

Zirconocene–Iridium Hydrido Complexes: Arene Carbon–Hydrogen Bond Activation and Formation of a Planar Square Zr₂Ir₂ Complex

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New early–late heterobimetallic hydrides (L₂ZrCl)(Cp*Ir)(μ-H)₃ (**1**; L = Cp derivative, Cp* = η⁵-C₅Me₅) were synthesized from zirconocene derivatives (L₂ZrCl₂) and LiCp*IrH₃ via a salt elimination reaction and structurally characterized by NMR and X-ray analyses. Upon treatment of **1** with an alkyllithium reagent, hydride abstraction complex **4** underwent thermolytic ligand elimination at the Zr–Ir system to yield a novel planar square complex (L₂Zr)₂(Cp*Ir)₂(μ₃-H)₄ (**2**). When a labeling study of the reaction was conducted, it was found that the conversion of **1** to **2** involves rapid aromatic and benzylic C–H activation by a coordinatively unsaturated dinuclear complex (L₂Zr)(Cp*Ir)(H)₂ (**3**).

Low-valent group 4 *dⁿ* metal complexes (*n* ≠ 0) have been recognized as useful organometallic reagents in synthetic reactions such as oxidative couplings of carbon–carbon and carbon–heteroatom multiple bonds.^{1,2} Ligand elimination from group 4 *d⁰* metal hydrides such as oligomeric zirconocene hydrides accompanied by dihydrogen elimination can result in the formation of key *dⁿ* metal species.³ A number of these group 4 metallocene hydrides have been synthesized and well characterized.^{4–6} However, only two studies have been conducted on early–late heterobimetallic (ELHB) hydrides of group 4 metallocene and late-transition-metal units. Therefore, the chemistry of ELHB hydrides has not been investigated in detail. It is of particular interest to study ligand elimination from these types of ELHBs for the formation of low-valent bimetallic complexes; it is also important to study their cooperative reactivity in regio- and chemoselective reactions.^{7,8} In this paper, we report the

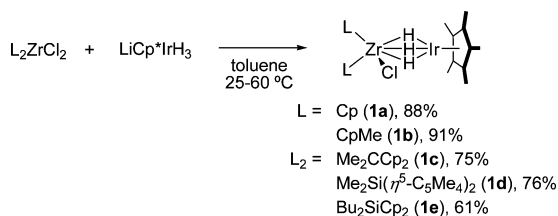
syntheses of and ligand elimination from new ELHB hydrides (L₂ZrX)(Cp*Ir)(μ-H)₃ (L = cyclopentadienyl derivative; X = Cl, alkyl, aryl, etc.).

Our initial efforts have been devoted to the synthesis and isolation of (L₂ZrCl)(Cp*Ir)(μ-H)₃ (**1**) according to a method used in the case of mono-Cp*-type ELHB hydrides (Cp*MCl₂)-(Cp*Ir)(μ-H)₃ (M = Ti, Zr, Hf).⁹ Thus, salt elimination of Cp₂ZrCl₂ and LiCp*IrH₃ was carried out at 25–60 °C in toluene to obtain **1a** in 88% isolated yield. The proposed structure of **1a** was supported by NMR, elemental analyses, and analogy with the X-ray structures of **1b–1e**. In the ¹H NMR spectrum of **1a** at 22 °C (–14.09 ppm, C₆D₆),¹⁰ the single resonance peak for the three hydrides is observed to undergo a significant upfield shift as compared to the peak observed in the ¹H NMR spectrum of (Cp₂ZrCl){Os(PMe₂Ph)₃}(μ-H)₃ (–7.05 ppm in C₆D₆). Because we successfully synthesized structurally prototypical **1a**, we also carried out the

