Organometallics **1991,** *10,* 2827-2834

dergoes further oxidation only at the very positive potential $E_{pa}(4^{+/2+})$ = 1.59 V near the anodic border of the electrochemical window (≈+1.75 V in TBAP/DME, Figure 1).

This oxidative stability of 4^+ could have been predicted from the aforementioned data since for this ion the factors that lead to anodic shifts of $E_{1/2}$ operate in unison. Explicitly, the very anodic potential $E_{pa}(4^{+/2+})$ may be rationalized by the facts that ionization occurs from a $C_{12}H_{12}M^+$ cation, the ligand combination in *unsymmetrical* and the redox orbital is *singly occupied*, no assistance to ionization being furnished by a release of pairing energy.

Experimental Section

Materials. $(\eta^6\text{-}C_6H_6)_2V$ (**1**),[29] $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)V$ (**2**),[2] $(\eta^6\text{-}C_6H_6)_2Cr$ (**3**),[30] and $(\eta^5\text{-}C_5H_5)(\eta^7\text{-}C_7H_7)Cr$ (**4**)[31] were synthesized as previously reported. Dimethoxyethane (DME) was purified by refluxation and distillation from potassium benzophenone. The supporting electrolyte $(n\text{-}Bu)_4NClO_4$ was recrystallized three times from DME and dried in vacuo at 110 °C.

Apparatus. Cyclic voltammetry was performed with electrochemical equipment from AMEL (Milano) consisting of a Model 552 potentiostat, Model 568 function generator, Model 563 multipurpose unit, Nicolet Model 3091 storage oscilloscope, and Kipp and Zonen Model BD 90 x/y recorder. The electrochemical cell was operated under an atmosphere of argon, with glassy carbon, platinum rod, and saturated calomel (SCE) serving as working, counter, and reference electrodes, respectively. For temperature control, the cell was immersed in a thermostated cooling bath.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the donors of the Fonds der Chemischen Industrie for the support of this work.

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Characterization of the Heterobimetallic μ-(η^1-C:η^2-O,O′) Carbon Dioxide Complexes $(\eta^5\text{-}C_5H_5)(CO)_2MCO_2M'(Cl)(\eta^5\text{-}C_5H_5)_2$ (M = Fe, Ru; M′ = Ti, Zr)

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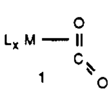
Received September 13, 1990

Heterobimetallic CO_2 adducts $Cp(CO)_2MC(O)OM'(Cl)Cp_2$ [M = Ru, M′ = Zr (**9a**), Ti (**9b**); M = Fe, M′ = Zr (**10a**), Ti (**10b**)] were prepared by treating the metallocarboxylates $CpM(CO)_2CO_2^-Na^+$ (M = Ru, Fe) with the appropriate zirconocene and titanocene dichloride at low temperatures. The metallocarboxylates $CpM(CO)_2CO_2^-Na^+$ are available from the reaction of a cold $CpM(CO)_2^-Na^+$ (−78 °C) solution with 1 equiv of CO_2, and $CpRu(CO)_2^-Na^+$ is prepared by sonication of Rp_2/sodium metal in tetrahydrofuran (THF). The solution stability of these bimetallocarboxylates, decreasing in the order RuZr (**9a**) ≫ FeZr (**10a**) > RuTi (**9b**) > FeTi (**10b**), determines how readily that they are isolated and characterized. The heterobimetallic CO_2 adduct **9a** is available analytically pure; IR, ^1H, and ^{13}C NMR spectral data are complete for **10a**, and IR spectral data for all four bimetallocarboxylates, as well as for the isotopomer $Cp(CO)_2Ru^{13}C(O)OZr(Cl)Cp_2$ (**9a**-^{13}C), are consistent with similar μ-(η^1-C:η^2-O,O′) carboxylate structures. All four bimetallic CO_2 adducts decompose in benzene solution to give similar products, $Cp_2M_2(CO)_4$ and μ-oxo $(Cp(Cl)M')_2O$; **10a**, **9b**, and **10b** decompose at or below room temperature, and **9a** slowly degrades above 40 °C. Protonating **9a** and **10a** with HBF_4 also deoxygenates the ligated CO_2 and affords $CpM(CO)_3^+BF_4^-$ (M = Ru, Fe) and $[Cp_2(Cl)Zr]_2O$ in moderate yields.

