

### Preliminary communication

## A new route to early-late heterobimetallic $\mu$ -alkylidene complexes

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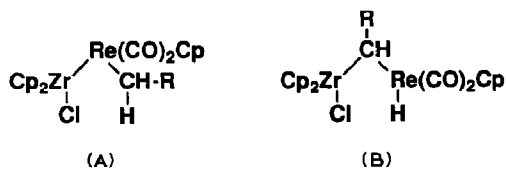
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### Abstract

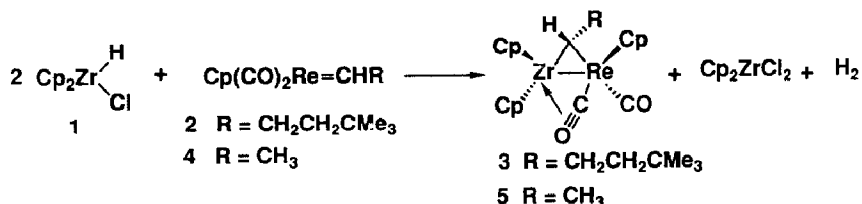
The reaction of two equivalents of  $\text{Cp}_2\text{ZrHCl}$  (**1**) with  $\text{Cp}(\text{CO})_2\text{Re}=\text{CHR}$  (**2**,  $\text{R} = \text{CH}_2\text{CH}_2\text{CMe}_3$ ; **4**,  $\text{R} = \text{CH}_3$ ) led to the formation of the heterobimetallic  $\mu$ -alkylidene complexes  $\text{Cp}_2\text{Zr}(\mu\text{-CHR})(\mu, \eta^1, \eta^2\text{-CO})\text{Re}(\text{CO})\text{Cp}$  (**3**,  $\text{R} = \text{CH}_2\text{CH}_2\text{CMe}_3$ ; **5**,  $\text{R} = \text{CH}_3$ ).

The isolobal relationship between the carbon–carbon double bond of alkenes and the carbon–metal double bond of metal carbene complexes [1] has led us to explore the reactions of rhenium carbene complexes  $\text{Cp}(\text{CO})_2\text{Re}=\text{CHR}$  with  $\text{Cp}_2\text{ZrHCl}$  (**1**), a reagent well known to add its Zr–H bond across the carbon–carbon double bond of alkenes [2]. Depending upon the regiochemistry of the addition, this approach might have initially produced either a new metal–metal bonded compound **A** or a new  $\mu$ -alkylidene complex **B**. Here we report that the reaction of  $\text{Cp}_2\text{ZrHCl}$  with rhenium carbene complexes produces new heterobimetallic bridging alkylidene complexes.

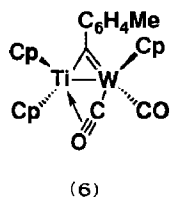


The reaction of  $\text{Cp}(\text{CO})_2\text{Re}=\text{CHCH}_2\text{CH}_2\text{CMe}_3$  (**2**) [3] with two equivalents of  $\text{Cp}_2\text{ZrHCl}$  (**1**) in benzene-*d*<sub>6</sub> was followed by 200 MHz <sup>1</sup>H NMR. Gas evolution occurred during the reaction which was complete after 20 min. The reaction proceeded cleanly to give  $\text{Cp}_2\text{ZrCl}_2$  ( $\delta$  5.87 ppm),  $\text{H}_2$  ( $\delta$  4.46 ppm) and the new heterobimetallic  $\mu$ -alkylidene complex  $\text{Cp}_2\text{Zr}(\mu\text{-CHR})(\mu, \eta^1, \eta^2\text{-CO})\text{Re}(\text{CO})\text{Cp}$  (**3**). In a preparative reaction, **1** (295 mg, 1.14 mmol) and **2** (195 mg, 0.48 mmol) in 30 ml of toluene were stirred for 30 min at room temperature. As the reaction proceeded, gas

evolved and **1** dissolved. Toluene was evaporated and the residue was extracted with diethyl ether (20 ml). The ether solution was filtered and evaporated. Pentane (20 ml) was added to the resulting yellow glass, the mixture was filtered, and pentane was evaporated to give  $\text{Cp}_2\text{Zr}(\mu\text{-CHR})(\mu\text{-}\eta^1, \eta^2\text{-CO})\text{Re}(\text{CO})\text{Cp}$  (**3**) (118 mg, 63%) as a yellow, crystalline solid. A  $^1\text{H}$  NMR study showed that the heterobimetallic compound **3** was also produced from the reaction of **2** with one equivalent of  $\text{Cp}_2\text{ZrH}_2$  in benzene- $d_6$ .



