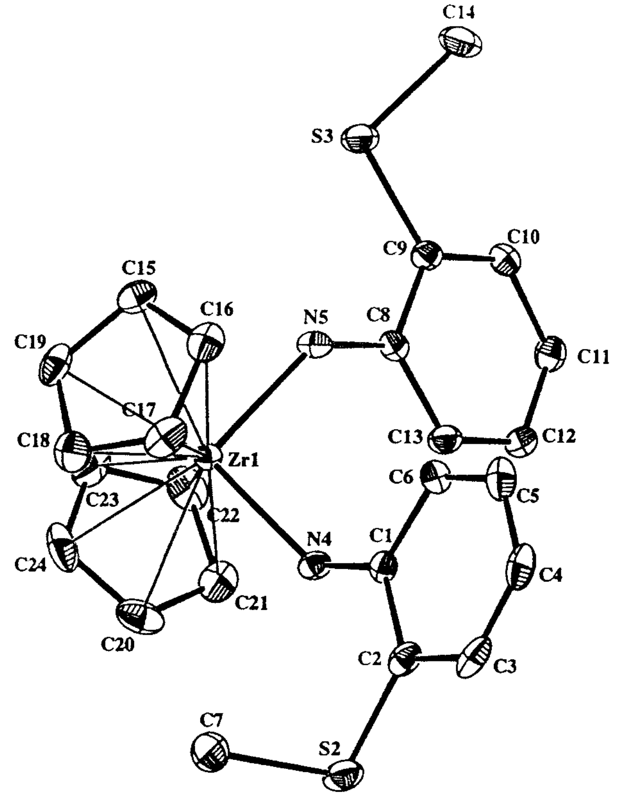

Figure 1. ORTEP drawing of complex **2** with the atom-labeling scheme.

Table 1. Selected Bond Distances (Å) and Angles (deg) (with Esds in Parentheses) for 2[a]

Zr(1)−CE(1)	2.2338(4)	S(2)−C(2)	1.768(6)
Zr(1)−CE(2)	2.2324(4)	S(2)−C(7)	1.807(6)
Zr(1)−N(4)	2.122(3)	S(3)−C(9)	1.770(5)
Zr(1)−N(5)	2.110(4)	S(3)−C(14)	1.790(6)
N(4)−C(1)	1.378(5)	N(5)−C(8)	1.399(5)
CE(1)−Zr(1)−CE(2)	128.33(2)	N(4)−Zr(1)−N(5)	98.90(14)
Zr(1)−N(4)−C(1)	134.7(3)	Zr(1)−N(5)−C(8)	133.6(3)

[a] CE(1) and CE(2) are the centroids of the C15···C19 and C20···C24 cyclopentadienyl rings, respectively.

The phenyl groups are pointing away from each other, and the methylmercapto moieties are oriented in such a way that steric interactions are reduced to the minimum. Zr−S distances are very long, and therefore, existence of a Zr−S bond, in the solid state, can also be ruled out.

Reaction of Cp_2ZrCl_2 (**1**) with 1 equiv of lithium 2-(methylmercapto)phenylamide afforded the monoamide complex **3** (eq 2). When the reaction is carried

$$\underset{\mathbf{1}}{Cp_2ZrCl_2} + Li(NHC_6H_4\text{-}o\text{-}SMe) \rightarrow \underset{\mathbf{3}}{Cp_2ZrCl(NHC_6H_4\text{-}o\text{-}SMe)} + LiCl \quad (2)$$

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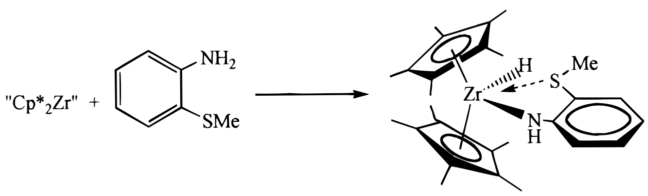
Scheme 1



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out by addition of complex **1** to the lithium amide solution, complex **2** is quantitatively formed instead of complex **3**. To avoid the second chloride substitution, the reaction has to be carried out by slow addition of the lithium amide solution to the zirconium complex solution, and even under these conditions, complex **3** is always isolated contaminated with ca. 15% of the disubstituted compound **2**. Nevertheless, it was possible to characterize it spectroscopically.