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Scheme 1. Formation of **1**

salt metathesis of several zirconocene dichlorides with LiCp*IrH₃. **1b–1e** were obtained from (CpMe)₂ZrCl₂ and *ansa*-L₂ZrCl₂ (L₂ = Me₂CCp₂, Me₂Si(C₅Me₄)₂, Bu₂SiCp₂) in good isolated yields (Scheme 1). However, sterically demanding Cp*₂ZrCl₂ could not readily form a ELHB hydride. The structures of **1b–1e** were elucidated by NMR, X-ray diffraction, and elemental analyses. The crystal structure of **1b** is shown in Figure 1, and the three hydrides of **1b–1e** were located in the X-ray study. As shown in the figure, this structure has no direct Zr–Ir bond,^{7a,b} but the distance between Zr and Ir is found to be 2.784–2.806 Å, which is comparable to the Zr–Ir distance of {Cp*Zr(CH₂SiMe₃)₂}(Cp*Ir)(μ-H)₃ [2.751 Å], exhibiting cooperative C–H activation of pyridines.⁸

To evaluate the lability of the hydride ligands in the present ELHB hydrides, we attempted the substitution of a polar chloro ligand with a hydride. Cautlon carried out the synthesis of dinuclear Zr–Os and Zr–Re hydrides using Schwartz's reagent Cp₂Zr(H)Cl.⁶ By following the same method, we reacted Cp₂Zr(H)Cl and MeCCp₂Zr(H)Cl with LiCp*IrH₃ in toluene at ambient temperature, and the resultant mixtures in both cases instantly afforded a dark-red crystalline solid. Crystallography of the obtained complexes revealed the presence of a planar square (L₂Zr)₂(Cp*Ir)₂(μ₃-H)₄ complex (**2**; Scheme 2). The crystal structure of (Cp₂Zr)₂(Cp*Ir)₂(μ₃-H)₄ (**2a**) is shown in Figure 2. **2a** has four triply bridging hydrides and two Zr–Ir distances [2.8156(6) and 2.7987(6) Å], whose lengths are comparable

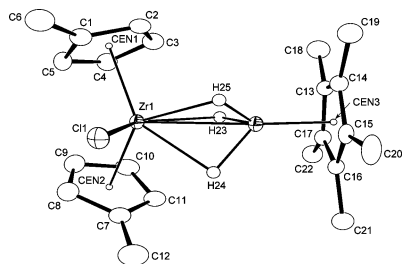


Figure 1. Molecular structure of **1b** (thermal ellipsoids are drawn at the 50% probability level). Selected bond distances (Å) and angles (deg): Zr1–Ir1 2.7950(3), Zr1–Cl1 2.4857(9), CEN1–Zr1 2.267, CEN2–Zr1 2.268, CEN3–Ir1 1.864; Ir1–Zr1–Cl1 101.31(2), CEN3–Ir1–Zr1 169.6, CEN1–Zr1–CEN2 125.0.

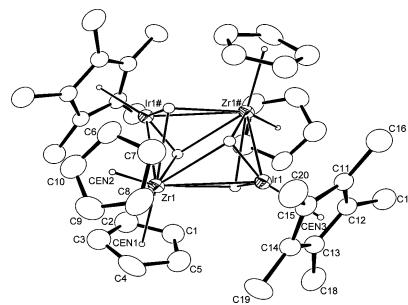
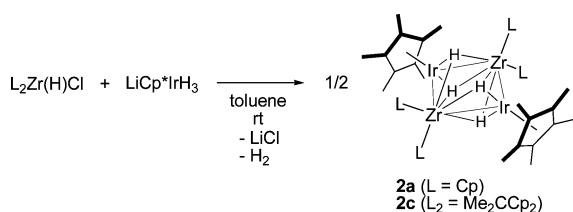
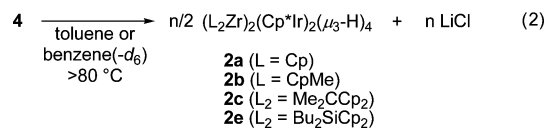
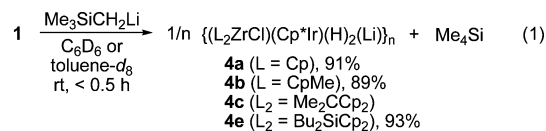
Scheme 2. Reaction of a Schwartz-Type Complex and LiCp*IrH₃