Introduction

Although numerous organotransition-metal carbon dioxide complexes **1** and **2** are known,[1] none undergo hydride transfer or net hydrogenation at the ligated CO_2. Bimetallic CO_2 complexes, represented by μ-(η^1-C:η^2-O,O′) **3** and μ-(η^1-C:η^1-O) **4** structures, potentially could facilitate CO_2 activation and reduction if the appropriate electron-rich (ML_x) and oxophilic ($M'L_y$) metal centers are paired. Relatively little is known, however, concerning the reactivity of ligated carbon dioxide.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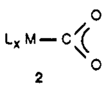
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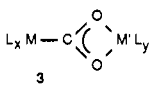
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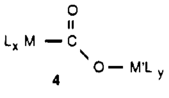
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Several examples documenting reactions between mononuclear CO_2 complexes **1**/**2** and electrophiles have been reported. Anionic metallocarboxylates **2**[2,3] bind alkali- or

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[1] (a) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661; *Carbon Dioxide Activation by Metal Complexes*; VCH Publishers: Weinheim, Federal Republic of Germany, 1988. (b) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (c) *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed.; ACS Symposium Series 363; American Chemical Society: Washington, DC, 1988. (d) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135. (e) Inoue, S.; Koinuma, H. *Rev. Inorg. Chem.* **1984**, *6*, 291. (f) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (g) Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651. (h) Behr, A. In *Catalysis in C_1 Chemistry*; Keim, W., Ed.; D. Reidel Publishers: Boston, MA, 1983, p 169. (i) Ito, T.; Yamamoto, A. In *Organic and BioOrganic Chemistry of Carbon Dioxide*, Inoue, S., Yamazaki, N., Eds.; Wiley: New York, 1982; Chapter 3. (j) Sneedon, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, F. W., Eds.; Pergamon: New York, 1982; Vol. 8, Chapter 50.4.

[2] Recent selected examples include the following. (a) $FpCO_2^-Li^+$, Na^+, or K^+ [Fp = $Cp(CO)_2Fe$]: Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 794; *Organometallics* **1985**, *4*, 1467. See also ref. 3. (b) $Cp(PPh_3)(CO)FeCO_2^-Li^+$ or K^+: Gibson, D. H.; Ong, T.-S. *J. Am. Chem. Soc.* **1987**, *109*, 7191. (c) $Cp(PPh_3)(NO)ReCO_2^-Li^+$ or K^+: Senn, D. R.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *Inorg. Chem.* **1987**, *26*, 2737. (d) $Cp(NO)(CO)ReCO_2^-Na^+$ or Et_3NH^+: Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982. (e) $Cp(N_2Ar)(CO)ReCO_2^-Li^+$, Na^+, or Ca^{2+}: Barrientos-Penna, C. F.; Gilchrist, A. B.; Klahn-Oliva, A. H.; Hanlan, A. J. L.; Sutton, D. *Organometallics* **1985**, *4*, 478. (f) $(CO)_5WCO_2^{2-}(Li^+)_2$: Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, *109*, 2956.

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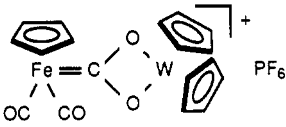
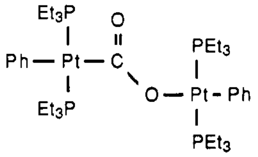
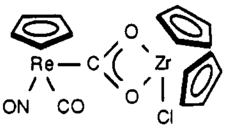
alkaline-earth-metal counterions $(M')^{q+}$ as bimetallocarboxylate structures **3**, an ion-pair interaction that promotes CO_2 binding to the initial metalate L_xM^-.[4] For one metallocarboxylate, $(FpCO_2)_2Mg(THF)_x$, this interaction also drastically alters its reactivity toward electrophilic alkylating reagents.[3c] Several examples of bridging carboxylate or μ-CO_2 complexes in which a group IV metalloid substituent ($M' = R_3Si$, Ge, Sn, Pb) forms either a chelating (η^2-O,O′) carboxylate **3** or an (η^1-O) metalloester **4** have been reported,[2c,3b] although information on their reaction chemistry is not available. Finally, protonation of several CO_2 complexes affords coordinated carbon monoxide.[5,6]

