

Figure 2. Stereoscopic view of the packing. Dotted lines indicate the hydrogen bonds.

metry are connected by the O(5 γ)-H...N(1') hydrogen bonds. These hydrogen bonds connect the molecules to form a hydrogen-bonded molecular layer. The flexible THF moieties lie between these layers and do not make close contacts with any parts of the other molecules. TPD also has a similar hydrogen bonding scheme and the propyl moiety is dynamically disordered.

The great reactivity of the ring-opened derivatives toward the formation of the thiazolium ring seems to result in part from flexibility of the substituent at S(1) and preserved capability of easy rotation about the N(3)-C(4) single bond as observed in this structure.

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Syntheses and Spectroscopic Studies of Metal-Metal Bonded Complexes (Zr-Fe)

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The preparation of the metal-metal bonded complex $Cp_2ZrClFeCp(CO)_2$ has been achieved by the reaction of Cp_2ZrCl and strong nucleophile $NaFeCp(CO)_2$. The more soluble metal-metal bonded complexes $Cp_2ZrRFeCp(CO)_2$ ($R=CH_3, n-C_4H_9$) have also been prepared through the reaction of Cp_2ZrRCl and $NaCpFe(CO)_2$. The complexes were characterized by IR, Raman, 1H NMR and Mass spectra. The complete absorption ($100-3800cm^{-1}$) spectra for the three metal-metal bonded molecules are reported and the bands of each vibration were assigned.

Introduction

There is increasing evidence that binuclear transition metal complexes will play important roles in the development of organotransition metal chemistry. In one role, these simple compounds can serve as models for more complex systems. In a second role, bimetallic compounds containing early transition metal and late transition metal should prove unique and

useful in their own right. This potential is suggested by recent studies revealing bimetallic mechanisms in reactions previously believed to take place at a single metal site.¹ Especially interesting are the recent applications of mixed-metal systems in organic synthesis.²

In view of the importance of biheterometallic compounds containing early and late transition metals, we have attempted to form metal-metal bonds containing zirconium. The first

report of the apparent formation of a metal-to-metal bond between zirconium and other transition metal atom was made by Renault *et. al.*,³ who reported the synthesis of $\text{Cp}_2(\text{CH}_3)\text{ZrMoCp}(\text{CO})_2$ by the reaction of $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ and $\text{HMoCp}(\text{Co})$, with accompanying production of CH_4 . No structural or spectroscopic information was given in that report, but it was postulated that the product had a Zr-Mo bond. In 1981, Norton* postulated that this compound actually had a supported metal-metal bond, and the support is a four electron donor CO ligand. It thus appeared that no compounds with unsupported Zr-transition metal bonds had been substantiated; although they clearly would be of interest both in their own right and as models for reactions in which Zr-to-metal bonding would be an important interaction.

Described herein are the syntheses and the characterization of Zr-to-metal bonded complexes formed through the reaction of a group IV-B metal, Cp_2ZrCl_2 , and its alkyl derivatives, with a strongly nucleophilic iron carbonylate anion.

Experimental

All syntheses described were done in carefully dried and degassed solvents, under N_2 or *in vacuo*, and with the use of Schlenk type glassware. All materials were of highest commercial grade and were purified appropriately before use.

The Cp_2ZrCl_2 was obtained from Aldrich Chemical Co., and the $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Cl}$ were prepared from the reaction of $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$ with PbCl_2 following the procedure of Wailes⁵ with some modifications. The $\text{Cp}_2\text{Zr}(\text{C}_6\text{H}_7)\text{Cl}$ was prepared according to the literature method.⁶ The $\text{NaCpFe}(\text{CO})_2$ was prepared according to the standard procedure.⁷ Infrared spectra were measured on a Digilab FTS-15B. Raman spectra were obtained with a Jarrel-Ash 25-300 Raman spectrometer using the 488nm line of an Ar⁺ laser as an exciting source.

NMR spectra were measured on a Bruker WP 250, and mass spectra on a Perkin-Elmer RMV-6D spectrometer. The elemental analyses were performed by Galbraith Labs., Knoxville, TN.

