

## Synthesis of a Zirconium Sandwich Complex and Crystallographic Characterization of Its Adduct with Tetrahydrofuran

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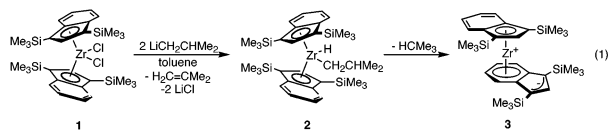
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The discovery of metal sandwich compounds, more commonly known as metallocenes, spawned the modern field of organometallic chemistry.<sup>1</sup> Interest in such molecules as related to group 4 transition metals originated with Wilkinson's attempt to prepare the parent titanocene,  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}^{\text{II}}]$ , over 50 years ago<sup>2</sup> and since that time has expanded to include numerous examples of M(IV), bent metallocene derivatives.<sup>3</sup> Subsequent attempts to prepare the parent sandwich compounds have been frustrated by their ability to activate cyclopentadienyl C–H bonds<sup>4</sup> or to bind relatively inert molecules such as dinitrogen.<sup>5</sup>

Preparation and crystallographic characterization of a titanium sandwich compound with sterically demanding cyclopentadienyl ligands was first described by Lawless<sup>6</sup> and more recently expanded by Mach.<sup>7</sup> Synthesis of the heavier group 4 congeners has not been achieved, owing to the greater thermodynamic driving force for these elements to attain their highest oxidation state.<sup>8</sup> Numerous catalytic processes<sup>9</sup> have implicated the existence of zirconocene, while other studies have successfully trapped the molecule with donor ligands.<sup>10</sup> In this communication, we report the synthesis of a zwitterionic, bis-indenyl zirconium sandwich complex, crystallographic characterization of its adduct with tetrahydrofuran, and preliminary reactivity studies.

Recent work in our laboratory has focused on the application of early transition metal alkane reductive elimination reactions to the hydrogenation of  $\text{P}_4$ <sup>11</sup> and the activation of molecular nitrogen.<sup>12</sup> Kinetic studies in the latter case demonstrated accelerated rates of alkane loss with addition of  $[\text{SiMe}_3]$  substituents to the cyclopentadienyl ligands. Having obtained these results, we became interested in studying the related bis-indenyl zirconium alkyl hydride complexes and determining the rate and products of their alkane reductive elimination reactions.

Synthesis of the desired zirconocene alkyl hydride complex,  $(\eta^5\text{-C}_9\text{H}_5\text{-1,3-(SiMe}_3)_2)_2\text{Zr}(\text{CH}_2\text{CHMe}_2)\text{H}$  (**2**), was achieved by addition of two equivalents of  $\text{LiCH}_2\text{CHMe}_2$  to a toluene solution of the corresponding dichloride complex, **1**, at 22 °C (eq 1). One equivalent of isobutene was also observed by  $^1\text{H}$  NMR spectroscopy and confirmed by mass spectrometry. Benzene- $d_6$  solutions of **2** undergo facile reductive elimination at ambient temperature, affording one equivalent of isobutane and a new burgundy zirconium complex, **3**. Rapid reductive elimination has thwarted all attempts to isolate **2** in the solid state. However, **3** may be obtained in multigram quantities by alkylation of **1**, followed by filtration and recrystallization from cold pentane.



Solution molecular weight determinations for **3** by cryoscopy and ebulliometry in benzene both provided values of  $570 \pm 60$

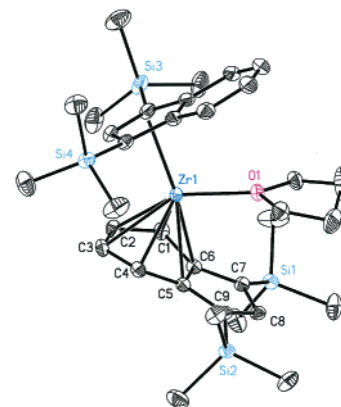


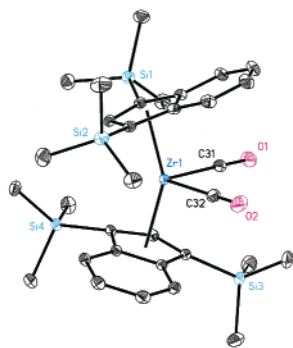
Figure 1. ORTEP diagram of **3-THF** with 30% probability ellipsoids.

amu, consistent with a monomeric bis-indenyl zirconium sandwich complex ( $\text{MW}_{\text{calc}} = 610$  amu). The possibility of a dinitrogen complex was ruled out by performing successful syntheses of **3** both in an argon atmosphere and under vacuum. Elemental analysis was also consistent with an empirical formula of  $[(\text{C}_9\text{H}_5\text{-1,3-(SiMe}_3)_2)_2\text{Zr}]$ .

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3** in benzene- $d_6$  and cyclohexane- $d_{12}$  are nearly identical and display a total of 8 and 12 ligand resonances, respectively, inconsistent with a  $\text{C}_{2v}$  symmetric zirconium sandwich complex. Instead, the NMR data indicate a  $\text{C}_s$  symmetric molecule with *inequivalent* indenyl rings. Moreover, the  $^1\text{H}$  NMR spectrum in benzene- $d_6$  displays benzo protons that are shifted upfield to 4.00 and 5.28 ppm, indicative of coordination of the six-membered ring to the zirconium center.<sup>13</sup> On the basis of these data and crystallographic characterization of its adduct with THF (vide infra), the most plausible structure for **3** is a zirconium sandwich in which one of the indenyl ligands has undergone a haptotropic rearrangement (eq 1).<sup>14</sup> Formally, **3** can be viewed as a 14-electron, zwitterionic zirconium sandwich complex.

