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Synthesis and Reactivity of Early−Late Heterobimetallic Hydrides of Group 4 Metals and Iridium Supported by Mono(η^5-C_5Me_5) Ancillary Ligands: Bimetallic Carbon−Hydrogen Bond Activation

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Summary: Early−late heterobimetallic (ELHB) hydrido complexes comprising group 4 metals and iridium with mono(pentamethylcyclopentadienyl) (η^5-C_5Me_5 = Cp) ligands have been synthesized and structurally characterized. The hydrocarbyl complexes {Cp*M(CH_2SiMe_3)$_2$}(Cp*Ir)(μ-H)$_3$ (**3b**, M = Zr; **3c**, M = Hf) derived from (Cp*MCl_2)(Cp*Ir)(μ-H)$_3$ (**1b**, M = Zr; **1c**, M = Hf) displayed the cooperative C−H activation of methoxyarenes and pyridines.*

Over the past two decades, the study of early−late heterobimetallic (ELHB) complexes has been a major focus in multinuclear organotransition-metal chemistry because of the potential use of their cooperativity using both the Lewis acidity of the early metal and d-electron richness of the late metal in a single complex.[1] However, owing to the different intrinsic characteristics of the two metals, the behavior and reactivity of bimetallic systems are often nearly identical with those of the corresponding mononuclear metal complexes: i.e., one metal site functions independently from the other or preferentially to the other. Therefore, cooperative reactivity resulting from direct metal−metal interactions is still uncommon and should be distinguished from that of the not ideally behaving ELHBs where one metal unit serves as a metalloligand.[2] In our laboratory we have focused on the reaction chemistry of the Cp*Ru-based homo- and heterometallic hydrides.[3,4] For instance, upon dihydrogen elimination, (Cp*MH_3)(Cp*Ru)(μ-H)$_3$ (M = Mo, W) was found to selectively hold polar molecules such as $^iPrNH_2$ and PR_3 (R = Me, OMe) at the early-metal site.[4b] Currently our research interest is focused on anisotropic bimetallic complexes with the mono-Cp* ancillary ligand on each metal. There is a great deal of research on the synthesis of ELHBs with a group 4 metal unit, mostly by the following three methods: salt metathesis of early-metal halides and anionic late metals,[5] alkane or amine elimination of early-metal alkyls or amides with late-metal carbonyl hydrides,[6] and the insertion of low-valent early metals into the σ- or π-bond between late metals and heteroatoms.[7] Salt metathesis is likely to be the most reliable method for the synthesis of ELHB hydrides between group 4 and group 9 metals, due to the availability of group 4 metal halides and LiCp*IrH_3.[8] Here, we report the synthesis and cooperative reactivity of complexes of the type (Cp*MX_2)(Cp*Ir)(μ-H)$_3$ (M = Ti, Zr, Hf; X = Cl, alkyl).

(Cp*$TiCl_2$)(Cp*Ir)(μ-H)$_3$ (**1a**) was straightforwardly synthesized from a 1:1 mixture of available Cp*$TiCl_3$ and LiCp*IrH_3 in 83% yield and identified by NMR, elemental analysis, and crystallography (Scheme 1). The molecular structure is shown in Figure 1 with selected bond distances and angles. Although no direct metal−metal bond is found in **1a**, the distance of 2.5637(4) Å between Ti1 and Ir1 is sufficiently suitable for a metal−metal interaction.[9] The collinear Ti1−Ir1−CEN2 (178.5°) is reminiscent of reported dinuclear complexes with the (Cp*Ir)(μ-H)$_3$ fragment: (η^5-C_5Me_4EtRu)(Cp*Ir)(μ-H)$_3$, 177.6°; [(Cp*Ir)$_2$(μ-H)$_3$]ClO_4, 179.3°.[4a,10] The titanium center has a three-legged piano-stool geometry with an average titanium angle of 103°: Cl1−Ti1−Cl2 (99.50(2)°), Cl1−Ti−Ir1 (104.81(2)°), and Cl2−Ti1−Ir1 (105.08(2)°). In the ^1H NMR spectrum, the signal for the bridging hydrides (δ −9.55 ppm) is comparable with that of bridging hydrides in the aforementioned Ru−Ir trihydride (δ −17.37 ppm in C_6D_6) and cationic Ir−Ir trihydride (δ −15.33 ppm in $CDCl_3$), indicating that the 28-electron complex **1a** shows fair Lewis acidity due to the Cp*$TiCl_2$ unit.[4a,11] The NMR-scale reaction carried out in C_6D_6 at room temperature showed that the formation of **1a** involves disproportionation