Examples of bimetallic CO_2 complexes retaining only organotransition-metal groups (M and M′) are now available. Geoffroy's FeW μ-(η^1-C:η^2-O,O′) metallocarboxylate[7] and Bennett's Pt_2 bridging (η^1-C:η^1-O) CO_2 adduct[8] represent clear examples of structures **3** and **4**, respectively. We previously reported a ReZr μ-(η^1-C:η^2-O,O′) metallocarboxylate **5** that maintains its (η^2-O,O′) chelation of zirconium even in coordinating solvents.[9] In contrast, zirconocene carboxylates $Cp_2(Cl)\overline{\text{ZrOC(O)}}R$ (**6**) (R = H, Me, Ph, *t*-Bu) equilibrate with nonchelated (η^1-O) carboxylate structures, e.g., $Cp_2(Cl)(THF)ZrOC(O)R$.[10] Other bimetallic μ-(η^1-C:η^1-O) CO_2 complexes **4** have been reported.[11,12] Of the known bimetallocarboxylates only a bis(cobalt macrocycle) μ-CO_2 compound[11a] had incorporated CO_2 by treating a metallocarboxylate **2** with a metal electrophile $(L_yM')^+$. The metallocarboxylate ligand on other examples of bimetallic CO_2 complexes **3** and **4** derives from carbon monoxide through subsequent coordinated ligand reactions.







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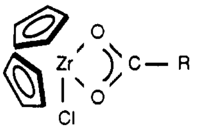
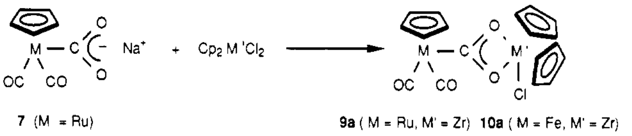


6a R = CH_3

6b R = H

We now report full details on converting CO_2 via the new metallocarboxylate $Cp(CO)_2RuCO_2^-Na^+$ ($RpCO_2^-Na^+$) (**7**) and its known iron congener $FpCO_2^-Na^+$ (**8**)[13] to RuZr (**9a**), RuTi (**9b**), FeZr (**10a**), and FeTi (**10b**) bimetallic CO_2 adducts (eq 1). This work emphasizes their relative ease of synthesis and stability as well as deduction of their structures from IR, ^1H, and ^{13}C NMR spectral data.



7 (M = Ru)
8 (M = Fe)
9a (M = Ru, M′ = Zr) **10a** (M = Fe, M′ = Zr)
9b (M = Ru, M′ = Ti) **10b** (M = Fe, M′ = Ti)

(1)

Experimental Section

Synthetic manipulations were performed by using a combination of standard Schlenk-line (for syringe–septum solution transfer), glovebox, and vacuum-line (for CO_2 transfer)[14] procedures. Infrared spectra of methylene chloride or tetrahydrofuran (THF) solutions and of KBr pressed disks were recorded on Perkin-Elmer spectrophotometers, Model Numbers 297 and 1610 (FT), over the carbonyl ν(CO) and carboxylate $\nu(CO)_2$ frequency range (2200–1200 cm^{-1}). NMR spectral data (δ values downfield from internal Me_4Si) were obtained in $CDCl_3$, C_6D_6 (^1H, ^{13}C), and THF (^{13}C) solutions with Varian Model XL-200 and IBM-WP100 spectrometers. Combustion microanalyses were done by Desert Analytics, Tucson, AZ, and by Robertson Laboratories, Madison, NJ.

Organic and inorganic reagents were obtained commercially and used as received; titanocene and zirconocene chlorides Cp_2MCl_2 were dried on the vacuum line and stored under nitrogen. Dichloromethane was distilled under nitrogen from P_2O_5; THF and diethyl ether were distilled from sodium benzophenone ketyl. Further drying of the carbon dioxide, Matheson "bone dry" grade, entails passage through a 1 cm × 1 m glass column that is packed with a 25% P_2O_5 powder dispersion on activated silica gel (70–200 mesh) containing 1% Congo Red indicator. Metal carbonyl dimers

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(3) (a) Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363. (b) Giuseppetti, M. E.; Cutler, A. R. *Organometallics* **1987**, *6*, 970. (c) Forschner, T.; Menard, K.; Cutler, A. *J. Chem. Soc., Chem. Commun.* **1984**, 121.

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(5) (a) Aresta, M.; Quaranta, E.; Tommasi, I. *J. Chem. Soc., Chem. Commun.* **1988**, 450. (b) Tsai, J.-C.; Khan, M.; Nicholas, K. M. *Organometallics* **1989**, *8*, 2967; **1991**, *10*, 29.