The structure of **3** was established spectroscopically [4\*]. The elemental composition of the heterobimetallic complex **3** was determined by high resolution mass spectroscopy. The three different cyclopentadienyl groups of **3** give rise to three resonances in the  $^1\text{H}$  NMR at  $\delta$  5.68, 5.32 and 4.75 ppm and in the  $^{13}\text{C}$  NMR at  $\delta$  108.5, 106.9, and 87.4 ppm. The proton on the bridging alkylidene carbon appears downfield at  $\delta$  6.79 as a doublet of doublets with unequal coupling ( $J$  9.4, 6.3 Hz) to the diastereotopic protons of the neighboring methylene group. Single frequency  $^1\text{H}$  decoupling at  $\delta$  6.79 ppm resulted in collapse of a doublet ( $J(\text{CH})$  120 Hz) in the  $^{13}\text{C}$  NMR at  $\delta$  111.3 ppm to a singlet and allowed assignment of this signal to the bridging alkylidene carbon. The IR spectrum of **3** has strong bands at 1902 and 1669  $\text{cm}^{-1}$ , consistent with the presence of one terminal and one bridging carbonyl group. In the  $^{13}\text{C}$  NMR spectrum, these two carbonyl groups give rise to resonances at  $\delta$  207.4 and 205.5 ppm. This implicates a  $\mu\text{-}\eta^1, \eta^2\text{-CO}$  bridging mode since a symmetrically bridged  $\mu\text{-CO}$  group would have led to a significantly farther downfield  $^{13}\text{C}$  resonance [5].



Stone has reported the synthesis of the closely related heterobimetallic  $\mu$ -alkylidyne complexes  $\text{Cp}_2\text{M}(\mu\text{-CC}_6\text{H}_4\text{Me})(\mu\text{-}\eta^1, \eta^2\text{-CO})\text{W}(\text{CO})\text{Cp}$  (**6**,  $\text{M} = \text{Ti}$ ; **7**,  $\text{M} = \text{Zr}$ ) from the reaction of  $\text{Cp}_2\text{M}(\text{CO})_2$  with  $\text{Cp}(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_4\text{Me}$ . Both **6** and **7** exhibit terminal and bridging carbonyl bands in the IR, similar  $^{13}\text{C}$  NMR chemical shifts for the terminal and bridging carbonyls, and three different Cp resonances in

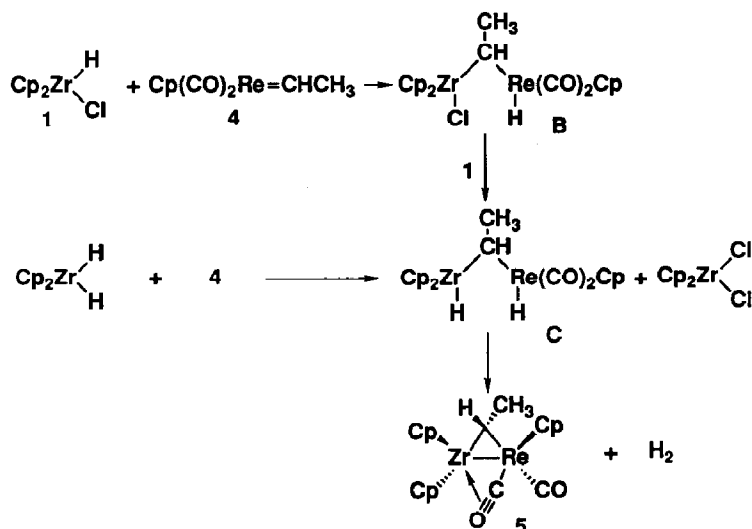
\* Reference number with asterisk indicates a note in the list of references.

both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The X-ray crystal structure of **6** confirmed the presence of the  $\mu\text{-}\eta^1,\eta^2\text{-CO}$  unit.