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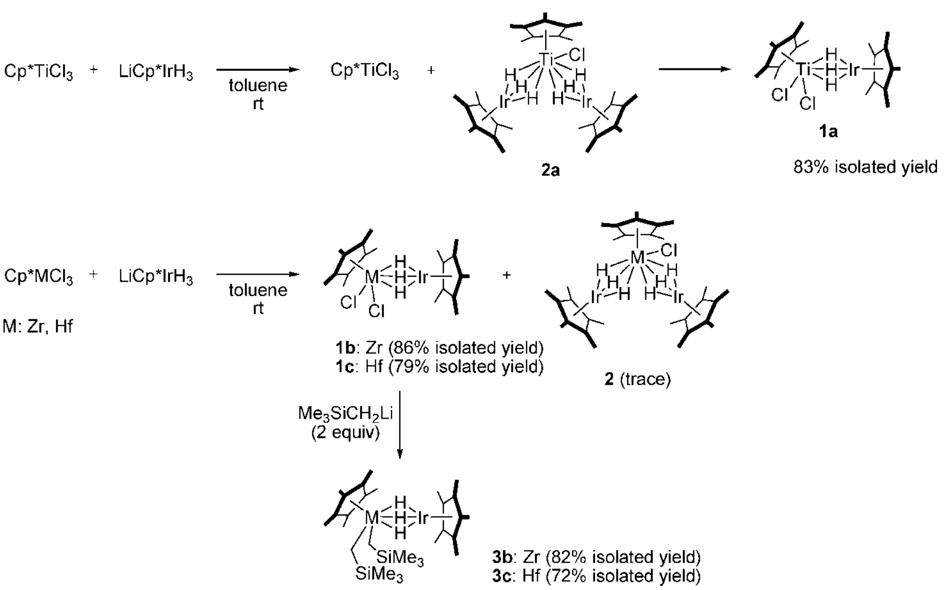
Scheme 1. Synthesis of 1 and 3



between an initially formed complex, which was assigned to the trinuclear (Cp*TiCl){(Cp*Ir)(μ-H)$_3$}$_2$ (**2a**), and the residual Cp*TiCl$_3$.[12] Under the same conditions of salt metathesis, (Cp*ZrCl$_2$)(Cp*Ir)(μ-H)$_3$ (**1b**) and (Cp*HfCl$_2$)(Cp*Ir)(μ-H)$_3$ (**1c**) were obtained in 86% and 79% isolated yields, respectively (Scheme 1), and these complexes were also characterized by NMR and X-ray analyses.[13]

