Carbon Dioxide Insertion into the Fe–Zr and Ru–Zr Bonds of the Heterobimetallic Complexes $Cp(CO)_2M–Zr(Cl)Cp_2$: Direct Production of the μ-η^1(*C*):η^2(*O,O'*)-CO_2 Compounds $Cp(CO)_2M–CO_2–Zr(Cl)Cp_2$

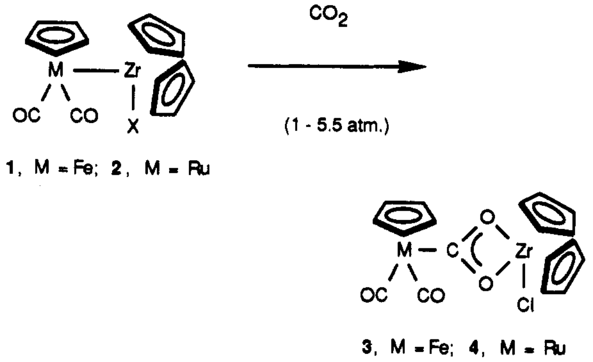
John R. Pinkes, Bryan D. Steffey, Jose C. Vites, and Alan R. Cutler*

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180

Received October 14, 1993[•]

Summary: The Fe–Zr and Ru–Zr heterobimetallic compounds $Cp(CO)_2M–Zr(Cl)Cp_2$ *incorporate carbon dioxide under mild conditions and give their respective* μ-η^1*(C):*η^2*(O,O') bimetallocarboxylates* $Cp(CO)_2M–CO_2–Zr(Cl)Cp_2$*. With* $Cp(CO)_2Fe–Zr(Cl)Cp_2$*, 1 equiv of* CO_2 *or* $^{13}CO_2$ *(99% labeled) quantitatively adds at above 0 °C in THF. The resulting* CO_2 *adduct,* $Cp(CO)_2Fe–CO_2–Zr(Cl)Cp_2$*, was independently synthesized and fully characterized.* $Cp(CO)_2Fe–^{13}CO_2–Zr(Cl)Cp_2$ *equilibrates with its isotopomer* $Cp(^{13}CO)(CO)Fe–CO_2–Zr(Cl)Cp_2$ *at room temperature. Results of control experiments preclude ionization of* $Cp(CO)_2Fe–Zr(Cl)Cp_2$ *to* $Cp(CO)_2Fe^-/^+(THF)Zr(Cl)Cp_2$ *in order to add* CO_2*. Operation of a* CO_2 *insertion pathway that requires bifunctional activation of the* CO_2 *is discussed. Analogous Ru–Zr* CO_2 *insertion chemistry requires more forcing conditions: 3–5 atm of* CO_2 *and 3 days.*

The challenge of developing carbon dioxide fixation as a potential source of C_1 organic feedstocks is that the limiting step often entails binding CO_2 at a transition-metal center.[1,2] The electron-rich transition-metal complexes that ligate CO_2 irreversibly reduce it to carbon monoxide.[3] These degradative processes can be circumvented by incorporating CO_2 into organotransition-metal systems via ligand reactions,[4] typically "insertion" of exogenous CO_2 into metal–hydride and some metal–alkyl bonds to produce O-bound carboxylato compounds.[5] We now report that the Fe–Zr and Ru–Zr bimetallic complexes $Cp(CO)_2M–Zr(Cl)Cp_2$ (**1** and **2**)[6] add CO_2 to give the stable bimetallocarboxylates $Cp(CO)_2M–CO_2–Zr(Cl)Cp_2$ (**3** and **4**) (eq 1), which represent the first examples of inserting CO_2 into transition-metal–transition-metal bonds.



(1)

The carbon dioxide complexes **3** and **4** typify an emerging theme that heterobimetallic complexes facilitate the binding of CO_2 at transition-metal centers.[7–9] Our recently reported RuZr CO_2 complex $Cp(CO)_2Ru–CO_2–Zr(Cl)Cp_2$ (**4**),[10] for example, is much more stable than its metallocarboxylate precursor, $Cp(CO)_2Ru–CO_2^-K^+$. This stabilization is associated with an electronic "push–pull" that results from coupling electron-rich ruthenium and oxophilic zirconium moieties[11] through the μ-η^1(C):η^2(O,O') carboxylate bridge.