Preparation of $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{FeCp}(\text{CO})_2$. To a stirred solution of $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Cl}$ (1.5 mmol in 30 ml THF) was added 20 ml of THF solution containing 1.3 mmol of $\text{NaCpFe}(\text{CO})_2$. After stirring for 30 min., the solution was filtered and, then, the solvent was removed at 25°C under reduced pressure and dried at 40°C on a vacuum line. A minimum amount of THF was added to dissolve the product, and the solution was filtered to remove NaCl. The solvent was removed under reduced pressure, followed by an addition of a minimum amount of benzene to the resulting orange solid. This mixture was filtered and washed three times with cyclohexane to remove unreacted $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{Cl}$ and dried *in vacuo* for three hours. The air-sensitive orange product was decomposed in a sealed melting point capillary without melting at 142-145°C. Yield: 62%. ¹H NMR(d_6 -THF); 6.25(5H), 4.35(5H), 1.20(3H)ppm. IR(in THF); 1946, 1893 cm^{-1} . Anal. Calcd for $\text{ZrFeC}_{16}\text{H}_{16}\text{O}_2$: C, 52.29; H, 4.36. Found: C, 53.01; H, 4.40.

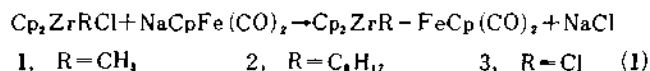
Preparation of $\text{Cp}_2\text{Zr}(\text{C}_6\text{H}_7)\text{FeCp}(\text{CO})_2$. To a stirred THF solution of $\text{Cp}_2\text{Zr}(\text{C}_6\text{H}_7)\text{Cl}$ (1.2 mmol) was added a THF solution of $\text{NaCpFe}(\text{CO})_2$ (1.2 mmol) dropwise. The reaction was continued for 40 min. and, then, the solution was filtered. The solvent was removed at 25°C under reduced pressure. The resulting reddish orange solid was extracted with benzene

(6 ml) and dried. The orange solid was washed with cyclohexane to remove unreacted $\text{Cp}_2\text{Zr}(\text{C}_6\text{H}_7)\text{Cl}$ and dried *in vacuo* overnight. mp: 112-115°C. Yield: 75%. ¹H NMR(d_6 -THF); 6.34(5H), 4.68(5H), 1.42-2.23 (14H, featureless), 1.08(3H) ppm. IR (nujol): 1978, 1937 cm^{-1} . Anal. Calcd for $\text{ZrFeC}_{25}\text{H}_{32}\text{O}_2$: C, 58.70; H, 6.26. Found: C, 58.96; H, 6.32.

Preparation of $\text{Cp}_2\text{ZrClFeCp}(\text{CO})_2$. To a stirred THF solution of Cp_2ZrCl_2 (0.8 mmol) was added a THF solution of $\text{NaCpFe}(\text{CO})_2$ (0.8 mmol). The reaction was continued for 1.5h and, then, the solution was filtered. The solvent was removed and the residue was extracted with THF (3 ml). Benzene was layered on the solution. The resulting orange solid was filtered. The orange solid was washed with hexane and dried *in vacuo* overnight. mp: 142-145°C. Yield: 78%. ¹H NMR(d_6 -THF); 6.38(5H), 4.89(5H)ppm. IR(in THF): 1955, 1904 cm^{-1} . Anal. Calcd for $\text{ZrFeC}_{17}\text{H}_{15}\text{O}_2\text{Cl}$: C, 47.06; H, 3.49. Found: C, 47.86; H, 3.56.

Results and Discussion

The reactions of Cp_2ZrRCl and Cp_2ZrCl_2 with $\text{NaCpFe}(\text{CO})_2$ result in the formation of the zirconium-iron bonded complexes **1**, **2** and **3**, respectively, in high yields (eq. 1). The structures of the compounds were deduced from their IR, ¹H NMR, Mass spectra and elemental analysis.



The ¹H NMR spectrum of **1** taken in THF-*d*₆ contained peaks only at δ 6.25, 4.35, and 1.20. The integrated intensity ratio of these three peaks is exactly 10:5:3. The peak at δ 6.25 is assigned to cyclopentadienyl protons on the zirconium site and one at δ 4.35 is assigned to those attached to the iron. The band at δ 1.20 is assigned to the methyl protons on the zirconium site. In the case of **3**, there are two peaks in the cyclopentadienyl region. One peak is observed at 6.38ppm due to the equivalent cyclopentadienyl protons on the zirconium and another peak is found at 4.89ppm due to those on the iron. The slight difference in the chemical shift can be explained by the inductive effect. The withdrawing effect of Cl compared to CH₃ agrees with the arguments made below about the δ (C-H) out of plane bending mode of infrared spectrum, which is quite sensitive to charge density on the group IV-B metal.