For studying ligand exchange reactions on ELHBs, we then attempted to convert **1** into the corresponding perhydride or hydrocarbyl derivatives. Treatment of **1b** with LiBEt$_3$H or MeLi unfortunately resulted in unidentified complex mixtures.[14] On the other hand, Me$_3$SiCH$_2$Li acted as an excellent alkylating agent for **1b**,**c** (but not for **1a**) to afford the desired {Cp*M(CH$_2$SiMe$_3$)$_2$}(Cp*Ir)(μ-H)$_3$ (**3b**, M = Zr; **3c**, M = Hf) in excellent yields. **3b**,**c** were highly soluble in pentane but sufficiently crystalline to be isolated in pure form and were structurally characterized. The ^{1}H NMR spectra of **3** showed an upfield shift of the M−H resonance from those of **1** in addition to the typical geminal coupling of diastereotopic MCH$_2$SiMe$_3$ methylene protons (^2J = 11.4 Hz for **3b**,**c**). Since **3** appeared to be inert both to thermolysis in aromatic hydrocarbons and to hydrogenolysis, our attention was focused on the reactions with heteroatom-containing organic substrates that could serve as Lewis bases to the early-metal site for promoting the ligand exchange reactions. Several groups have intensively studied isotope labeling of organic substrates using the C−H activation chemistry of homogeneous cationic iridium complexes such as [IrH$_2$(Me$_2$CO)$_2$(PPh$_3$)$_2$]X (X = BF$_4$, SbF$_6$)[15] and Cp*(PMe$_3$)Ir(Me)(X) (X = OTf, BAr$^F_4$).[16,17] These previous studies led us to test the H/D exchange reaction between methoxyarenes and C$_6$D$_6$ using **3** as a neutral precursor complex. Thus, 1,4-dimethoxybenzene and 2-methoxynaphthalene were chosen as substrates for the H/D exchange reaction and heated at 100−120 °C in C$_6$D$_6$ under the influence of **3**, Cp*IrH$_4$, or Cp*Zr(CH$_2$SiMe$_3$)$_3$.[18] The aromatic C−H and methyl ether C−H in 1,4-dimethoxybenzene were effectively deuterated by using **3b**. Among those complexes **3b** proved to be the most active precursor complex (Figure 2).[19] The reaction of 2-methoxynaphthalene can reflect the regiochemical preference of active species. **3b** efficiently promoted deuterium incorporation into the aryl and methyl groups, with rapid exchange at H^6 and H^7.[20] However, when Cp*IrH$_4$ was used, no H/D exchange was observed at H^1 and H^3 and at the methyl ether C−H.[21] Although the active species in the aforementioned H/D exchange reactions

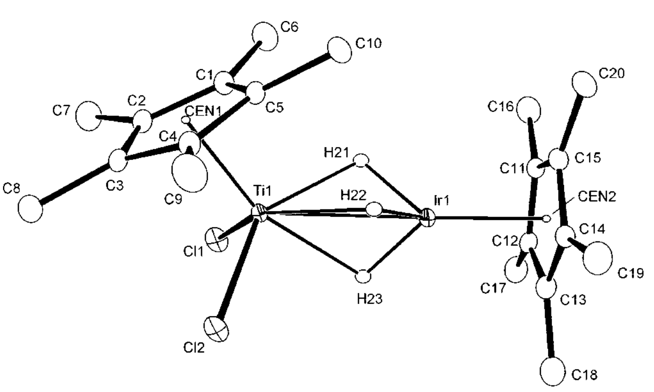


Figure 1. ORTEP diagram of **1a**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, except bridging hydrides, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti1−Ir1 = 2.5637(4), Ti1−Cl1 = 2.3069(5), Ti1−Cl2 = 2.3159(5), CEN1−Ti1 = 2.066, CEN2−Ir1 = 1.864; Cl1−Ti1−Cl2 = 99.50(2), CEN2−Ir1−Ti1 = 178.48, CEN1−Ti1−Ir1 = 124.38, CEN1−Ti1−Cl1 = 110.55, CEN1−Ti1−Cl2 = 109.60, Ir1−Ti1−Cl1 = 104.813(18), Ir1−Ti1−Cl2 = 105.082(19).

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(12) **2a** was obtained from a 1:1 mixture of **1a** and LiCp*IrH$_3$.

(13) Unlike **1a**, the dinuclear complexes **1b**,**c** were isolated by recrystallization, because no disproportionation between (Cp*MCl){(Cp*Ir)(μ-H)$_3$}$_2$ (**2b**, M = Zr; **2c**, M = Hf) and Cp*MCl$_3$ occurred.

(14) (Cp*ZrMe$_2$)(Cp*Ir)(μ-H)$_3$ can be obtained from Cp*ZrMe$_2$Cl and LiCp*IrH$_3$ in 84% yield but it completely decomposed at ambient temperature within 24 h. This observation may be related to the disappointing result of the attempted reduction and methylation of **1b**.

