Reactions of an Imidozirconocene Complex with Cyclopentadienylmetal Carbonyl Complexes: C—H Activation versus Oxygen Atom Abstraction

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The transient monomeric imidozirconocene complex Cp₂-Zr=NR (**1**), which is generated reversibly from isolable Cp₂-(THF)Zr=N-*t*-Bu (**2**), contains one of the few metal—heteroatom multiple bonds capable of undergoing intermolecular C—H activation.[1-6] For example, this intermediate reacts with the C—H bond of benzene to give the corresponding phenylamidozirconocene complex **3a**.[1,2] In the course of attempting to extend the scope of this C—H activation process, we have found that **1** undergoes two unusual types of reaction with certain other cyclopentadienyl-substituted metal complexes: (a) a surprisingly facile cyclopentadienyl C—H activation leading to the formation of substituted η^1: η^5-cyclopentadienyl zirconocene amido complexes and (b) oxygen atom abstraction from metal-bound CO ligands to give isonitrile complexes and the new dinuclear (μ-oxo)(μ-imido)zirconocene complex **11**.

The above reactions were discovered during the course of an investigation of substituent effects on the C—H activation of **1** with arenes which revealed that the efficiency of the reaction depends on the electrophilicity of substituents on the benzene ring. Thus, treatment of **2** with neat *m*-dichlorobenzene for 2 days at 70 °C cleanly gave one product, Cp₂Zr(C₆H₃Cl₂)-(NH-*t*-Bu) (**3b**), in 90% yield by ¹H NMR spectroscopy (Scheme 1). Compound **3b** was isolated in pure form in 51% yield; an X-ray crystallographic analysis was performed, and an ORTEP diagram is shown in Figure 1. To our knowledge,[1-6] this is the first M=N C—H activation product that has been characterized by X-ray diffraction. In contrast, the reactions of **2** with 1,3-disubstituted benzenes containing electron-donating groups (X = Me, OMe, *t*-Bu) are slow and give several products. Thermolysis of **2** in mesitylene (1,3,5-trimethylbenzene) proceeded very slowly, leading to a complex mixture of products. From the mixture, we were able to isolate two unexpected major products, Cp₂Zr(CH₂C₆H₃Me₂)(NH-*t*-Bu) (**4**) and [CpZr(NH-*t*-Bu)(η^1: η^5-C₅H₄)]₂ (**5**) (Scheme 1).[7] It is noteworthy that the dimeric Cp-bridged zirconocene amido complex **5** was produced by cyclopentadienyl C—H activation[8-13]
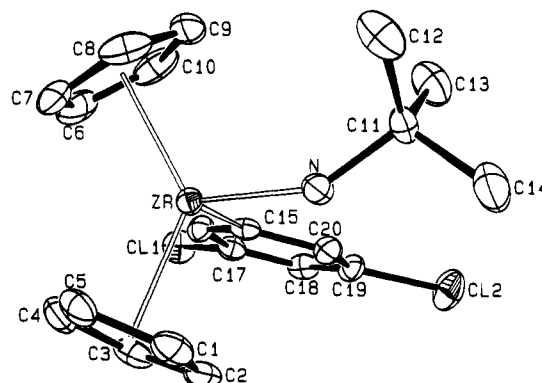
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(7) The ratio of the two major products **4** and **5** varies with the concentration of **2** in mesitylene. The **4/5** ratios are 2/1 (0.13 M 2), 1.4/1 (0.26 M 2), and 0.8/1 (0.57 M 2) (¹H NMR). The dimeric compound **5** was isolated in 15% yield (from the reaction of 3.6 × 10⁻¹ M 2 in mesitylene), and **4** was isolated in 20% yield from the reaction of 6.8 × 10⁻² M 2 in mesitylene. Approximately 20% of uncharacterized products (¹H NMR) were generated during thermolysis at 75 °C.