In the mass spectrum of **1**, the principal spectral peaks in 100-1000 *m/e* are shown in Table 1. The assignment of all mass spectral peaks to the molecular ion and its fragment clearly identified the methyl compounds as **1**. The peak at *m/e* 412 is the molecular ion peak corresponding to the formula of **1**. It was also found that the dominant fragmentation route was the loss of CH₃, followed by two CO's. They led to peaks at *m/e* 397 [$\text{M}-\text{CH}_3$]⁺, *m/e* 369 [$397-\text{CO}$]⁺ and *m/e* 356 [$412-2\text{CO}$]⁺, respectively. This fragmentation pattern demonstrates the presence of the Zr-CH₃ bond.

In the infrared spectrum taken immediately after dissolution in THF solution, ν (CO) bands were observed at 1893 and 1946 cm^{-1} for **1** and at 1904 and 1955 cm^{-1} for **3**, as shown in Figure 1. Two peaks in the carbonyl region are expected for the iron complexes with $\text{FeCp}(\text{CO})_2$ moieties.⁸⁻¹⁰ The slight

Table 1. Principal Mass Spectral Peaks for $Cp_2Zr(CH_3)FeCp(CO)_2$ in the Region 100–1000 m/e

m/e	Relative Abundance	Corresponding Ion
412	0.08	$Cp_2ZrCH_3FeCp(CO)_2^+$
397	0.04	$Cp_2ZrFeCp(CO)_2^+$
369	0.03	$Cp_2ZrFeCp(CO)^+$
356	0.05	$Cp_2ZrCH_3FeCp^+$
341	0.15	$Cp_2ZrFeCp^+$
282	0.06	$ZrCH_3FeCp(CO)_2^+$
254	0.11	$ZrCH_3FeCp(CO)^+$
234	0.5	$Cp_2ZrCH_3^+$
220	0.6	Cp_2Zr^+
192	0.11	$FeCH_3Cp(CO)_2^+$
186	0.32	$FeCp_2^+$
177	0.25	$FeCp(CO)_2^+$
149	0.37	$FeCp(CO)^+$
121	1	$FeCp^+$

difference in CO frequency number of both compounds can be interpreted as the difference in electron withdrawing strength of Cl and CH_3 group. Peaks marked with a D are due to the parent dimer $[FeCp(CO)_2]_2$ decomposed from the products, **1** and **3**, in THF solution. The nujol mull spectra contain only two ν (CO) bands for each, shifted as expected by solid state and solvent effect from their solution frequencies. Those for the methyl derivative, for example, are shifted from 1946 and 1893 cm^{-1} to 1941 and 1872 cm^{-1} in nujol, respectively. A complex containing this group should have an infrared active symmetric mode and an infrared active antisymmetric mode. The nujol mull spectrum of **2** has two bands at 1978 and 1937 cm^{-1} . They correspond well with those of **1**. There is no carbonyl band in the 1500–1700 cm^{-1} region, as would be characteristic of the $\mu-\eta^1, \eta^2$ -CO group. These complexes are good examples of unsupported Zr-transition metal bonded compounds. In the lower frequency (700–900 cm^{-1}) region, the most significant bands are peaks characteristic of the cyclopentadienyl ligand. The peak at 803 cm^{-1} in **1** and that at 808 cm^{-1} in **3** are assigned as the δ (C–H) band, the out-of-plane bending mode of the hydrogens on the cyclopentadienyl ligand of the group IV-B metals.

The δ (C–H) band of η^5 - C_5H_5 coordinated to Zr, which is known to be quite sensitive to the electronegativity of the X and Y moieties in Cp_2ZrXY compounds.^{11–13} is shifted from 814 cm^{-1} in Cp_2ZrCl_2 ¹⁴ to 808 cm^{-1} in **3** and to 802 cm^{-1} in **1**. It has been shown that the more electropositive the group IV-B metal becomes the higher is the frequency of this mode in its bis cyclopentadienyl complexes. In this sense, the shift to lower frequency of **1** compared to the starting material may mean that the group IV-B metal compound is slightly more negative than the starting material.