Continuing these studies on late–early bimetallic CO_2 complexes required reproducibly synthesizing and fully

---

[•] Abstract published in *Advance ACS Abstracts*, December 1, 1993.

(1) Reviews on CO_2 complexes: (a) *Catalytic Activation of Carbon Dioxide*; ACS Symposium Series 363; Ayers, W. M., Ed.; American Chemical Society: Washington, DC, 1988. (b) For recent tabulations of CO_2 complexes, see: Tanaka, H.; Tzeng, B.-C.; Nagao, H.; Peng, S.-M.; Tanaka, K. *Inorg. Chem.* **1993**, *32*, 1508. Gibson, D. H.; Ong, T.-S.; Ye, M. *Organometallics* **1991**, *10*, 1811.

(2) Reduction of CO_2 by electrocatalysis or photoelectrocatalysis/photochemical activation of CO_2 may engender CO_2 binding and ligand reactions at transition-metel centers: (a) Hammouche, M.; Lexa, D.; Momenteau, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1991**, *113*, 8455. (b) Bruce, M. R. M.; Megehee, E.; Sullivan, B. P.; Thorp, H. H.; O'Toole, T. R.; Downard, A.; Pugh, J. R.; Meyer, T. J. *Inorg. Chem.* **1992**, *31*, 4864.

(3) Recent examples include the following. (a) Reductive disproportionation: Alvarez, R.; Atwood, J. L.; Carmona, E.; Pérez, P. J.; Poveda, M. L.; Rogers, R. D. *Inorg. Chem.* **1991**, *30*, 1493. (b) Oxygen atom abstraction: Fu, P.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1992**, *11*, 2607. Hall, K. A.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 10402.

(4) Examples of homogeneous catalytic hydrogenation[4a,b] and hydrosilation[4c] of CO_2: (a) Tsai, J.-C.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 5117. (b) Graf, E.; Leitner, W. *J. Chem. Soc., Chem. Commun.* **1992**, 623. (c) Eisenschmid, T. C.; Eisenberg, R. *Organometallics* **1989**, *8*, 1822.

(5) Selected examples: (a) Sullivan, B. P.; Meyer, T. J. *Organometallics* **1986**, *5*, 1500. (b) Darensbourg, D. J.; Wiegreffe, H. P.; Wiegreffe, P. H. *J. Am. Chem. Soc.* **1990**, *112*, 9252. (c) Darensbourg, D. J.; Hanckel, R. K.; Bauch, C. G.; Pala, M.; Simmons, D.; White, J. N. *J. Am. Chem. Soc.* **1985**, *107*, 7463. (d) Darensbourg, D. J.; Pala, M. *J. Am. Chem. Soc.* **1985**, *107*, 5687.

(6) (a) Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665; *Organometallics* **1984**, *3*, 504. (b) Casey, C. P. *J. Organomet. Chem.* **1990**, *400*, 205.

(7) Bifunctional activation of CO_2, $L_xM–CO_2–M'$, was established for ion pairing anionic metallocarboxylates $L_xMCO_2^-$ to alkali- or alkaline-earth-metal counterions $(M')^+$:[1b,8] (a) Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1982**, *104*, 5082. Floriani, C. *Pure Appl. Chem.* **1983**, *55*, 1. (b) Bianchini, C.; Meli, A. *J. Am. Chem. Soc.* **1984**, *106*, 2698. (c) Schmidt, M. H.; Miskelly, G. M.; Lewis, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 3420. (d) Group 1 and 2 counterions influence metal alkyl–CO_2 insertions[5b] and catalytic electrochemical CO_2 reduction by Fe(0) porphyrins.[2a]

(8) Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363.

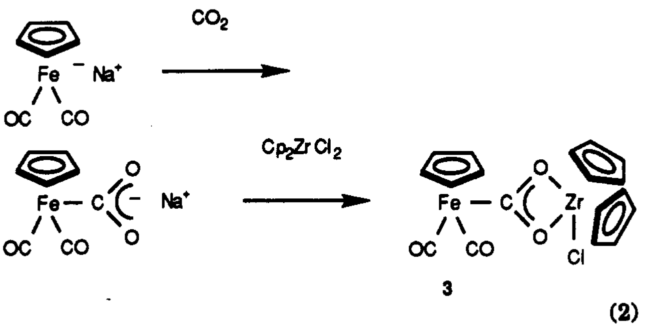
(9) Examples of bimetallic CO_2 complexes retaining only organotransition-metal groups: (a) Gibson, D. H.; Ye, M.; Richardson, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 9716. (b) Pilato, R. S.; Housmekerides, C. E.; Jernakoff, P.; Rubin, D.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 2333. (c) Housmekerides, C. E.; Ramage, D. L.; Kretz, C. M.; Shontz, J. T.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, *31*, 4453. (d) Szalda, D. J.; Chou, M. H.; Fujita, E.; Creutz, C. *Inorg. Chem.* **1992**, *31*, 4712 and references therein.