The bright yellow complex **3** is extremely air sensitive, soluble in THF and toluene, and partially soluble in pentane. Its ^{1}H NMR spectrum shows singlets at 1.98, 5.88, and 7.65 (broad signal) ppm, which are assigned to the methyl group, the cyclopentadienyl rings, and the proton bonded to the nitrogen atom, respectively. The high-field shift of the methyl signal suggests that there is no bond between the sulfur atom and the zirconium center. Aromatic protons appear as multiplet signals between 6.81 and 7.49 ppm. The ^{13}C{^{1}H} NMR spectrum is consistent with the bonding mode proposed on the basis of the ^{1}H NMR spectrum.

In an effort to gain deeper insight on the bonding modes of the 2-(methylmercapto)amide group, the reaction between "Cp*$_2$Zr" (Cp* = η^5-C_5Me_5) (generated in situ by reaction of $Cp^*_2ZrCl_2$ and 2 equiv of Li^{t}Bu) and 2-(methymercapto)aniline has been carried out and gives, through an oxidative-addition process, the hydride–amide complex **4**.

Complex **4** was isolated as a pale yellow solid, and it is air sensitive and very soluble in most organic solvents. It has been characterized by elemental analysis and IR and ^{1}H and ^{13}C NMR spectroscopic techniques. The ^{1}H NMR spectrum shows singlets at 1.83 and 2.31 ppm which correspond to the Cp* ligand and the methyl group bonded to the sulfur atom, respectively. The spectrum also shows two more signals at 3.18 and 4.20 ppm assigned to the NH and hydride groups. Both signals are in the expected range,[12] but it was not possible to unequivocally assign them. Furthermore, aromatic protons give rise to multiplet signals between 6.43 and 7.11 ppm. The signal attributed to the methyl group is located at a relatively low field when compared with that in other zirconium complexes reported in this paper. It might be indicative of the existence of an interaction between the sulfur atom and the zirconium center in this complex. In the same way, the ^{13}C NMR spectrum shows that the carbon atoms directly bonded to the sulfur atom are shifted to lower field than that in other zirconium complexes.

Reaction of $Cp_2Zr(NHC_6H_4$-*o*-SMe$)_2$ (2) with [Rh(μ-Cl)(COD)]$_2$. Complex **2** reacts with [Rh(μ-Cl)(COD)]$_2$ in toluene, at 100 °C, to give, by slow cooling to room temperature, amber-colored crystals which were identified, by an X-ray diffraction study, as a rhodium(I) thiolate dimer complex **5** (Scheme 2).

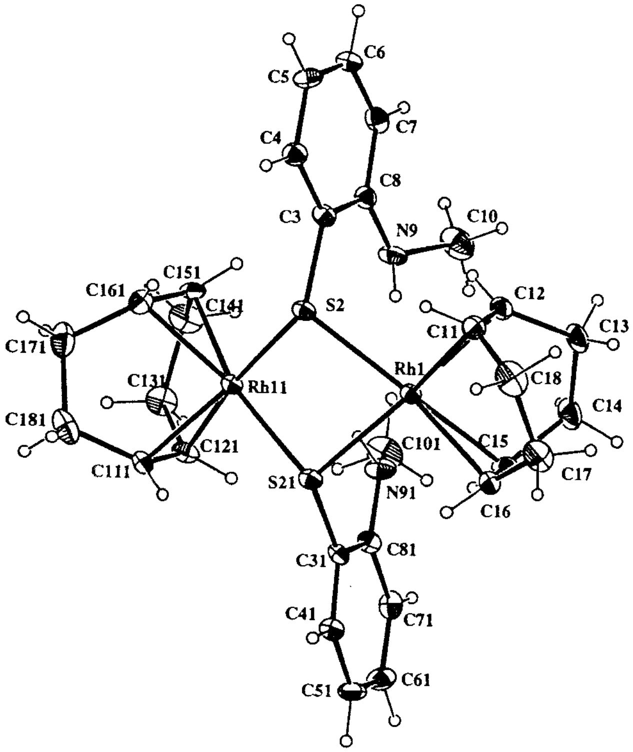

Figure 2. ORTEP drawing of complex **5** with the atom-labeling scheme.