Figure 2. Molecular structure of **2a** (thermal ellipsoids are drawn at the 50% probability level). Selected bond distances (Å) and angles (deg): Zr1–Ir1 2.8158(6), Zr1#–Ir1 2.7987(6), Zr1–Zr1# 3.648, Ir1–Ir1# 4.268, CEN1–Zr1 2.307, CEN2–Zr1 2.289, CEN3–Ir1 1.1.964; Ir1–Zr1–Ir1# 98.95(2), Zr1–Ir1–Zr1# 81.05(2), CEN3–Ir1–Zr1 137.25, CEN1–Zr1–CEN2 123.25.

to those of the corresponding bonds in **1** [2.793–2.806 Å]. With regard to the metal–metal distances and metal–ligand environments, the core structures of **2a** and **2c** are almost identical. For example, both of the structures show significantly narrow Cp(CEN)–Zr–Cp(CEN) bite angles for those of L₂ZrCl₂ (**2a**, 123.25° vs 129.3°; **2c**, 112.95° and 113.49° vs 116.6°)¹¹ and relatively long Cp(CEN)–Ir distances (**2a**, 1.964 Å; **2c**, 1.962 Å vs 1.805–1.986 Å).¹²

On the basis of the above results, we hypothesized that hydride ligands were rapidly eliminated from in situ formed perhydrides such as (L₂ZrH)(Cp*Ir)(μ-H)₃¹³ and **2** was formed via the coordinatively unsaturated intermediate (L₂Zr)(Cp*Ir)(H)₂ (**3**). Thus, **1a** was treated with Me₃SiCH₂Li as a base to remove chloro and hydride ligands. The reaction proceeded rapidly at room temperature with quantitative extrusion of Me₄Si to yield a dark-red solution. The product complex was, however, identified to be {(Cp₂ZrCl)(Cp*Ir)(H)₂(Li)}_n (**4a**) from its ¹H, ¹³C, and ⁷Li NMR spectra. The structural formula of **4a** was further elucidated by carrying out protonation of **4a** using PhC≡CH and, consequently, reproducing **1a**. **4b, 4c**, and **4e** were also synthesized from **1b**, **1c**, and **1e**, respectively, in high yields (eq 1); however, **1d** yielded Me₂Si(*η*⁵-C₅Me₄)₂Zr(CH₂SiMe₃)₂ as the major product. The competitive Zr–Ir degradation occurring in the above reactions suggested that the preferential occurrence of nucleophilic hydride abstraction or substitution on the zirconium center depends on the zirconocene substituent. Interestingly, **4a–4c** and **4e** underwent LiCl elimination in toluene or benzene above 80 °C to afford **2a–2c** and **2e** (eq 2).



This finding prompted us to investigate the reaction pathway of the conversion of **1** to **2**; for this purpose, we

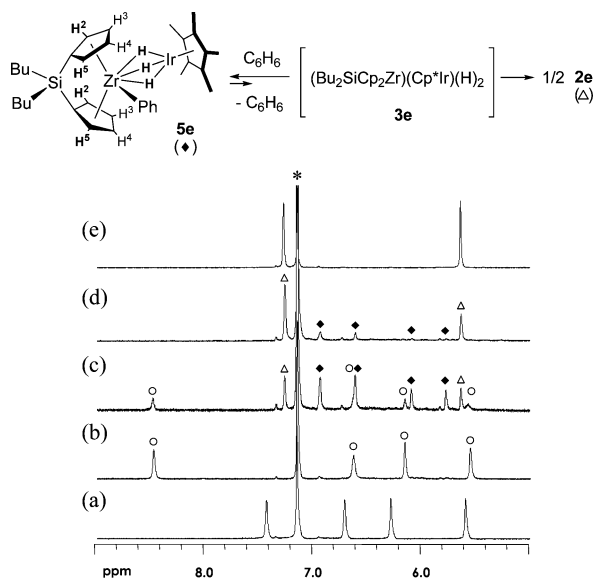
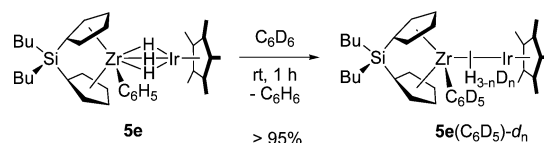