All of the bands in the 500–700 cm^{-1} region are due to the δ (M–C–O) or δ (M–C) vibrations. The peaks at 658, 600 and 542 cm^{-1} are assigned to coupled δ (M–C–O) and δ (M–C) modes of terminal carbonyls in **1**. The band at 510 cm^{-1} is due to the coupled δ (M–C–O) and δ (M–C) modes, as expected in this region.¹⁵

The far infrared spectrum of a nujol mull of **1** on a

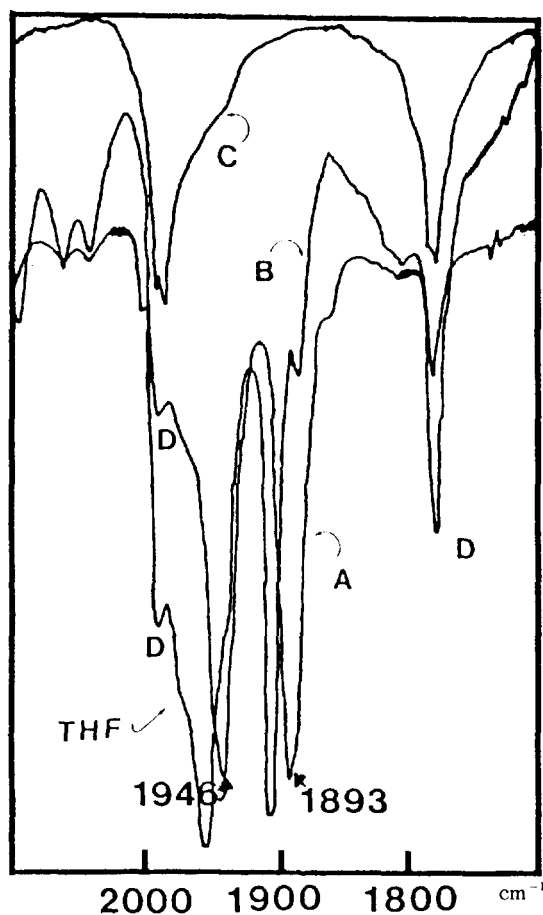


Figure 1. The ν (CO) region of the infrared spectrum of A = $Cp_2Zr(CH_3)FeCp(CO)_2$, B = $Cp_2ZrClFeCp(CO)_2$, C = $[FeCp(CO)_2]_2$ in THF, and D = $[FeCp(CO)_2]_2$ decomposed from the products, A and B, in THF solution.

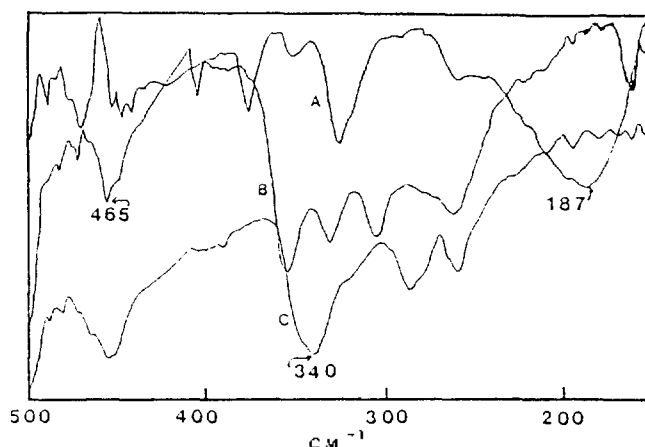
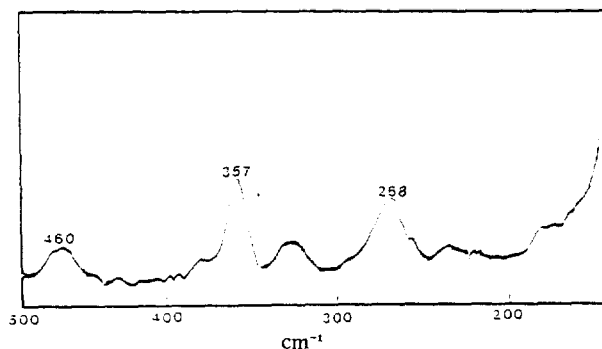