An ORTEP view of the molecule with the atom-labeling scheme is shown in Figure 2. Table 2 lists the most significant intramolecular distances and bond angles with their standard deviations.

The crystal structure shows that coordination around each rhodium atom is approximately square planar. Two bridging sulfur atoms and a chelating cyclooctadiene are bonded to each metal atom. The Rh_2S_2 ring is puckered, the dihedral angle between the S(2)–Rh(1)–S(21) and S(2)–Rh(11)–S(21) planes being 145.80(5)°. The amine–thiolate bridging groups are in a syn configuration with respect to the four-membered ring Rh_2S_2 core.

The Rh–S bond lengths (Rh(1)–S(2) = 2.351(2) Å, Rh(1)–S(21) = 2.362(2) Å) are in the short range of bond lengths found for binuclear thiolate-bridged complexes; the longest related bond was reported for [Rh(μ-SC_6F_5)(COD)]$_2$ (average 2.41 Å),[13] and the shortest was reported for [Rh(μ-$S(CH_2)_3NMe_2$)(COD)]$_2$ (average 2.34 Å).[14] The Rh–C bond distances fall in the range 2.139(9)–2.177(10) Å, which are normal values for Rh(I) complexes containing COD ligands trans to S donor atoms.[15]

Complex **5** is air stable and rather insoluble in toluene or pentane and has been characterized by ^{1}H NMR and IR spectra. The ^{1}H NMR spectrum of complex **5** shows signals for the cyclooctadiene ligand at 1.60 and 2.12

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Scheme 2

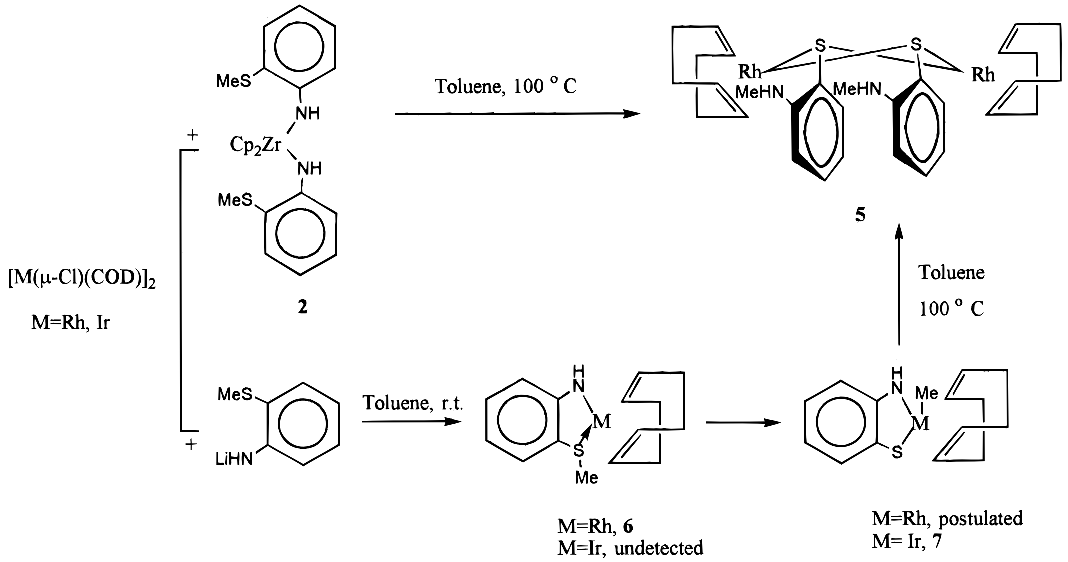

Table 2. Selected Bond Distances (Å) and Angles (deg) (with Esds in Parentheses) for 5