Figure 3. ^1H NMR spectra for conversion of **1e** to **2e**- d_n in C_6D_6 . The asterisk, \circ , \blacklozenge , and \triangle denote the peaks assigned to the solvent, **4e**, **5e**(C_6D_5)- d_n , and **2e**- d_n . (a and b) Spectra obtained before and after the addition of $\text{Me}_3\text{SiCH}_2\text{Li}$ to **1e** at ambient temperature. (c and d) Spectra obtained after thermolysis at 60°C for 16 and 70 h, respectively. (e) Spectrum of **2e** prepared in C_6H_6 and purified.

analyzed the highly soluble **1e** by NMR monitoring (C_6D_6 solvent, 60°C).^{14,15} The ^1H NMR spectra obtained in the aromatic proton region are shown in Figure 3. In the spectra obtained during the conversion of **1e** to **2e**- d_n , two sets of four inequivalent Cp–H signals were observed; one set was assigned to **4e** (\circ), and the other was assigned to an intermediate **5e**(C_6D_5)- d_n (\blacklozenge). The signal intensities of **2e**- d_n peaks increased gradually with a simultaneous decrease in the intensities of the peaks assigned to **4e** and **5e**(C_6D_5)- d_n (b \rightarrow c \rightarrow d). Moreover, it was revealed that selective deuterium incorporation into the Cp–H at C2 and C5 and into the hydrides of **5e** and **2e** was successfully achieved.¹⁶

Thus, on the basis of the above results, we speculate the reaction pathway for the conversion of **1** to **2** as follows. Initially, the nucleophilic abstraction of acidic hydride from **1** results in the formation of complex **4** by the reaction shown in eq 1. Then, LiCl elimination from **4** under thermolytic conditions yields the electronically unsaturated species **3** as an unstable intermediate; this intermediate is also thought to be a key species in the rapid reaction between Schwartz-type reagents and $\text{LiCp}^*\text{IrH}_3$. This highly reactive **3** is

Scheme 3. Rapid Arene Exchange on **5e**



expected to undergo oxidative addition reaction with C–H(D) of the aromatic solvent and Cp–H.¹⁷ During such an oxidative addition/reductive elimination process, **3**- d_n can incorporate deuterium into Cp–H. In the case of *ansa*-type **3e** and **5e** ($\text{L}_2 = \text{Bu}_2\text{SiCp}_2$), the most remote Cp–H from the Cp^*Ir unit would be selectively split and deuterated by **3e**- d_n , along with flipping of the Si–Zr–Ir angle of **5e** during the equilibrium between **3e** and **5e**. This would result in selective deuterium incorporation onto the four ring carbons (not only C₅ but also C₂) β to the bridging silicon at the same rate (6.09 and 5.77 ppm). Finally, **3** is dimerized to **2**, which is the most thermodynamically stable complex.

In addition, it should be noted that nondeuterated **5e**, obtained as a major product from **1e** in C_6H_6 (60°C , 24 h), underwent rapid ligand exchange with the solvent C_6D_6 (Scheme 3). To the best of our knowledge, the reaction proposed in our study is one of the most reactive C–H or C–D activations in simple arenes by structurally well-defined transition-metal hydrides.¹⁸

In summary, we have demonstrated that ELHBs (**1**) derived from L_2ZrCl_2 and $\text{LiCp}^*\text{IrH}_3$ undergo thermolytic ligand elimination upon treatment with an alkyl lithium reagent, giving rise to a novel planar square complex **2**. The conversion of **1** to **2** occurs competitively with the oxidative addition of aromatic and benzylic C–H to the transient intermediate **3**.

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Supporting Information Available: Experimental details for the synthetic procedure and spectral data, crystallographic data of **1b**–**1e**, **2a**–**2c**, and **2e**, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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