(6) Anionic metallocarboxylates also are involved in pH-dependent equilibria that link (η^1-C) metallocarboxylate–metallocarboxylic acid–carbonyl ligands: Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139. Katz, N. E.; Szalda, D. J.; Chou, M. H.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 6591 and references cited.

(7) Pilato, R. S.; Housmekerides, C. E.; Jernakoff, P.; Rubin, D.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 2333. Representative of six bimetallic CO_2 complexes that result from treating an oxo complex $Cp_2M'{=}O$ (M′ = Mo, W) with a carbonyl compound $CpFe(CO)_3^+$, $Cp^*Ru(CO)_3^+$, $Cp'Mn(NO)(CO)_2^+$, or $Cp^*Re(NO)(CO)_2^+$ ($Cp^* = \eta^5$-C_5Me_5, $Cp' = \eta^5$-C_5H_4Me). An X-ray crystallographic structure determination of $Cp^*(CO)(NO)ReCO_2WCp_2^+BF_4^-$ rigorously defines the μ-(η^1-C:η^2-O,O′) carboxylate ligand.

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(10) (a) Cutler, A.; Raja, M.; Todaro, A. *Inorg. Chem.* **1987**, *26*, 2877. (b) X-ray crystallographic structure determination of **6** [R = CH_2CH_2COFc, Fc = (η^5-C_5H_4)FeCp]: Ma, Y.; Zhu, Y.; Wang, X.; Ma, C. *Polyhedron*, **1989**, *8*, 929. The (η^2-O,O′) chelation of carboxylate ligands by zirconocene systems is well documented: Thewalt, U.; Klima, S.; Berhalter, K. *J. Organomet. Chem.* **1988**, *342*, 303 and references cited.

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(12) Bridging CO_2 complexes involving three or more metal centers (μ_3-CO_2) also have been reported: (a) Lundquist, E. G.; Huffman, J. C.; Folting, K.; Mann, B. E.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 128. Caulton's thoroughly characterized μ_3-(η^1-Os,Rh,Rh′) carboxylate $[(COD)Rh]_2Os(\mu\text{-}H)_2(CO_2)(PMe_2Ph)_3$ is a product of adding CO_2 to $(COD)RhH_3Os(PMe_2Ph)_3$. (b) Beck, W.; Raab, K.; Nagel, V.; Steimann, M. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 526. Balbach, B. K.; Helus, F.; Oberdorfer, F.; Ziegler, M. L. *Ibid.* **1981**, *20*, 470; *Z. Naturforsch., B* **1982**, *37B*, 157. (c) John, G. R.; Johnson, B. F. G.; Lewis, J.; Wong, K. C. *J. Organomet. Chem.* **1979**, *169*, C23. Eady, C. R.; Guy, J. J.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1976**, 602.

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(14) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

$(Cp(CO)_2M)_2$ (M = Fe (Fp_2)[15] and M = Ru (Rp_2))[16] were prepared by literature procedures and judged pure by IR and ^{1}H NMR spectroscopy. Authentic samples and spectral data of FpH,[13b,17] FpCl,[18] $FpCO^+BF_4^-$,[19] RpH,[16,20] RpCl,[16,21] $RpCO^+BF_4^-$,[22] and $[Cp_2(Cl)Zr]_2O$ (**11a**)[23] were available from previous studies for direct comparison. The yellow, sparingly soluble heterobimetallic complex $Cp(CO)_2RuZr(Cl)Cp_2$ (**13**) was prepared by treating $Cp(CO)_2Ru^-K^+$ with Cp_2ZrCl_2 according to Casey's procedure:[24] IR (THF) 1973, 1914 cm^{-1}; IR (KBr) 1952, 1891, 1884 (sh) cm^{-1} (Figure 1).

Synthesis of $(\eta^5\text{-}C_5H_5)(CO)_2RuCO_2Zr(Cl)(\eta^5\text{-}C_5H_5)_2$ (9a). A 30-mL centrifuge tube, which had been oven-dried for 12 h (140 °C), was transferred to the glovebox and charged with $(Ru(CO)_2Cp)_2$ (222 mg, 0.50 mmol), two freshly cut pieces of sodium (200 mg, 8.8 mmol), and 15 mL of THF. The tube was sealed with a rubber septum, centered in an ultrasonic cleaning bath containing ice water, and sonicated[13b,25] for 2.5 h. An IR spectrum of the resulting yellow-brown supernatant solution after centrifugation established quantitative conversion of Rp_2 (ν(CO) 2006 (sh), 1996, 1964, 1953, 1936, 1784 cm^{-1}) to its sodium metalate[20-22] Rp^-Na^+ (ν(CO) 1907, 1825 cm^{-1}). The presence of small amounts of RpH (ν(CO) 2022, 1958 cm^{-1}) was avoided by prior flushing of the IR cell with Rp^-Na^+ solution (0.5 mL) in order to remove traces of adsorbed water.