Rh(1)−C(11)	2.139(9)	Rh(1)−S(2)	2.351(2)
Rh(1)−C(12)	2.169(9)	Rh(1)−S(21)	2.362(2)
Rh(1)−C(15)	2.134(10)	C(8)−N(9)	1.384(12)
Rh(1)−C(16)	2.177(10)	N(9)−C(10)	1.432(14)
S(2)−C(3)	1.773(9)		
C(3)−S(2)−Rh(1)	115.0(3)	N(9)−C(8)−C(3)	120.9(9)
Rh(1) −S(2)- Rh(11)	95.30(9)	C(8)−N(9)−C(10)	122.0(9)
S(2)−Rh(1)−S(21)	78.69(9)		

(methylene) and 4.12 ppm (olefinic protons). The thiolate moiety exhibits a doublet at 2.80 ppm assigned to the methyl group, a broad signal at 3.65 ppm due to the amminic proton, and several multiplet signals between 6.38 and 7.07 ppm for the aromatic protons.

To establish the mechanism of the unexpected reaction, we carried out the experiment in an NMR tube with toluene-d_8 as the solvent. After 30 min at room temperature, the ^1H NMR spectrum shows that the starting compounds $[Rh(\mu\text{-}Cl)(COD)]_2$ and the zirconium complex **2** react in a practically quantitative way to form $Cp_2ZrCl(NHC_6H_4\text{-}o\text{-}SMe)$ (**3**) and a new rhodium complex that was identified as $[Rh(NHC_6H_4\text{-}o\text{-}SMe)(COD)]$ (**6**) on the basis of their spectroscopic data (see below).

To confirm the formation of the rhodium amide complex **6**, its synthesis was alternatively carried out by reacting $[Rh(\mu\text{-}Cl)(COD)]_2$ with $Li(NHC_6H_4\text{-}o\text{-}SMe)$, prepared in situ (Scheme 2).

Complex **6** was isolated as a green compound that is air stable in the solid state, and it has been characterized by elemental analysis and ^1H and ^{13}C NMR and IR spectroscopies. It is rather soluble in THF and toluene, only sparsely soluble in pentane. ^1H NMR shows that the olefinic protons of the COD group give rise to two different multiplet signals at 3.72 and 4.49 ppm, indicating different groups in a trans position, suggesting coordination of the sulfur atom as drawn in Scheme 2. The methylene groups appear at 1.85 and 2.23 ppm as complex signals. The singlet at 1.95 ppm can be assigned to the methyl group bonded to the sulfur atom, and the aromatic protons appear as multiplet signals between 6.38 and 7.07 ppm. Finally, the proton bonded to the nitrogen atom gives rise to a broad signal at 4.30 ppm. ^{13}C NMR data are consistent with the proposed bonding mode.

According to these results, we can conclude that the first step of the reaction between complex **2** and $[Rh(\mu\text{-}Cl)(COD)]_2$ is the transfer of the amide ligand from the zirconium center to the rhodium and of the chloride from the rhodium to the zirconium atoms to yield complex **6** and $Cp_2ZrCl(NHC_6H_4\text{-}o\text{-}SMe)$ (**3**).

To verify the next reaction step, a solution of complex **6** in toluene-d_8 was heated to 100 °C for 1 h, and at the same time, in an independent experiment, a 1:2 mixture of $[Rh(\mu\text{-}Cl)(COD)]_2$ and $Cp_2Zr(NHC_6H_4\text{-}o\text{-}SMe)_2$ was also dissolved in toluene-d_8 and heated to the same temperature. After 2 h, the signals assigned to the rhodium thiolate complex **5** appear, indicating that the transformation has taken place in both cases, approximately in a 43% yield. From these results one can conclude that the zirconium complexes play no role in the thermal rearrangement of **6** to give the thiolate complex **5**. Such rearrangement can take place through an oxidative addition of the S−Me bond at the rhodium(I) atom followed by a reductive-elimination step to form the N−Me bond (Scheme 2). Attempts to isolate or detect the possible rhodium(III) intermediate complex, by heating it up at a lower temperature, have been unsuccessful.

Reaction of $[Ir(\mu\text{-}Cl)(COD)]_2$ with $Li(NHC_6H_4\text{-}o\text{-}SMe)$. Considering the evolution of complex **6** to a thiolate compound, which involves a sulfur−carbon bond breaking, we decided to further explore the reactivity of the 2-(methylmercapto)phenylamide ligand with an iridium center, which could stabilize higher oxidation states better than rhodium.