(10) (a) Vites, J. C.; Steffey, B. D.; Giuseppetti-Dery, M. E.; Cutler, A. R. *Organometallics* **1991**, *10*, 2827. (b) Steffey, B. D.; Vites, J. C.; Cutler, A. R. *Organometallics* **1991**, *10*, 3432.

(11) Recent examples of FeZr or RuZr heterobimetallic complexes with bridging ligands: (a) Berno, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1990**, *9*, 1995. (b) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 8466; *Organometallics* **1992**, *11*, 876. Lemke, F. R.; Bullock, R. M. *Organometallics* **1992**, *11*, 4261. (c) Reviews on heterobimetallic chemistry: Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41. Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167.

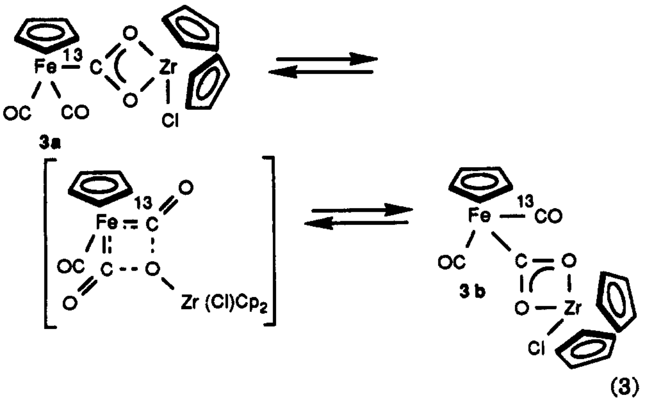
0276-7333/94/2313-0021$04.50/0

characterizing the Fe–Zr bimetallocarboxylates Cp$(CO)_2$Fe–CO_2–Zr(Cl)Cp_2 (**3**) and Cp$(CO)_2$Fe–$^{13}CO_2$–Zr(Cl)Cp_2 (**3a**) (eq 2). The Fe–Zr CO_2 adduct **3** had been



(2)

reported[10a] as an impure material; it now was obtained analytically pure after a prompt workup involving removal of the THF.[12] Although stable as a solid, THF solutions of **3** at room temperature degraded to $[CpFe(CO)_2]_2$ and $[Cp_2(Cl)Zr]_2O$ with a half-life ($\tau_{1/2}$) of 4.0 h. IR spectral carboxylate $\nu(CO_2)$ assignments for **3**, which define a chelating η^2(O,O′) metallocarboxylate structure,[10] were confirmed by comparison with those for **3a**. In addition to its solution degradation, **3a** more rapidly ($\tau_{1/2}$ = 1.5 h) exchanges the ^{13}C label between the carboxylate and terminal carbonyl sites (eq 3).[13] The resulting isotopomer Cp(^{13}CO)(CO)Fe–CO_2–Zr(Cl)Cp_2 (**3b**)[14] is presumably derived from equilibrium concentrations of the metalloanhydride species depicted in eq 3.



(3)

Incorporating carbon dioxide into the Fe–Zr bond of Casey's heterobimetallic compound Cp$(CO)_2$Fe–Zr(Cl)-Cp_2 (**1**) proved to be surprisingly straightforward.[16] Treatment of a THF solution of **1** above 0 °C with 1 equiv of CO_2 quantitatively converted it to Cp$(CO)_2$Fe–CO_2–Zr(Cl)Cp_2 (**3**) (eq 1). Also evident in these reaction mixtures was $[CpFe(CO)_2]_2$ (cf. Figure 1) and $[Cp_2(Cl)Zr]_2O$ that accompanied the generation of **1**. Using 99% ^{13}C-labeled CO_2 in this insertion reaction likewise afforded Cp$(CO)_2$Fe–$^{13}CO_2$–Zr(Cl)Cp_2 (**3a**).