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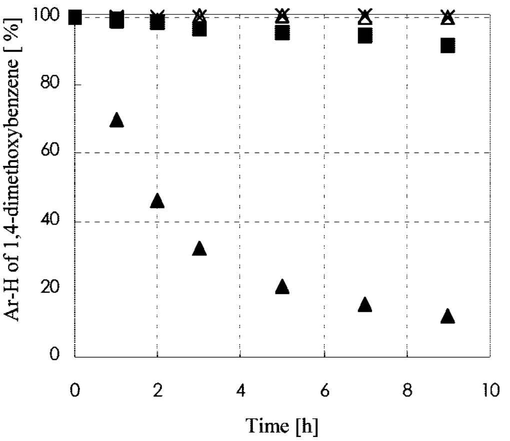
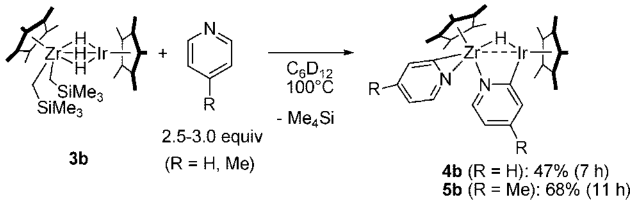


Figure 2. H/D exchange reaction of 1,4-dimethoxybenzene and C_6D_6: (■) Cp^*IrH_4; (▲) **3b**; (△) **3c**; (×) $Cp^*Zr(CH_2SiMe_3)_3$. The reaction was carried out in C_6D_6 at 120 °C using a J. Young valved NMR tube in the presence of a precursor complex (13 mol %); $[1,4\text{-dimethoxybenzene}]_0 = 0.11$ M.

is difficult to identify, the key structure after the initial Me_4Si elimination from **3** could be found out in substoichiometric reactions with less reactive arene substrates. Since nonsubstituted pyridine is known to be resistant to the H/D exchange by cationic iridium,[16j] the thermolysis of **3** in the presence of a 2.5−10-fold molar excess of pyridine was performed in C_6D_{12}, whereby **3b**,**c** both reacted with 2 mol equiv of pyridine at 100 and 140 °C, respectively, yielding the bis(pyridyl) complexes **4b**,**c** (Scheme 2). However, due to the following side reactions of **4**, we have not been able to optimize the reaction conditions to ensure clean conversion of **3** into **4**.[22] γ-Picoline more successfully underwent C−H cleavage by **3b** at 100 °C to afford the bis(picolyl) complex **5b** (78% conversion, 68% yield). From the crystallographic analysis of **5b**, which has η^2-picolyl-κ^2C,N and μ-picolyl-κ^2C,N ligands, illustrated in Figure 3, it can be seen that C−H activation of pyridine occurred formally over the two metal centers of **3** with loss of two Me_3SiCH_2 and two bridging hydride ligands. As a result, the metal−carbon bond was formed at each metal site in **3b** with the exceptionally short Zr−Ir distance of 2.5111(7) Å.[23,24] Moreover, the reaction between **3b** and excess pyridine was performed at 100 °C under two different reaction conditions: replacement of the solvent by C_6D_6 and use of pyridine-d_5. In both cases H/D exchange occurred in μ-H and pyridyl H^6 and $H^{6'}$ of **4b** and H^2 (D^2) and H^6 (D^6) of free pyridine but not in the methyl group C−H of eliminated Me_4Si.[25,26] In addition, under the latter conditions deuterium incorporation into the methyl group C−H of the Cp*Zr moiety was confirmed by ^1H and ^{13}C NMR spectra. Although the mechanism with respect to how C_6D_6 solvent interacts with the ELHB still remains elusive, these observations suggest the intermediate tucked-in complexes $\{(\eta^5:\eta^1\text{-}C_5Me_4CH_2)MR\}(Cp^*Ir)(\mu\text{-}H)_3$ (M = Zr, Hf; R = CH_2SiMe_3, pyridyl, picolyl, etc.) and reversible C−H activation of pyridine by **4** and **5**. The possible mechanism is as follows (Scheme 3):[27] the coordinatively unsaturated **3** associatively loses