In this context, we carried out the reaction between $[Ir(\mu\text{-}Cl)(COD)]_2$ and $Li(NHC_6H_4\text{-}o\text{-}SMe)$, prepared in situ in THF at room temperature (Scheme 2), which renders complex **7** as a purple crystalline solid. This compound was shown to be the most stable one under these conditions. It can be described as $Ir(Me)(SC_6H_4\text{-}o\text{-}NH)(COD)$, as a result of the proposed oxidative addition on the initially formed $Ir(NHC_6H_4\text{-}o\text{-}SMe)(COD)$ complex.

Complex **7** is very soluble in THF or toluene and partially soluble in pentane. It has been characterized by IR and ^{1}H and ^{13}C NMR spectroscopies. Its ^{1}H NMR spectrum shows a singlet signal at 1.09 ppm which is assigned to methyl group, and the ^{13}C NMR spectrum shows the resonance of the carbon atom of the methyl group at 54.1 ppm.[16] Both values indicate that the methyl group is no longer bonded to the sulfur atom but to the iridium center, and therefore, an oxidative addition of the S−Me bond has taken place. Besides, both the ^{1}H and ^{13}C NMR spectra indicate that the environment of the COD group is asymmetric, giving place to four different signals for the olefinic protons as well as for the olefinic carbon atoms.

On the basis of these results with the iridium complex, we can establish that in the reaction of **2** and [Rh(μ-Cl)(COD)]$_2$, the formation of **5** can take place by a reductive elimination in the undetected Rh(Me)(SC$_6$H$_4$-*o*-NH)(COD).

Concluding Remarks

In this paper we have reported the synthesis of some zirconium amide complexes, accessible by halide displacement or by N−H oxidative addition of 2-(methylmercapto)aniline to "Cp*$_2$Zr". We have studied the reaction of Cp$_2$Zr(NHC$_6$H$_4$-*o*-SMe)$_2$ with [Rh(μ-Cl)(COD)]$_2$, which occurs with transfer of the amide ligand from the zirconium to the rhodium atom to form an rhodium amide complex Rh(NHC$_6$H$_4$-*o*-SMe)(COD) while the chloride ligand is transferred to the zirconium yielding complex **3**. This reactivity is particularly intriguing because bonds between hard ligands and soft late transition metals are unfavorable. That is why there are not many amide complexes of low oxidation state metals known and bidentate phosphine−amide ligands have been used to prepare amide complexes of these metals. In our case, coordination of the soft base (S) to rhodium or iridium may assist the concomitant coordination of the amide group, hard base, forming a five-membered ring, stabilizing complex **6**. When the rhodium amide thioether complex **6** is heated to 100 °C, conversion to the bridged thiolate complex, **5**, takes place. However, it was not possible to detect the postulated Rh(III) intermediate compound, whereas for iridium, this is the most stable compound. Oxidative addition of the S−Me bond can possibly take place, rendering the alkyl−amide−thiolate Ir(III) complex. The bond between the amide group and iridium in the 3+ oxidation state could account for a N(pπ)−Ir(dπ) interaction, making complex **7** the most stable one.

Experimental Section

General Procedures. All reactions and product manipulations were carried out under dry nitrogen using standard Schlenk and drybox techniques. Toluene was distilled from sodium, pentane from sodium/potassium alloy, and diethyl ether and THF from sodium benzophenone, under nitrogen. All solvents were deoxygenated prior to use.

The following reagents were prepared by literature procedures: Cp*H,[17] Cp*$_2$ZrCl$_2$,[18] and [Rh(μ-Cl)(COD)]$_2$.[19] The commercially available compounds 2-(methylmercapto)aniline, LiMe in diethyl ether, RhCl$_3$·nH$_2$O, Cp$_2$ZrCl$_2$, Li^{t}Bu, and Li^n-Bu were used as received from Aldrich.

^{1}H and ^{13}C NMR measurements were obtained on either a 200 Gemini or 300 Unity Varian Fourier transform spectrometer. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in units of parts per million relative to SiMe$_4$.