Addition of an excess (>3 equiv) of THF to a pentane solution of **3** followed by solvent removal and recrystallization from heptane at  $-35$  °C afforded bright red crystals identified as **3-THF** (eq 2). Dissolution of pure **3-THF** in benzene- $d_6$  resulted in a 2:1 mixture of **3-THF** and **3** along with free THF. Complete (>95%) conversion to **3-THF** may be achieved by addition of more than 3 equiv of THF to benzene- $d_6$  solutions of **3**.

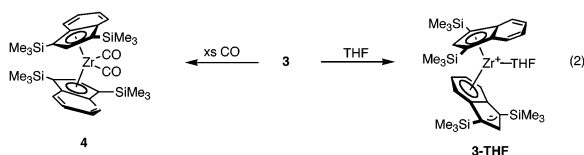
X-ray diffraction on single crystals of **3-THF** reveals a  $\text{C}_s$  symmetric zirconium complex with a centrally bound THF ligand (Figure 1). The molecule contains one commonly observed  $\eta^5$  indenyl ligand, while the other is bound through the benzo ring. The coordinated six-membered ring is no longer planar with a dihedral angle of  $19^\circ$  between the planes defined by  $\text{C1-C2-C3-C4}$  and  $\text{C1-C6-C5-C4}$ . Relatively short Zr–C1 and Zr–C4 distances of 2.340(2) and 2.355(3) Å, respectively, are also observed and are suggestive of localization in the benzo ring. This



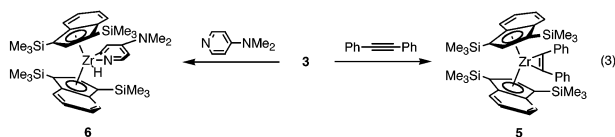
**Figure 2.** ORTEP diagram of **4** with 30% probability ellipsoids.

coordination environment is similar to that observed previously for a series of arene complexes of niobium<sup>15</sup> and tantalum<sup>16</sup> while formal  $\eta^2$  hapticity for a Cp ring has been reported for both titanium<sup>17</sup> and tantalum<sup>18</sup> complexes. Thus **3** and **3-THF** may be viewed as either Zr(II) complexes with an  $\eta^6$  indenyl ligand or as Zr(IV) compounds with a bound  $\eta^2, \eta^1, \eta^2, \eta^1$  six-membered ring.

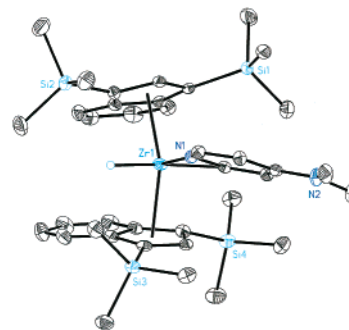
Preliminary reactivity studies were carried out with **3** to establish the molecule as a source of low-valent zirconium. Addition of one atmosphere of CO to a pentane solution of **3** resulted in isolation of forest green crystals identified as  $(\eta^5\text{-C}_9\text{H}_5\text{-1,3-(SiMe}_3)_2)_2\text{Zr}(\text{CO})_2$  (**4**) (eq 2).<sup>19</sup> Both NMR spectroscopic data and X-ray



diffraction studies (Figure 2) demonstrate  $\eta^5$  coordination of both indenyl ligands. Likewise, reaction of **3** with one equivalent of  $\text{PhC}\equiv\text{CPh}$  afforded the alkyne adduct,  $(\eta^5\text{-C}_9\text{H}_5\text{-1,3-(SiMe}_3)_2)_2\text{Zr}(\text{PhCCPh})$  (**5**), with  $\eta^5$  indenyl ligands as judged by its  $C_{2v}$  symmetry in benzene- $d_6$  solution (eq 3). Complexation of ligands more potent than THF is effective in promoting haptotropic rearrangement, resulting in familiar bent zirconocene derivatives.



Sandwich compound **3** also promotes the oxidative addition of carbon–hydrogen bonds. One equivalent of (dimethylamino)pyridine (DMAP) reacts with **3** to provide golden yellow crystals of  $(\eta^5\text{-C}_9\text{H}_5\text{-1,3-(SiMe}_3)_2)_2\text{Zr}(\eta^2\text{-cyclo-NC}_3\text{H}_3\text{-4-NMe}_2)\text{H}$  (**6**) (eq 3). Both the solution- and solid-state structure (Figure 3) of **6** contain  $\eta^5$  indenyl rings with central coordination of the pyridyl nitrogen and a transoid arrangement of the C–H fragments arising from oxidative addition.



**Figure 3.** ORTEP diagram of **6** with 30% probability ellipsoids.

In conclusion, alkane reductive elimination has provided the first example of a zirconium sandwich compound that undergoes haptotropic rearrangement to yield a zwitterionic zirconium sandwich with an  $\eta^6$  indenyl ligand. Reconstitution of  $\eta^5$  hapticity may be achieved by addition of strong donor ligands or by oxidative addition. Further studies exploring the chemistry of this unique molecule are currently under investigation.

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**Supporting Information Available:** Experimental procedures, NMR spectra for selected compounds (PDF); crystallographic data for **3-THF**, **4** and **6** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (19) Spectroscopic data can be found in the Supporting Information.

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