Scheme 2. Reaction of 3b with Pyridines



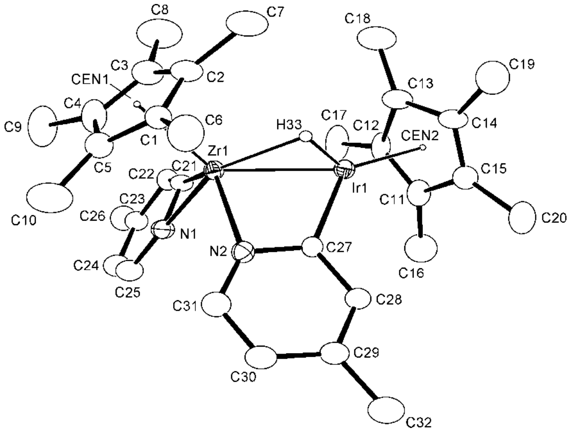


Figure 3. ORTEP diagram of **5b**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms except bridging hydrides are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−Ir1 = 2.5111(7), Zr1−N1 = 2.233(7), Zr1−N2 = 2.230(6), Zr1−C21 = 2.229(8), Zr1−C27 = 2.645(7), Ir1−C27 = 2.028(8), CEN1−Zr1 = 2.241, CEN2−Ir1 = 1.967, N1−C21 = 1.345(10), N2−C27 = 1.355(10); N1−Zr1−C21 = 35.1(3), N1−Zr1−N2 = 87.9(2), Zr1−N2−C27 = 91.8(5), N1−Zr1−Ir1 = 118.04(17), N2−Zr1−Ir1 = 76.31(17), CEN1−Zr1−Ir1 = 129.15, CEN1−Zr1−N1 = 111.84, CEN2−Ir1−Zr1 = 146.07, CEN2−Ir1−C27 = 134.69.

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(18) See the Supporting Information.

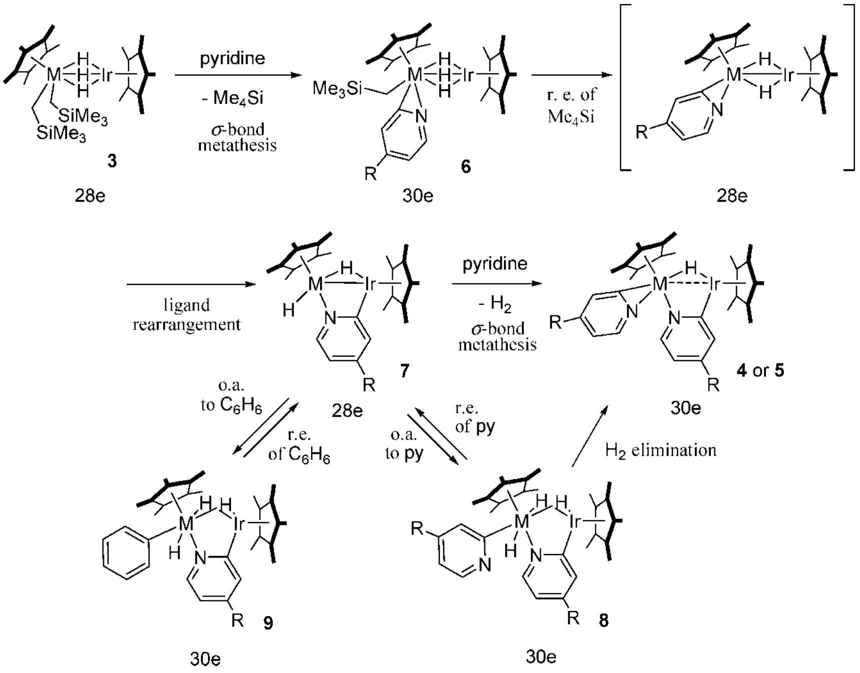
(19) After the reaction was performed with **3b** at 120 °C for 9 h, deuterium incorporations into the aryl and methyl groups were estimated by NMR to be 88% and 29%, respectively. Also, distribution of 1,4-dimethoxybenzene isotopomers was determined by GC-MS analysis of the deuterated and non-deuterated samples: d_9 (<1%), d_8 (5%), d_7 (11%), d_6 (18%), d_5 (24%), d_4 (22%), d_3 (11%), d_2 (5%), d_1 (2%), d_0 (<1%).