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Figure 1. ORTEP diagram for the molecular structure of Cp₂Zr(C₆H₃-Cl₂)(NH-*t*-Bu) (**3b**). Selected bond distances (Å): Zr—N, 2.060(3); Zr—C15, 2.337(3). Selected bond angles (deg): N—Zr—C15, 97.01(12); Zr—N—C11, 147.6(2). C₂₀H₂₃NCl₂Zr crystallizes in the monoclinic space group *C2/c*; *a* = 32.901(7) Å, *b* = 8.123(3) Å, and *c* = 15.226-(4) Å; β = 111.491(18)°. Of 2784 reflections collected (−103 °C, Mo Kα: 3.0 < 2Θ < 45.0°), 1932 ($F^2 > 3\sigma(F^2)$) were refined to R = 0.026, R_w = 0.028.

Scheme 1
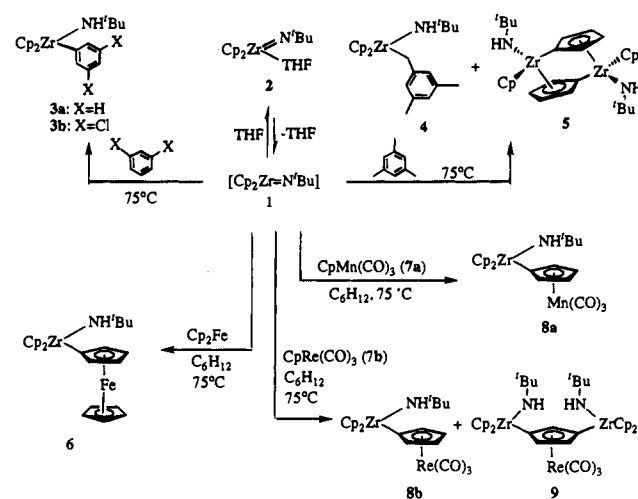
of another equivalent of **1** due to the modest reactivity of mesitylene. NMR data[14] supported the proposal that the two zirconium centers in **5** were linked by the η^1: η^5-C₅H₄ ring rather than coordinated by a fulvalenide ligand.[15]

The discovery of cyclopentadienyl C—H activation of **2** in mesitylene in spite of the low concentration of Cp-containing complexes led us to explore the possibility of C—H activation with other compounds containing cyclopentadienyl rings. Heating the imido complex **2** at 4.0 × 10⁻² M concentration for 1.5 days at 75 °C in the presence of 3 equiv of Cp₂Fe in C₆H₁₂ yielded one clean product (>90% by ¹H NMR; 61% isolated), Cp₂Zr(NH-*t*-Bu)(η^1: η^5-C₅H₄)FeCp (**6**) (Scheme 1).[16] The reactions of **2** with cyclopentadienyl(carbonyl)metal complexes were studied under similar conditions. Treatment of **2** with 3 equiv of CpMn(CO)₃ (**7a**) at 75 °C in C₆H₁₂ showed selectively the cyclopentadienyl C—H activation of **7a**, leading to Cp₂Zr(NH-*t*-Bu)(η^1: η^5-C₅H₄)Mn(CO)₃ (**8a**) (>90% by ¹H NMR; 38% isolated) (Scheme 1). The cyclopentadienyl C—H bond of

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(14) The NMR data for the η^1:η^5-C₅H₄ ligand in **5** showed four quartet peaks at 6.38, 6.01, 5.48, and 5.14 ppm in the ¹H NMR spectrum and five peaks at 138.5 ppm (Cp*Z*r*C*), 125.0, 115.9, 115.0, and 114.3 ppm (*C*H) in the ¹³C NMR spectrum.

