Synthesis of an Early–Late Heterobimetallic Imido Complex: Cooperative Reactivity with N–H, O–H, and S–H Bonds and Formation of a Novel Aminophosphine Complex

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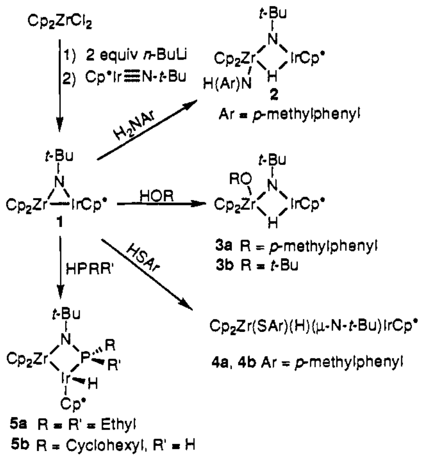
Although many early-late heterobimetallic compounds have been prepared,[1] cooperative reactivity involving both metal centers is rarely observed.[2–7] We wish to report here the synthesis of $Cp_2Zr(\mu\text{-N-}t\text{-Bu})IrCp^*$ (**1**), to our knowledge the first example of an early–late heterobimetallic imido complex.[8] We have compared the reactivity of complex **1** with X–H bonds containing both hard (N and O) and soft (S and P) heteroatoms.[9,10] Both the Zr and Ir centers participate in the reaction of **1** with N–H and O–H bonds, to give compounds in which the Ir–Zr bond is broken, the heteroatom is bound to Zr, and the hydride is bridging between the two metal centers.[11,12] The reaction of **1** with the S–H bond of *p*-thiocresol seems to give a similar compound as the major product. The reaction of **1** with P–H bonds proceeds differently, resulting in an unusual insertion of phosphide (PR_2) into the Ir–N bond to give heterobimetallic aminophosphine complexes.[13–15]

The chemistry we have observed is summarized in Scheme I. The bridging imido complex **1** was synthesized by sequential addition of 2 equiv of *n*-BuLi and 1 equiv of $Cp^*IrN\text{-}t\text{-Bu}$ to a solution of Cp_2ZrCl_2 in THF at −30 °C, followed by warming to room temperature and stirring for 2 days. Negishi and coworkers have established that the addition of *n*-BuLi to Cp_2ZrCl_2 initially forms $Cp_2Zr(n\text{-Bu})_2$, which *β*-hydrogen eliminates to form butane and the zirconocene butene complex ($Cp_2Zr(CH_2{=}CHCH_2CH_3)$).[16] Dark brown crystals of imido complex **1** suitable for an X-ray diffraction study were obtained in 60% yield from diethyl ether at −30 °C.[17] An ORTEP drawing of the structure is shown in Figure 1. The Zr–N bond length of 2.08(1) Å is normal for Zr bridging imido dimers,[18–23] and the Ir–N distance of 1.887(3) Å is comparable to that observed in a related bridging Ir imide ($Cp^*Ir(1)(\mu\text{–N-}t\text{-Bu})Ir(2)Cp^*(PMePh_2)$; Ir(1)-N = 1.81(1) Å).[24] The 2.598(2) Å metal–metal distance and an acute Zr-N-Ir angle (81.6(5)°) are consistent with the presence of an Ir–Zr bond.

Scheme I



Addition of *p*-toluidine to **1** at 25 °C resulted in an immediate color change from brown to red. Crystals of the N–H addition product **2** ($Cp_2Zr(NHAr)(\mu\text{-H})(\mu\text{-N-}t\text{-Bu})IrCp^*$) were isolated in 60% yield from a mixture of toluene and pentane at −30 °C. Slow crystallization from a toluene solution of **2** gave crystals suitable for X-ray analysis, and an ORTEP drawing is shown in Figure 1.[25] One interesting feature of this structure is the hydride bridging the Ir and Zr centers, giving a formal 18-electron configuration at Zr and a 16-electron configuration at Ir. The Ir imide (1.896(6) Å) and Zr imide (2.175(6) Å) bonds are slightly longer than those in **1**. The Ir-Zr distance has lengthened to 2.977(1) Å, and the Zr-N1-Ir angle has increased to 93.7(3)°, indicative of a weakened or absent bonding interaction between Ir and Zr.

The solution ^1H NMR spectrum of the N–H addition product **2** at room temperature has no observable resonances attributable to either the N–H or the hydride groups. However, upon cooling of the solution to −40 °C in toluene-d_8 the N–H resonance becomes apparent at 4.72 ppm and the hydride at −5.47 ppm. This fluxional process has been studied by a spin saturation transfer experiment, in which the Ir–H and N–H groups were observed to exchange with each other at −51 °C. A very weak infrared metal hydride stretching absorption was observed at 2096 cm^{-1} (Nujol). Complex **1** does not react with $t\text{-BuNH}_2$ or $i\text{-PrNH}_2$. Presumably this is due to the lower acidity of these alkylamines rather than increased steric bulk since *t*-BuOH reacts readily with **1**, as discussed below.