Synthesis of Cp$_2$Zr(NHC$_6$H$_4$-*o*-SMe)$_2$ (2). To a solution of 2-(methylmercapto)aniline (0.5 mL, 3.9 mmol) in 5 mL of Et$_2$O, 2.5 mL of Li^{n}Bu (1.6 M) was added. The reaction mixture was allowed to react at room temperature for 30 min and then cooled at −78 °C, and 0.58 g (2.0 mmol) of Cp$_2$ZrCl$_2$ was added. Subsequently, the cooling bath was removed and the mixture was stirred at room temperature for 1 h. After this time, the solvent was removed under vacuum and the residue extracted with 2 × 20 mL of toluene at 80 °C. The filtrate was pumped dry and washed with 2 × 10 mL of pentane to yield 0.75 g (76%) of **2**. IR (Nujol/PET= polyethylene, cm^{-1}): 3618 (w), 3302 (m), 1611 (m), 1587 (m), 1564 (m), 1288 (s), 1262 (s), 1018 (m), 854 (w), 827 (s), 808 (s), 768 (m). ^{1}H NMR (C$_6$D$_6$): δ 2.07 (s, 6 H, CH$_3$), 3.70 (br, 2 H, N−H), 5.82 (s, 10 H, Cp), 6.64, 7.36 (m, 8 H, C$_6$H$_4$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 16.7 (s, CH$_3$), 110.8 (s, Cp), 119.0, 120.4, 128.5, 130.5 (s, CH), 122.9 (s, C−N), 155.9 (s, C−S). Anal. Calcd for C$_{24}$H$_{26}$N$_2$S$_2$Zr: C, 57.90; H, 5.26; N, 5.63. Found: C, 57.60; H, 5.30; N, 5.60.

Synthesis of Cp$_2$ZrCl(NHC$_6$H$_4$-*o*-SMe) (3). A solution of Li(NHC$_6$H$_4$-*o*-SMe), prepared in situ by reaction of 2-(methylmercapto)aniline (0.2 mL, 1.6 mmol) with Li^{n}Bu (1 mL, 1.6 mmol) in 5 mL of Et$_2$O, was slowly added to a suspension of Cp$_2$ZrCl$_2$ (0.47 g, 1.6 mmol) in Et$_2$O at 0 °C. Then the mixture was stirred at room temperature for 1 h, and the solvents were removed under vacuum. The residue was extracted with toluene (2 × 10 mL), and after filtration, the toluene was evaporated and the yellow solid was washed with pentane and dried under vacuum to give 0.34 g (54%) of product **3**. ^{1}H NMR (C$_6$D$_6$): δ 1.98 (s, 3 H, CH$_3$), 5.88 (s, 10 H, Cp), 6.81−7.49 (m, 4 H, CH), 7.65 (br, 1H, NH). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 15.9 (s, CH$_3$), 112.6 (s, Cp), 121.4, 123.4, 127.4, 127.7 (s, CH), 125.5 (s, C−N), 155.0 (s, C−S).

Synthesis of Cp*$_2$ZrH(NHC$_6$H$_4$-*o*-SMe) (4). A suspension of Cp*$_2$ZrCl$_2$ (0.97 g, 2.2 mmol) in 5 mL of THF was treated with 2.6 mL (4.5 mmol) of Li^{t}Bu (1.7 M in hexane), and the mixture was stirred at room temperature for 30 min. After this time, it was cooled to −78 °C and 0.28 mL (2.2 mmol) of 2-(methylmercapto)aniline was added, the cooling bath removed, and the mixture stirred at room temperature for 1 h. The solvents were evaporated under vacuum, the residue was extracted with pentane (2 × 10 mL), and the solution was evaporated to ca. 1 mL and cooled at −30 °C for 24 h, yielding 0.77 g (69%) of **4**. IR (Nujol/PET, cm^{-1}): 3717 (w), 3684 (m), 3486 (w), 3361 (w), 3289 (w), 1611 (s), 1584 (s), 1565 (m), 1308 (s), 1255 (s), 1031 (m), 854 (s), 518 (s). ^{1}H NMR (C$_6$D$_6$): δ 1.83 (s, 30 H, Cp*), 2.31 (s, 3 H, CH$_3$), 3.18, 4.20 (br, 1 H, N−H, Zr−H), 6.43, 7.11 (m, 4 H, CH). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 11.5 (s, Cp*), 11.9 (s, CH$_3$), 115.3 (s, Cp*), 111.8, 115.8, 127.6, 128.7 (s, CH), 129.2 (s, C−N), 159.5 (s, C−S). Anal. Calcd for C$_{27}$H$_{38}$NSZr: C, 64.74; H, 7.85; N, 2.79. Found: C, 64.25; H, 7.80; N, 2.75.