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Scheme 2
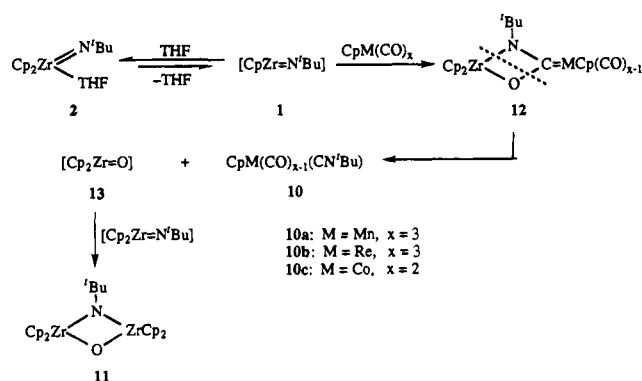
CpRe(CO)$_3$ (**7b**) was even more susceptible to reaction with **2**, leading to both the singly and doubly C—H activated products, Cp$_2$Zr(NH-*t*-Bu)(η^1: η^5-C$_5$H$_4$)Re(CO)$_3$ (**8b**) and (Cp$_2$ZrNH-*t*-Bu)$_2$(η^1: η^1: η^5-C$_5$H$_3$)Re(CO)$_3$ (**9**) (Scheme 1). The ratio of products **8b** and **9** was dependent upon the starting ratio of **7b** to **2**.[17] Heating **2** in the presence of 0.5 equiv of **7b** in cyclohexane for 7 days at 75 °C yielded mostly **9** (*ca.* 80% by ^{1}H NMR), which was isolated in 59% yield. We were not able to establish the regiochemistry of **9** definitively due to similar 1,2 and 1,3 H—H coupling constants in Cp—metal systems, but we believe that the two Cp$_2$ZrNH-*t*-Bu groups in **9** must be in the 1,3-positions of the Cp ring due to their steric bulk.

Studies with other cyclopentadienyl metal carbonyl complexes gave complex mixtures of products in cyclohexane solvent, as indicated by the appearance of numerous Cp and *t*-Bu absorptions in the ^{1}H NMR spectrum of the reaction mixture. Changing the reaction solvent to THF, however, led to the identification of a second reaction pathway. For example, treatment of **2** with 3 equiv of CpCo(CO)$_2$ in THF at 75 °C yielded CpCo(CO)(CN-*t*-Bu) (**10c**)[18,19] (>90% by ^{1}H NMR; 28% isolated) and a new binuclear complex identified by spectroscopic and elemental analysis as (Cp$_2$Zr)$_2$(μ-O)(μ-N-*t*-Bu) (**11**) (>90% by ^{1}H NMR; 30% isolated) (Scheme 2).

Preliminary ^{1}H NMR investigations suggest that the reaction of **2** with CpV(CO)$_4$, CpFe(CH$_3$)(CO)$_2$, or (C$_6$H$_6$)Cr(CO)$_3$ in THF also yields **11** and the corresponding deoxygenated metal carbonyl isocyanide complexes. The rates of the reaction of **2** with CpV(CO)$_4$ and (C$_6$H$_6$)Cr(CO)$_3$ were relatively fast, the reactions occurring even at 25 °C.
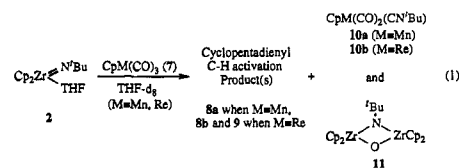
The observations described above induced us to re-examine the reactions of CpM(CO)$_3$ (M = Mn, Re) with **2** in THF rather than cyclohexane. The coordinating ability of THF repressed the formation of free Cp$_2$Zr=N-*t*-Bu, significantly decreasing the reaction rate, and thus heating the reaction mixture to 105 °C was required. The cyclopentadienyl C—H activated products were still the major species formed (from **7a**, *ca.* 60% of **8a**, 30% of **10a** and **11**; from **7b**, 85% of **8b** and **9**, 14% of **10b** and **11** (^{1}H NMR; eq 1).