Addition of *p*-cresol to **1** at 25 °C gave the dinuclear O–H activation product $Cp_2Zr(OAr)(\mu\text{-H})(\mu\text{-N-}t\text{-Bu})IrCp^*$ (**3a**, 56%

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(17) Crystal parameters for **1** at −110 °C: space group *Cc*, $a = 14.476(5)$ Å, $b = 15.406(3)$ Å, $c = 10.398(3)$ Å, $\alpha = \gamma = 90.0°$, $\beta = 96.93(2)°$, $V = 2302.0(20)$ Å^3, $Z = 4$, $d(\text{calc}) = 1.79$ g/cm^3, $R = 3.1$, $R_w = 3.9$.

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(25) Crystal parameters for **2** at −106 °C: space group: *Pbca*, $a = 13.824(4)$ Å, $b = 23.470(4)$ Å, $c = 21.272(5)$ Å, $\alpha = \beta = \gamma = 90.0$ °C, $V = 6901.2(47)$ Å^3, $Z = 8$, $d(\text{calc}) = 1.57$ g/cm^3, $R = 3.02$, $R_w = 2.90$.

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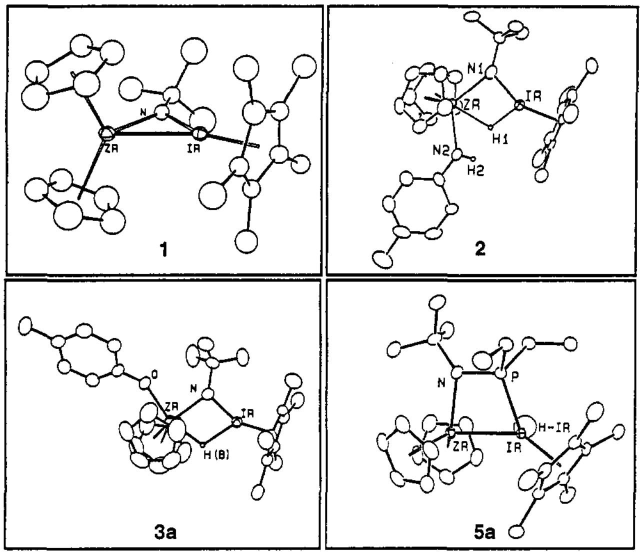

Figure 1. ORTEP drawings of **1**–**3a** and **5a**. Most of the hydrogens have been omitted for clarity in the structures of **2**, **3a**, and **5a**. The hydrogens were not located in the structure of **1**. Selected bond distances (Å): **2**, Ir–N(1) 1.896(6), Zr–N(1) 2.175(6), Zr–N(2) 2.220(7), Zr–H(1) 2.03(6), Ir–H(1) 1.58(6); **3a** Ir–N 1.889(6), Zr–N 2.149(6), Zr–O 2.083(5), Ir–Zr 3.020(1), ∠Ir–N–Zr 96.6(3)°; **5a** Zr–N 2.164(3), Ir–P 2.235(1), Ir–H 1.39(6).

yield). Unlike its nitrogen analog, this compound does not exhibit fluxional behavior in the ^{1}H NMR spectrum at room temperature. A hydride resonance was observed at −7.24 ppm (benzene-d_6) in the ^{1}H NMR spectrum, and an IR stretching absorption was observed at 1975 cm^{-1} (Nujol). Single crystals suitable for X-ray diffraction were grown by slow cooling of a 3:1 mixture of an ether and hexamethyldisiloxane solution from 80 °C to 25 °C.[26] An ORTEP drawing of **3a** is shown in Figure 1. The hydride and imide bridge Ir and Zr as in the *p*-toluidine addition product **2**, but the imido ligand rather than the hydride is in the central position of the equatorial wedge around Zr.

In contrast to the low reactivity of *t*-BuNH$_2$, addition of *t*-BuOH to **1** gave the dinuclear O–H activation product Cp$_2$Zr(O-*t*-Bu)(μ-H)(μ-N-*t*-Bu)IrCp* (**3b**) upon mixing at room temperature. Complex **3b** was isolated in 74% yield by crystallization from diethyl ether and was characterized by standard spectroscopic techniques and combustion analysis. Based on spectroscopic evidence, we believe it to have a structure analogous to **3a**. An Ir–H resonance was observed at −6.03 ppm (benzene-d_6) in the ^{1}H NMR spectrum, characteristic of the heterobimetallic bridging hydrides we have synthesized, and a broad metal hydride stretch was observed in the IR spectrum at 2024 cm^{-1} (Nujol).