(20) As for the reaction of 1,4-dimethoxybenzene, deuterium incorporations into the aryl and methyl groups of 2-methoxynaphthalene-d_n obtained from the **3b**-mediated H/D exchange in C_6D_6 at 100 °C for 53.5 h were estimated by NMR to be 74% (H1), 80% (H4), 80% (H5, H8), 92% (H7), and 31% (CH_3), respectively. Distribution of 2-methoxynaphthalene isotopomers was determined by GC-MS analysis of the deuterated and non-deuterated samples: d_{10} (1%), d_9 (6%), d_8 (17%), d_7 (32%), d_6 (28%), d_5 (12%), d_4 (3%), d_3 (<1%).

(21) The ^1H NMR signal for H3 of 2-methoxynaphthalene in C_6D_6 overlaps with those for H6 and C_6D_5H, but the signal for H4 with no overlap appeared as a doublet throughout the exchange reaction.

(22) In contrast to the reaction with γ-picoline, the lengthy reaction time after ca. 40% yield of **4b** reproducibly gave a pentane-insoluble unknown dark green solid at the expense of **4b**.

Scheme 3. Proposed Mechanism for the Formation of 4 and 5 (M = Zr, Hf; R = H, Me)



the Me_3SiCH_2 group from the early-metal site by the nucleophilic attack of the Lewis basic substrate followed by ligand rearrangement (**3** → **7**) and successive reaction with the second pyridine and dihydrogen elimination from the intermediate **7** or **8**, ultimately leading to **4** and **5** with a pyridyl ligand as a good π-acceptor to stabilize the low-valent species (**7** → **4**, **5** or **7** → **8** → **4**, **5**).

In conclusion, we have demonstrated that the newly developed group 4 metal−iridium ELHB hydrido complexes with mono-Cp* ligands, in particular, **3b**, acts as an active neutral precursor complex for the H/D exchange between methoxyarenes and C_6D_6 and shows a cooperative reactivity in the C−H activation of pyridine derivatives. Development of useful transformations on the basis of the relevant bond activation by the cooperatively working ELHBs is under investigation.

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Supporting Information Available: Text, figures, tables, and CIF files giving detailed experimental procedures, spectral data of new compounds, and crystallographic data for **1a**,**b**, **3b**,**c**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) The detailed dynamic structure of bis(pyridyl) complexes will be discussed elsewhere.

(25) Reaction of **3b** with pyridine (5 equiv) in C_6D_6 at 100 °C for 30 h gave deuterium incorporation into **4b** (bridging hydride (19%), C6 (30%) and C6′ of pyridyl ligands) and free pyridine (C2, C6 (19%)).

(26) Reaction of **3b** with pyridine-d_5 (6 equiv) in C_6D_{12} at 100 °C for 11 h resulted in formation of **4b**-d_n with deuterium incorporation into the methyl group of Cp*Zr (20%) and bridging hydride (60%) and with hydrogen incorporation into pyridyl ligands at C6 and C6′ (average 25%).

(27) An argument about whether the mechanism involves C−H activation via σ-bond metathesis or a reductive elimination/oxidative addition sequence might arise. Before the Me_4Si elimination from **3**, no deuterium incorporation into the bridging hydrides was observed. Thus, the initial C−H cleavage of pyridines via σ-bond metathesis at the considered d^0 early-metal site (**3** → **6**) is considered to be the major mechanism. Deuterium incorporation into μ-H of **4b** should be caused by oxidative addition of some low-valent intermediates to deuterated arenes: e. g. **7** → **8**, **9**. Additionally, we are not able to rule out the energetically less favored dihydride elimination as dihydrogen from the possible pyridyl or picolyl trihydride intermediates **8**.