The reaction of  $\text{Cp}(\text{CO})_2\text{Re}=\text{CHCH}_3$  (**4**) [3] with  $\text{Cp}_2\text{ZrHCl}$  (**1**) in benzene- $d_6$  was followed by 200 MHz  $^1\text{H}$  NMR. A clean reaction occurred to produce  $\text{Cp}_2\text{ZrCl}_2$  ( $\delta$  5.87 ppm) and  $\text{Cp}_2\text{Zr}(\mu\text{-CHCH}_3)(\mu\text{-}\eta^1,\eta^2\text{-CO})\text{Re}(\text{CO})\text{Cp}$  (**5**) [7\*]. The zirconium-rhenium bimetallic compound **5** was more readily isolated from the reaction of **4** with  $\text{Cp}_2\text{ZrH}_2$  since  $\text{H}_2$  is the only by-product. Addition of  $\text{Cp}_2\text{ZrH}_2$  (0.5 mmol) to a THF solution of  $\text{Cp}(\text{CO})_2\text{Re}=\text{CHCH}_3$  (**4**) (0.5 mmol, containing a small amount of  $\text{CpRe}(\text{CO})_3$  as an impurity) led to gas evolution. Solvent was evaporated and the residue was dissolved in 30 ml ether. The ether solution was filtered and concentrated to 3 ml to give **5** (44%) as a yellow solid. Analytically pure **5** [8\*] was obtained by washing with cold ether and with hexane at room temperature.

Although there are two possible diastereomers of **3** and **5** which differ in the relationship between the Cp ligand on rhenium and the alkyl substituent on the  $\mu$ -alkylidene group, only single diastereomers of **3** and of **5** were observed. If the two possible diastereomers of **5** were in rapid equilibrium, then only a single averaged NMR spectrum would be observed. When the  $^1\text{H}$  NMR of **5** was taken at  $-99^\circ\text{C}$  in THF- $d_8$ , only a single species was seen. Either only a single diastereomer is present or the two diastereomers have an extremely low barrier for interconversion. While we have no experimental evidence relating to the stereochemistry of **3** and **5**, we have depicted **3** and **5** as the least sterically crowded diastereomers.

A mechanistic hypothesis for the formation of these new heterobimetallic  $\mu$ -alkylidene complexes is shown in Scheme 1. Initial regioselective addition of the Zr-H bond of  $\text{Cp}_2\text{ZrHCl}$  across the  $\text{Re}=\text{C}$  double bond of **4** is suggested to produce a  $\mu$ -alkylidene intermediate **B**. Reaction of **B** with a second equivalent of  $\text{Cp}_2\text{ZrHCl}$  is suggested to result in exchange of hydride and chloride between the two zirconium centers and to produce the bimetallic dihydride **C** and  $\text{Cp}_2\text{ZrCl}_2$ . The dihydride **C** can also be produced by addition of a Zr-H bond of  $\text{Cp}_2\text{ZrH}_2$  across



Scheme 1

the Re=C double bond of **4**. Since the Re-H bond of putative intermediate **C** would be expected to be acidic in analogy with CpRe(CO)<sub>2</sub>H<sub>2</sub> [9] and since Zr hydrides are known to react with acids to produce H<sub>2</sub>, we suggest that intermediate dihydride **C** eliminates H<sub>2</sub> to form a metal-metal bond. Finally, coordination of the  $\pi$ -system of a rhenium carbonyl to zirconium would complete formation of **5**.

The only other compounds in which  $\mu$ -alkylidene ligands bridge a group 4 and later transition metal are those such as Cp<sub>2</sub>Ti( $\mu$ -CH<sub>2</sub>)( $\mu$ -Cl)Rh(1,5-cyclooctadiene) reported by Grubbs [10]. These compounds are formed by reaction of titanacyclobutanes with late transition metal chloride complexes. The two metal centers are held together primarily by the methylene and chloride bridges; there is at most a weak, dative metal-metal interaction. Complexes **3** and **5** are, therefore, the first compounds in which a  $\mu$ -alkylidene ligand bridges a group 4-late transition metal bond. Bergman has recently reported the synthesis of Cp<sub>2</sub>(CH<sub>3</sub>)Ta( $\mu$ -CH<sub>2</sub>)Pt(PMe<sub>3</sub>)<sub>2</sub> in which a methylene ligand bridges a group 5-late transition metal bond [11].