Synthesis of [Rh(μ-SC$_6$H$_4$-*o*-NHMe)(COD)]$_2$ (5). To a mixture of [Rh(μ-Cl)(COD)]$_2$ (0.095 g, 0.19 mmol) and Cp$_2$Zr(NHC$_6$H$_4$-*o*-SMe)$_2$ (0.19 g, 0.38 mmol), 3 mL of toluene was added and the solution was heated under reflux for 24 h. After this time, the solution was allowed to reach room temperature slowly, yielding crystals of **5** (83 mg, 62%). IR (Nujol/PET, cm^{-1}): 3387 (w), 3242 (m), 1573 (s), 1451 (m), 1298 (m), 1274 (m), 859 (m), 443 (m). ^{1}H NMR (C$_6$D$_6$): δ 1.60 (m, 8 H, COD), 2.12 (m, 8 H, COD), 2.80 (d, $^3J_{H-H}$ = 5.1 Hz, 6 H, CH$_3$), 3.65 (br, 2 H, NH), 4.12 (m, 8 H, COD), 6.38−7.07 (m, 8 H, CH). Anal. Calcd for C$_{30}$H$_{32}$N$_2$S$_2$Rh$_2$: C, 51.58; H, 5.77; N, 4.0. Found: C, 51.75; H, 5.84; N, 3.72.

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Synthesis of Rh(NH-C_6H_4-*o*-SMe)(COD) (6). To a solution of 2-(methylmercapto)aniline (40 μL, 0.32 mmol) in 5 mL of Et_2O, 0.2 mL (0.32 mmol) of Li^{n}Bu (1.6 M in hexane) was added and the mixture was stirred for 30 min. After this time, the solution was cooled to −78 °C and 0.079 g (0.16 mmol) of [Rh(μ-Cl)(COD)]$_2$ was added. The cooling bath was then removed, and the solution was stirred at room temperature for 30 min. The solvents were evaporated under vacuum, and the residue was extracted with 5 mL of toluene. After filtration, the solvent was removed under vacuum and the residue washed with 2 mL of pentane to yield 0.08 g (71%) of complex **6**. IR (Nujol/PET, cm^{-1}): 3611 (w), 3335 (w), 1597 (m), 1354 (m), 1328 (m), 1308 (m), 860 (m), 466 (m). ^{1}H NMR (C_6D_6): δ 1.85 (m, 4 H, COD), 1.95 (s, 3 H, CH_3), 2.23 (m, 4 H, COD), 3.72 (m, 2 H, COD), 4.30 (br, 1 H, N−H), 4.49 (m, 2 H, COD), 6.38−6.07 (m, 4 H). $^{13}C\{^1H\}$ NMR (C_6D_6): 23.8 (s, CH_3), 30.4, 32.0 (s, COD), 71.9 (d, $^1J_{Rh-C}$ = 11.1 Hz, COD), 84.8 (d, $^1J_{Rh-C}$ = 12.1 Hz, COD), 117.5 (s, C−N), 112.7, 115.9, 130.5, 131.6 (s, CH), 165.0 (s, C−S). Anal. Calcd for $C_{15}H_{16}NSRh$: C, 51.58; H, 5.77; N, 4.00. Found: C, 51.71; H, 5.43; N, 3.90.