The most straightforward mechanism for the deoxygenation reactions of **2** with metal carbonyl complexes involves an overall [2 + 2] cycloaddition between a CO ligand and the Zr=N moiety. This would produce μ-oxo azametallacyclobutane **12** (Scheme 2). Using CpCo(CO)$_2$ as an illustrative example, cleavage of the metallacyclobutane bonds in the opposite sense would then provide the transient complex Cp$_2$Zr=O (**13**) and **10c**. Confirmation of the carbon—oxygen bond cleavage[20] predicted by this process was obtained by treatment of **2** with CpCo(^{13}CO)$_2$; this led to CpCo(^{13}CO)(^{13}CN-*t*-Bu).[21] However, one puzzling aspect of this mechanism is the apparent reaction of the transient zirconocene oxo complex **13** with another equivalent of **1** to produce **11**, instead of polymerizing to form (Cp$_2$Zr=O)$_n$.[2] This is surprising because the reactions of **2** with carbonyl groups of organic compounds in THF generate the corresponding imine and (Cp$_2$Zr=O)$_n$ even in the presence of an excess of **2** at −43 °C where the reaction shows almost the same rate as the reaction of **2** with CpCo(CO)$_2$.[22] Proulx and Bergman have reported, in the "Wittig type" metathesis of CpTa(=CH$_2$)(CH$_3$) with PhRe(CO)$_5$, a similar overall [2 + 2] cycloaddition that leads to a product in which Cp$_2$(CH$_3$)Ta=O is weakly coordinated to a rhenium center.[23-25] The similarity of these reactions suggests the possibility that weak coordination of Cp$_2$Zr=O to a cobalt carbonyl fragment might prevent the highly reactive Zr=O moiety in **13** from self-oligomerization and allow it to react instead with **1**.[26] Further studies will be required to understand the apparently divergent behavior of Cp$_2$Zr=O generated from different sources.

Supplementary Material Available: Spectroscopic and analytical data on complexes **3b**, **4—6**, **8a**, **9**, and **11** and tables containing complete crystal and data collection parameters, positional parameters and estimated standard deviations, and intramolecular distances and angles for **3b** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(16) A referee has asked about the products formed on reaction of **2** with cyclopentadiene. Because of the ease of dimerization of this molecule, we have investigated the reactivity of **2** toward indene as an alternative. The final (presumably thermodynamic) product of this reaction (cyclohexane; 3 days at 75 °C) is the benzylic indenyl(amido)zirconocene C—H activation product, whose structure has been determined by X-ray diffraction. Another indenyl(amido)zirconocene complex was detected as a kinetic product during the reaction. Spectroscopic data on this material indicate that it is the vinylic C—H activation product, but we have so far not been able to isolate it. We do not yet understand why attack at the five-membered-ring hydrogens in indene appears to be favored over attack at the aryl hydrogens. This issue will be discussed, along with the details of the X-ray diffraction study, in a full paper.

(17) Heating >3 equiv of **7b** with **2** at 75 °C for 2 days gave **8b** as the major product. Under these conditions, *ca.* 80% of **8b** and 20% of **9** (^{1}H NMR) were generated. However, we were not able to isolate pure **8b** from this mixture because of the very similar solubilities of this complex and the excess **7b** still present in solution.

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(20) To confirm the source of oxygen in the oxozirconium product **11**, we carried out a deoxygenation reaction with an analogue of **2**, Cp$_2$Zr(N-2,6-(CH$_3$)$_2$C$_6$H$_3$)(THF). The experiment was carried out with the arylimido complex rather than **2** because the former does not react with benzene C—H bonds, allowing us to run the reaction in an aromatic rather than an oxygen-containing solvent. Reaction of the arylimido complex with CpCo(CO)$_2$ at 75 °C in C$_6$D$_6$ as well as THF-d_8 led to CpCo(CO)(CN-2,6-(CH$_3$)$_2$C$_6$H$_3$) in both solvents. Although "Cp$_2$Zr=O oligomer" was observed instead of the analogue of **11** in those reactions, the experiment in C$_6$D$_6$ demonstrates that THF is not required for the conversion of the starting terminal imido complex into an oxozirconium product.

(21) The reaction of **2** with CpCo(^{13}CO)$_2$ (86% ^{13}CO labeled) yielded CpCo(^{13}CO)(^{13}CN-*t*-Bu) with 84% incorporation of ^{13}C label. ^{13}C incorporation was determined by integration of relative mass peaks from EI mass spectroscopy.

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(25) Pilato, R. S.; Rubin, D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1990**, *29*, 1986.

(26) We also admit the possibility that the products **10** and **11** might be generated by direct reaction of Cp$_2$Zr=N-*t*-Bu (**1**) with **12** without the formation of free Cp$_2$Zr=O.