Figure 2. A. The far infrared spectrum of $Cp_2Zr(CH_3)FeCp(CO)_2$ as a nujol mull (500–100 cm^{-1}); B. The far infrared spectrum of $Cp_2Zr(CH_2Cl)FeCp(CO)_2$ as a nujol mull (500–100 cm^{-1}); C. The far infrared spectrum of Cp_2ZrCl_2 as a nujol mull (500–100 cm^{-1}).

polyethylene film is presented in Figure 2, along with those of Cp_2ZrCl_2 and $Cp_2Zr(CH_2)Cl$. Table 2 lists the bands of **1**

Table 2. The Far-IR and Raman spectral bands and assignments of $[\text{Cp}_2\text{ZrCH}_3\text{-FeCp}(\text{CO})_2]$ and $[\text{Cp}_2\text{ZrCl-FeCp}(\text{CO})_2]$

Far-IR		Raman
$\text{Cp}_2\text{ZrCH}_3\text{-FeCp}(\text{CO})_2$	$\text{Cp}_2\text{ZrCl-FeCp}(\text{CO})_2$	$\text{Cp}_2\text{ZrCH}_3\text{-FeCp}(\text{CO})_2$
187 (vs) $\nu(\text{Zr-Fe})$	181 $\nu(\text{Zr-Fe})$	127 (s) $\nu(\text{Cp-Zr-Cp})$
260 (w) $\nu(\text{Zr-Cp})$		268 (s) $\nu(\text{Zr-Cp})$
325 (s) $\nu(\text{Zr-Cp})$		325 (m) $\nu(\text{Zr-Cp})$
253 (w) $\nu(\text{Fe-Cp})$		357 (s) $\nu(\text{Fe-Cp})$
378 (m) $\nu(\text{Fe-Cp})$		460 (m) $\nu(\text{Zr-C})$
455 (s) $\nu(\text{Zr-C})$		
465 (m) $\nu(\text{Fe-C})$		

**Figure 3.** The Raman Spectrum of $\text{Cp}_2\text{Zr}(\text{CH}_3)\text{FeCp}(\text{CO})_2$ (500–150 cm^{-1})

in the region from 500 cm^{-1} to 50 cm^{-1} along with their assignments. Among the far infrared features, the dominant band, which is not present in the spectra of any of the starting materials, is a strong band at 187 cm^{-1} for **1** (181 cm^{-1} for **3**). It is assigned to the Zr-Fe stretching mode. This assignment at 187 cm^{-1} is in excellent agreement with the known $\nu(\text{M-M})$ assignment.¹⁶⁻¹⁸ Other far-infrared bands, such as the $\nu(\text{Fe-C})$, $\nu(\text{Zr-Cp})$, and $\nu(\text{Fe-C-O})$, were observed as expected from the spectra of the starting materials, but the $\nu(\text{Zr-Cl})$ stretch band at 285 cm^{-1} for **3** was absent. The bands at 455 and 465 cm^{-1} of **1** are assigned to the $\nu(\text{Zr-C})$ and $\nu(\text{Fe-C})$ stretch modes, respectively.

The Raman spectroscopy sometimes is valuable for determining the stretching modes of metal-metal bonds, when other large polarizable moieties do not scatter in the same region and the baseline is low. In Figure 3 is shown the Raman spectrum of **1**. Unfortunately, there is no relatively strong band

in that region (120–220 cm^{-1}). However, there are bands assignable to a bending and stretching mode of the Cp rings. The peak at 460 cm^{-1} is assigned as $\nu(\text{Zr-C})$. This is in good agreement with those of the infrared and far infrared spectra. The strong bands at 357, 268, and 127 cm^{-1} are assigned to $\nu(\text{Fe-Cp})$, $\nu(\text{Zr-Cp})$, and $\delta(\text{Cp-Zr-Cp})$, respectively.

In further studies, we are investigating the syntheses of Group IV(B) – other transition metal-metal bonded complexes. **Acknowledgements.** Author wish to express his thanks to Professor W.M. Risen at Department of Chemistry, Brown University for technical assistance and helpful discussions.

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