The formation of **3** implies that the electrophilic zirconium atom of Cp<sub>2</sub>ZrHCl adds to the carbene carbon of **2** as depicted in Scheme 1. This constitutes an unusual addition of an electrophile to the carbene carbon of a *d*<sup>6</sup> metal-carbene complex. In other research on the reactivity of **2**, we have found that both electrophiles and nucleophiles add to the carbene carbon of **2** [12]. The regiochemistry of the addition of zirconium hydride to **2** is the opposite of that found by Lukehart for the addition of metal hydrides to metal carbyne complexes [13]. For example, Lukehart has reported the addition of *trans*-Pt(PEt<sub>3</sub>)<sub>2</sub>H(S)<sup>+</sup> across the metal carbon triple bond of Cp(CO)<sub>2</sub>W $\equiv$ C-C<sub>6</sub>H<sub>4</sub>-*p*-CH<sub>3</sub> to produce Cp(CO)W( $\mu$ -CO)( $\mu$ -CHAr)Pt(PEt<sub>3</sub>)<sub>2</sub><sup>+</sup>.

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- 4 For **3**: <sup>1</sup>H NMR (270 MHz, benzene-*d*<sub>6</sub>)  $\delta$  6.79 (dd, *J* 9.4, 6.3 Hz;  $\mu$ -CH), 5.68 (s, C<sub>5</sub>H<sub>5</sub>), 5.32 (s, C<sub>5</sub>H<sub>5</sub>), 4.75 (s, C<sub>5</sub>H<sub>5</sub>), 3.08 (m, CHCHH), 2.75 (m, CHCHH), 1.41 (m, CH<sub>2</sub>CMe<sub>3</sub>), 1.11 (s, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, benzene-*d*<sub>6</sub>)  $\delta$  207.4 (s, CO), 205.5 (s, CO), 111.3 (d, *J* 120 Hz,  $\mu$ -CH), 108.5 (d, *J* 172 Hz, C<sub>5</sub>H<sub>5</sub>), 106.9 (d, *J* 174 Hz, C<sub>5</sub>H<sub>5</sub>), 87.4 (d, *J* 179 Hz, C<sub>5</sub>H<sub>5</sub>), 52.8 (t, *J* 119 Hz, CH<sub>2</sub>), 49.1 (t, *J* 122 Hz, CH<sub>2</sub>), 30.8 (s, C(CH<sub>3</sub>)<sub>3</sub>), 30.0 (q, *J* 122 Hz, C(CH<sub>3</sub>)<sub>3</sub>). IR (toluene): 1902 (vs), 1669 (s), cm<sup>-1</sup>. HRMS: found 626.0754; C<sub>24</sub>H<sub>29</sub>O<sub>2</sub> <sup>187</sup>Re<sup>90</sup>Zr calcd. 626.0776; 598 (*M* - CO); 570 (*M* - 2CO).
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- 7 **5** was also obtained from reaction of Li<sup>+</sup> Cp(CO)<sub>2</sub>Re(COCH<sub>3</sub>)<sup>-</sup> with excess Cp<sub>2</sub>ZrHCl. It is likely that alkylidene complex **4** is initially formed and then converted to **5**.
- 8 For **5**: <sup>1</sup>H NMR (200 MHz, benzene-*d*<sub>6</sub>)  $\delta$  6.97 (q, *J* 7.4 Hz,  $\mu$ -CH), 5.65 (s, C<sub>5</sub>H<sub>5</sub>), 5.28 (s, C<sub>5</sub>H<sub>5</sub>), 4.71 (s, C<sub>5</sub>H<sub>5</sub>), 2.92 (d, *J* 7.4 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, THF-*d*<sub>8</sub>)  $\delta$  207.4 (s, CO), 206.4 (s, CO), 109.1 (d, *J* 172 Hz, C<sub>5</sub>H<sub>5</sub>), 107.8 (d, *J* 172 Hz, C<sub>5</sub>H<sub>5</sub>), 102.0 (d, *J* 123 Hz,  $\mu$ -CH), 88.4 (d, *J* 179 Hz, C<sub>5</sub>H<sub>5</sub>), 40.3 (q, *J* 124 Hz, CH<sub>3</sub>). IR (toluene) 1901 (vs), 1666 (s) cm<sup>-1</sup>. HRMS: found 555.9990. C<sub>19</sub>H<sub>19</sub>O<sub>2</sub> <sup>187</sup>Re<sup>90</sup>Zr calcd. 555.9965. Anal. Found: C, 40.85; H, 3.37. C<sub>19</sub>H<sub>19</sub>O<sub>2</sub>ReZr calcd.: C, 40.98; H, 3.44%.

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