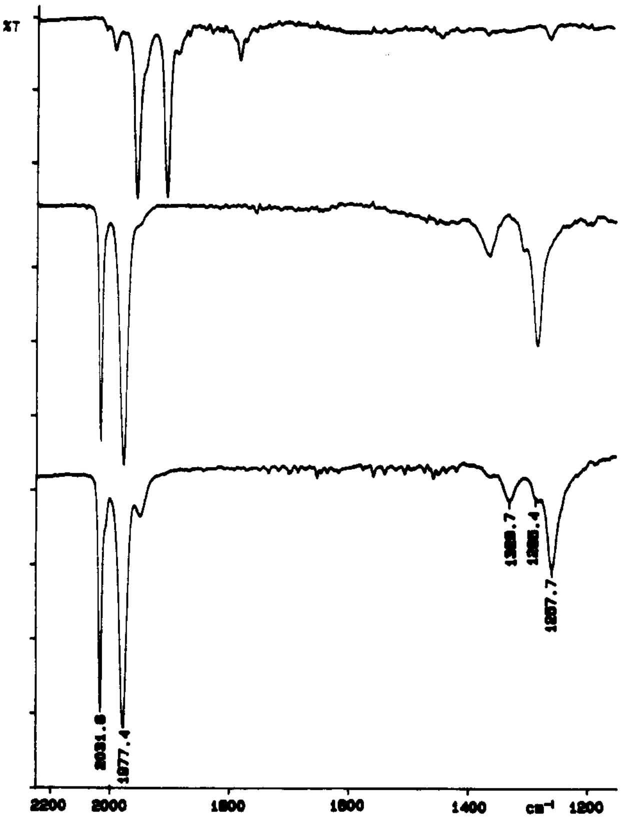


Figure 1. Infrared spectrum of Cp$(CO)_2$Fe–Zr(Cl)Cp_2 (**3**) (upper scan), the spectrum after addition of 1 equiv of CO_2 (middle scan), and the spectrum of purified Cp$(CO)_2$Fe–CO_2–Zr(Cl)Cp_2 (**1**) (bottom scan). Concentrations: 0.50 mmol of **1** or **3** in 5.0 mL of THF. ν(CO) bands at 1992, 1950, and 1781 cm^{-1} correspond to the $[Cp(CO)_2Fe]_2$ impurity.

Carboxylation of the Ru–Zr bimetallic complex Cp$(CO)_2$-Ru–Zr(Cl)Cp_2 (**2**), however, only reluctantly occurred with 3–5.5 atm of CO_2. Vigorously stirred suspensions of **2** in THF (room temperature) afforded clear solutions after 2–3 days under CO_2 pressure.[17] IR and NMR spectral analysis confirmed the presence of Cp$(CO)_2$Ru–CO_2–Zr(Cl)Cp_2 (**4**) in 22–38% yields, along with Cp$(CO)_2$RuH and $[Cp_2(Cl)Zr]_2O$. Both byproducts can be attributed to the previously documented slow decomposition of the product **4** in THF ($\tau_{1/2}$ = 12 h).[10a]

---

[12] A THF solution containing Cp$(CO)_2$Fe$CO_2^-K^+$ (1.00 mmol) was generated using 1.0 equiv of CO_2 (−196 to −78 °C) on a high-vacuum line[10a] and was treated with Cp_2ZrCl_2 (−78 °C). Rapid workup involving evaporation of THF and reprecipitation from benzene–hexane afforded Cp$(CO)_2$Fe–CO_2–Zr(Cl)Cp_2 (**3**) (80% yield) as a stable, pale yellowish white solid. IR (THF): ν(CO) 2032, 1977 cm^{-1}; $\nu_{asym}(CO_2)$ 1363, $\nu_{sym}(CO_2)$ 1283 cm^{-1}. ^1H NMR (C_6D_6): δ 6.09 (s, Cp_2Zr), 4.15 (s, CpFe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 229.2 (FeCO), 212.6 (μ-CO_2), 114.0 (Cp_2Zr), 85.9 (CpFe). Anal. Calcd for $C_{18}H_{15}O_4ClFeZr$: C, 45.25; H, 3.16. Found: C, 45.40; H, 3.05. Results using 99% ^{13}C-labeled CO_2: Cp$(CO)_2$Fe–$^{13}CO_2$–Zr(Cl)Cp_2 (**3a**). IR (THF): ν(CO) 2031, 1977 cm^{-1}; $\nu_{asym}(CO_2)$ 1330, $\nu_{sym}(CO_2)$ 1258 cm^{-1}. Once removed from THF, **3** is stable as a solid or even in benzene solution; <20% degradation over 4 h.