Synthesis of Ir(Me)(SC_6H_4-*o*-NH)(COD) (7). To a solution of 2-(methylmercapto)aniline (47 μL, 0.38 mmol) in 5 mL of THF was added 0.23 mL (0.37 mmol) of Li^{n}Bu (1.6 M in hexanes), and the mixture was stirred at room temperature for 30 min. After this time, the solution was cooled to −78 °C, and 0.125 g (0.19 mmol) of [Ir(μ-Cl)(COD)]$_2$ was added. The cooling bath was then removed, and the solution was stirred at room temperature for another 30 min. Solvents were evaporated under vacuum, and the residue was extracted with 5 mL of toluene. After filtration, the solvent was partially evaporated and could be isolated by slow diffusion pentane, 0.130 g (79%) of complex **7**, as purple crystals. IR (Nujol/PET, cm^{-1}): 3304 (m), 1573 (m), 1302 (m), 897 (m), 764 (s), 762 (s), 460 (m).^{1}H NMR (C_6D_6): δ 1.09 (s, 3H, Ir−Me), 1.65−2.26 (m, 8H, CH_2), 3.75 (m, 1H, =CH), 3.89 (m, 1H, =CH), 4.73 (m, 1H, =CH), 5.51 (m, 1H, =CH), 6.95 (m, 1H, Ph), 7.05 (m, 1H, Ph), 7.15 (m, 1H, Ph), 8.05 (m, 1H, Ph), 8.69 (br, 1H, NH). $^{13}C\{^1H\}$ NMR (C_6D_6): 24.7 (s, CH_2), 30.4 (s, CH_2), 31.2 (s, CH_2), 32.6 (s, CH_2), 54.1 (s, Me), 69.1 (s, =CH), 72.8 (s, =CH), 78.9 (s, =CH), 84.1 (s, =CH), 117.9, 118.5, 124.6, 132.6 (s, CH), 143.5 (s, N−C), 163.0 (s, S−C). Anal. Calcd for $C_{15}H_{16}NSIr$: C, 41.07; H, 4.59; N, 3.19. Found: C, 40.98; H, 4.57; N, 3.16.

X-ray Crystallographic Analysis for 2 and 5. Crystallographic data are summarized in Table 3. Diffraction data were obtained at 298 K on a Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation using a $\omega/2\theta$ scan technique. Cell parameters were determined by a least-squares fit on 25 reflections. Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction was carried out on the basis of an azimuthal scan.[20] For complex **5**, the asymmetric unit comprised one independent half molecule. The structures were solved by direct methods, SIR92.[21] Refinement was carried out by full-matrix least-squares techniques SHELXL-93.[22] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated positions, except the NH hydrogen for complex **5** which was located in a difference map and refined freely. Weights were optimized in the final refinement cycles. Other detailed data are supplied in the Supporting Information.

Table 3. Experimental Data for the X-ray Diffraction Studies

	5	2
mol formula	$C_{30}H_{40}N_2S_2Rh_2$	$C_{24}H_{26}N_2S_2Zr$
mol wt	698.58	497.81
cryst syst	monoclinic	orthorrombic
space group	$I2/a$	$P2_12_12_1$
radiation (Mo Kα)	λ = 0.710 70 Å	
a, Å	11.265(2)	8.2307(8)
b, Å	13.016(3)	14.7894(9)
c, Å	19.823(6)	18.684(2)
β, deg	105.15(2)	
V, Å^3	2805.5(12)	2274.3(4)
Z	4	4
μ cm^{-1}	13.48	6.80
D_{calcd}, g cm^{-3}	1.654	1.454
F(000)	1424	1024
cryst dimens, mm	0.15 × 0.20 × 0.40	0.53 × 0.25 × 0.16
θ range, deg	2.13−25.02	2.18−25.03
index ranges	$0 \le h \le 13$, $0 < k \le 15$, $-23 \le l \le 22$	$0 \le h \le 9$, $0 < k \le 17$, $0 \le l \le 22$
total no. of unique data	2469	2294
goodness of fit	1.145	0.727
R,^{a} R_w^{b}	0.0644, 0.1354	0.0228, 0.0572
largest diff peak and hole, e Å^{-3}	0.764 and −0.738	0.203 and −0.281

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Supporting Information Available: Tables of crystallographic details, atomic coordinates, bond lengths and angles, and anisotropic and isotropic displacement parameters for **2** and **5** (13 pages). Ordering information is given on any current masthead page.

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