Treatment of the heterobimetallic imido complex **1** with *p*-thiocresol at room temperature gave a 90:10 mixture of two compounds (**4a** and **4b**). The major product **4a** is spectroscopically similar to the *p*-toluidine and *p*-cresol addition products. A hydride resonance for **4a** was observed at −3.93 ppm (benzene-d_6) in the ^{1}H NMR spectrum, and a hydride stretching absorption was observed in the IR spectrum at 1974 cm^{-1} (Nujol). The minor product **4b** was observed to have diastereotopic Cp ligands by ^{1}H NMR spectroscopy, implying a chiral center at Ir. A hydride resonance for **4b** was not located in the ^{1}H NMR spectrum, possibly due to the low concentration of **4b** compared to **4a** in solution. We are currently investigating the structures of both **4a** and **4b**.

Diethylphosphine and the imido complex **1** reacted rapidly at 25 °C to give a red solution. Crystallization of the product from diethyl ether at −30 °C gave **5a** (Cp$_2$Zr(μ-*t*-BuNPEt$_2$)Ir(H)(Cp*)) in 63% yield. An X-ray diffraction study was performed on **5a**, and the ORTEP drawing is shown in Figure 1.[27] Instead of cleavage of the Ir–Zr bond, insertion of phosphide (PR$_2$) into the Ir–N bond occurs, leading to the structurally unique bimetallic aminophosphine complex **5a**. The P–N bond distance of 1.666(3) Å is indicative of a P–N single bond.[28] The Ir–Zr distance of 2.642(1) Å is similar to the distance found in the starting material **1**, indicating the presence of an Ir-Zr bond.

The aminophosphine complex is fluxional at room temperature on the ^{1}H and ^{13}C NMR time scales. At −40 °C, the cyclopentadienyl and ethyl groups are diastereotopic due to the chiral center formed at Ir by coordination of the phosphine. Warming to 50 °C caused coalescence of the cyclopentadienyl and ethyl ligands. One explanation for this fluxional behavior is the reversible dissociation of the phosphine ligand from the Ir center, causing epimerization at Ir. The addition of 10 equiv of cyclohexylphosphine or 5 equiv of trimethylphosphine to the aminophosphine complex **5a** did not result in displacement of the diethylphosphine ligand from Ir at 25 °C by ^{1}H NMR spectroscopy. This is not surprising since the intramolecular coordination of the diethylphosphine ligand would be expected to be favored over intermolecular coordination of cyclohexylphosphine or trimethylphosphine.

Addition of cyclohexylphosphine to **1** gave a rapid reaction at 25 °C to form **5b** (Cp$_2$Zr(μ-*t*-BuNP(Cy)(H))Ir(H)(Cp*)). Spectral data for **5b** indicate a structure similar to that of **5a**, as shown in Scheme I. The cyclohexylphosphine addition product **5b** does not exhibit fluxional behavior in the ^{1}H NMR between −90 and 50 °C. The cyclopentadienyl ligands on zirconium are diastereotopic at all temperatures (−90 to 50 °C). Only one of the two possible diastereomers of **5b** is formed, presumably due to an unfavorable steric interaction between the Cp* ligand and the cyclohexyl group on phosphorus.

In summary, the heterobimetallic imido complex **1** exhibits facile reactivity with many X–H bonds. Treatment of **1** with *p*-toluidine, *p*-cresol, 1,1-dimethylethanol, and *p*-thiocresol resulted in addition of X–H bonds across the metal–metal bond. However, treatment with phosphines led to an unusual phosphide insertion to give a bridging aminophosphine complex. Efforts are now underway to elucidate the mechanisms of several of these reactions and examine the reactivity of **1** with a wider range of substrates.

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Supplementary Material Available: Spectroscopic and analytical data for complexes **1**, **2**, **3a**, **3b**, **4a**, **4b**, **5a**, and **5b**; X-ray diffraction data (ORTEP diagrams, crystal and data collection parameters, positional and anisotropic thermal parameters, intramolecular distances and angles) for **1**, **2**, **3a**, and **5a** (31 pages). This information is provided with the archival edition of the journal, available in many libraries. Alternatively, ordering information is given on any current masthead page.

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(26) Crystal parameters for **3a** at −99 °C: space group: $P2_12_12_1$, a = 10.901(3) Å, b = 14.178(4) Å, c = 19.133(7) Å, $\alpha = \beta = \gamma$ = 90.0 °C, V = 2957.2(27) Å^3, Z = 4, d(calc) = 1.64g/cm^3, R = 3.11, R_w = 3.02.

(27) Crystal parameters for **5a** at −88 °C: space group: $P2_1/n$, a = 9.5153(14) Å, b = 19.3536(20) Å, c = 15.0471(20) Å, $\alpha = \gamma$ = 90.0°, β = 104.651(11)°, V = 2680.9(12) Å^3, Z = 4, d(calc) = 1.76 g/cm^3, R = 1.97, R_w = 2.25.

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