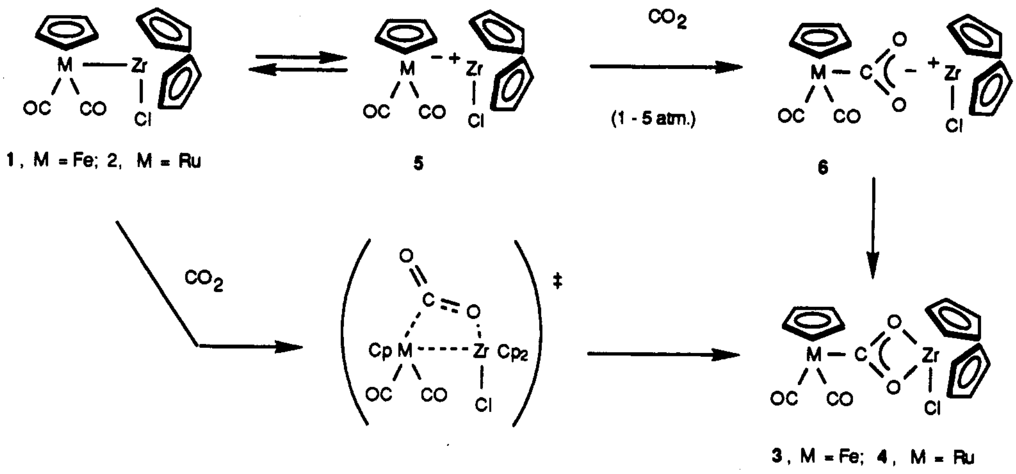
[13] (a) Analogous label shuttling between carboxylate and terminal carbonyl sites on Cp$(CO)_2$Fe—$^{13}CO_2^-Li^+$ or Cp$(CO)_2$Fe—$C^{18}O_2^-Li^+$,[13b] $[Cp(CO)_2Fe{=}C(^{17}O)O{-}WCp_2]^+$,[9b] and Cp$(CO)_2$Ru—$^{13}CO_2$—Zr(Cl)$Cp_2$[10b] has been noted. Metalloanhydride species (cf. eq 3) are proposed intermediates. (b) Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 794.

[14] IR (THF) of Cp(^{13}CO)(CO)Fe–CO_2–Zr(Cl)Cp_2 (**3b**) (ν(CO) 2014, 1958 cm^{-1}) and its ^{13}C NMR spectra are consistent with the presence of the monosubstituted Cp(^{13}CO)(CO)Fe moiety.[15] $[Cp(^{13}CO)(CO)Fe]_2$/[Cp-$(CO)_2Fe]_2$ and $[Cp_2(Cl)Zr]_2O$, as well as small amounts (<10%) of free CO_2 and $^{13}CO_2$ (IR $\nu(CO_2)$ 2336 and 2270 cm^{-1}) also were detected.

[15] (a) Alexander, J. J.; Wojcicki, A. J. *Inorg. Chem.* **1973**, *12*, 74. Alexander, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 1729. (b) Fettes, D. J.; Narayanaswamy, R.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2311. Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Dalton Trans.* **1985**, 1365. (c) Kazlauskas, R. J.; Wrighton, M. S. *Organometallics* **1982**, *1*, 602. (d) Bodnar, T. C.; Cutler, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5926.

[16] Cp$(CO)_2$Fe–Zr(Cl)Cp_2 (**1**) was generated as an orange THF solution (5 mL) by treating Cp$(CO)_2Fe^-K^+$ with Cp_2ZrCl_2 (0.50 mmol each):[6] IR ν(CO) 1955, 1905 cm^{-1}. On a high-vacuum line, 1.0 equiv of CO_2 was condensed; the mixture was warmed from −196 to −46 °C, stirred at −46 °C (0.5 h), and then warmed to room temperature over 2.5 h. IR spectral monitoring confirmed quantitative conversion of **1** to **3**: 70% yields of **3** were quantified by IR and NMR spectroscopy. Insertion of 99% ^{13}C-labeled CO_2 afforded Cp$(CO)_2$Fe–$^{13}CO_2$–Zr(Cl)Cp_2 (**3a**). Carboxylation of **1** in toluene solution was slower; only a 35% transformation to **3a** was realized after 5 h.

Scheme 1



(4)

(5)

Plausible pathways for adding CO_2 to the FeZr and RuZr bimetallic complexes $Cp(CO)_2M–Zr(Cl)Cp_2$ (1 and 2) include their prior ionization in THF, with the resulting metalates $Cp(CO)_2M^-$ then intercepting the CO_2 (Scheme 1; eq 4). Although the ionization of polar Fe–Zr or Ru–Zr bonds in the starting bimetallics 3 and 4 has not been detected, both $CpM(CO)_2^-$ ions and (solvated) zirconocene electrophiles[18] $Cp_2(X)Zr(THF)^+BPh_4^-$ independently exist. In the alternative pathway, CO_2 could insert into the Fe–Zr and Ru–Zr bonds via a bifunctional CO_2 activation step (Scheme 1; eq 5) similar to that promulgated by Floriani.[7a]

We favor the latter direct-insertion pathway for two reasons. First, ^{13}C-labeled CO_2 (1 atm in THF) does not exchange with unlabeled CO_2 in $Cp(CO)_2Fe–CO_2–Zr(Cl)Cp_2$ (**3**); neither $Cp(CO)_2Fe–{}^{13}CO_2–Zr(Cl)Cp_2$ (**3a**) nor **3b** were detected after 3 h at room temperature. This result establishes that heterolytic cleavage of **3** to give the ion pairs **6** and then **5**, the reverse of the postulated **5**–**6**–**3** transformations (eq 4), does not occur in THF. In independent studies, we had established that $Cp(CO)_2Fe-CO_2^-K^+$ will exchange with $^{13}CO_2$.[19] The more compelling second reason pertains to the lack of reactivity of $Cp(CO)_2Fe–Zr(Cl)Cp_2$ (1) toward carbon disulfide under conditions (1.0 equiv of CS_2 at 0 °C for 2.5 h, then warming to 22 °C) where CO_2 readily adds. If 1 did ionize, then the resulting $Cp(CO)_2Fe^-$ would have immediately added CS_2 and produced the well-known dithiocarboxylate compound $Cp(CO)_2FeCS_2^-$.[8,20] We independently established that $Cp(CO)_2FeCS_2^-K^+$ plus Cp_2ZrCl_2 at 0 °C affords the stable and fully characterized FeZr μ-$\eta^1(C)$:$\eta^2(S,S')$-dithiocarboxylate complex $Cp(CO)_2Fe–CS_2–Zr(Cl)Cp_2$.[21]

Although the Fe–Zr and Ru–Zr bonds of $Cp(CO)_2M–Zr(Cl)Cp_2$ (1 and 2) incorporate CO_2 to give their bimetallocarboxylates $Cp(CO)_2M–CO_2–Zr(Cl)Cp_2$ (3 and 4) under relatively mild conditions, further studies are required to firmly establish the mechanism of CO_2 insertion into Fe–Zr, Ru–Zr, and perhaps other polar, heterobimetallic complexes.

Acknowledgment. Support from the National Science Foundation (Grant CHE-8305484) is gratefully acknowledged.

OM930711O

---

[17] (a) Reactions were carried out in a Fischer–Porter glass pressure vessel[17b] that had been suitably modified so that it attached to a vacuum line. The glass pressure bottle was loaded with 4 in a glovebox and mounted on the vacuum line before condensing carefully dried CO_2 (in several portions) and THF. Results of control experiments using $Cp(CO)_2Ru^-Na^+$ and $Cp(CO)_2Ru–Zr(Cl)Cp_2$ (4) ruled out adventitious water as the source of the RpH. (b) Messerle, L. In *Experimental Organometallic Chemistry*; ACS Symposium Series 357; Wayda, A. L., Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 7, p 198.

[18] Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892. Borkowski, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *10*, 1268. Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

[19] Pinkes, J. R.; Chiuli, R. J.; Steffey, B. D.; Cutler, A. R. Manuscript in preparation.

[20] (a) Ellis, J. E.; Fennel, R. W.; Flom, E. A. *Inorg. Chem.* **1976**, *15*, 2031. (b) Giuseppetti-Dery, M.; Landrum, B. E.; Shibley, J. L.; Cutler, A. R. *J. Organomet. Chem.* **1989**, *378*, 421.

[21] Pinkes, J. R.; Cutler, A. R. Submitted for publication.