The solution of Rp^-Na^+ plus additional THF (15 mL) was transferred in the glovebox to an oven-dried Schlenk tube that was equipped with a vacuum-line adapter, a magnetic stirring bar, and a septum on the side arm. After being attached to the vacuum line, the raction tube was degassed by applying three freeze–thaw cycles. Dried CO_2 (24 mL, 1.0 mmol) was transferred from a gas-storage bulb to the reaction tube (at −196 °C), which then was isolated from the vacuum line and warmed to −78 °C with vigorous stirring. After 30 min nitrogen was admitted and an IR spectrum of the pale tan solution (a small quantity of white precipitate also was evident at −78 °C) was recorded. All Rp^-Na^+ was consumed, but only ν(CO) bands of RpH were evident at room temperature. The presence of a very low concentration of unreacted CO_2 was consistent with the intensity of its IR absorption at 2335 cm^{-1}.

Zirconocene dichloride, Cp_2ZrCl_2 (295 mg, 1.00 mmol), as a THF solution (5 mL) was added to the cold (−78 °C) solution of $RpCO_2^-Na^+$ (**7**), which then was warmed to −40 °C with stirring (1 h). An IR spectrum of the resulting light yellow-brown solution showed ν(CO) bands only at 2040 and 1982 cm^{-1}, which correspond to $Cp(CO)_2RuCO_2ZrClCp_2$ (**9a**). Warming the reaction mixture to room temperature gradually transforms it to RpH (IR spectral monitoring), and attempted workup affords greatly reduced yields of **9a** (<20%), along with variable concentrations of Rp_2, RpH, RpCl (ν(CO) 2047, 1995 cm^{-1}), $[Cp_2(Cl)Zr]_2O$ (**11a**), and other unidentified Cp_2Zr species (by ^{1}H NMR spectroscopy).

The reaction mixture was maintained at −40 °C for 8 h and then at −20 °C for 10 h. Solvent was evaporated by using the vacuum line, and the tan residue was extracted (22 °C) with benzene (200 mL). Removal of benzene left a tan solid, 351 mg, which was established to be a mixture of **9a** (85% pure, 67% yield) [^{1}H NMR (C_6D_6) δ 6.09 (s, Cp_2Zr), 4.58 (s, CpRu)] and $[Cp_2(Cl)Zr]_2O$ (**11a**) [δ 6.03 (Cp_2Zr)]. Occasionally, trace amounts of Cp_2ZrCl_2 (δ 5.90) were evident, although neither RpCl nor Rp_2 were detected [^{1}H NMR (C_6D_6) δ 4.32 and 4.72 (s, CpRu), respectively] under these conditions. Attempts to purify **9a** by column chromatography using activity 3 neutral alumina and benzene, flash-grade silica gel and hexane/dichloromethane at −30 °C or silanized silica gel (RP-18 or Rp-Ph, 40–63 mμ) and benzene or THF were unsuccessful.

Analytically pure **9a** was procured by washing the impure product with diethyl ether (4 mL), extracting with benzene (20 mL), and evaporating the benzene. The resulting white solid (52 mg) was characterized as $RpCO_2Zr(Cl)Cp_2$ (**9a**): IR (CH_2Cl_2) 2047, 1988 (CO), 1348, 1290 cm^{-1} (CO_2); IR (KBr) 2035, 1972 (CO), 1344, 1285 cm^{-1} (CO_2); ^{1}H NMR ($CDCl_3$) δ 6.21 (s, Cp_2Zr), 5.40 (s, CpRu); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 213.2 ($RuCO_2Zr$), 199.2 (CO), 114.2 (Cp_2Zr), 89.1 (CpRu). Anal. Calcd for $C_{18}H_{15}O_3ClRuZr$: C, 41.33; H, 2.89. Found: C, 41.37; H, 3.10.

Relatively pure samples of **9a** (90%) also were obtained by washing the crude product with hexane (20 mL), extracting with a minimum volume of diethyl ether (2 mL) to eliminate remaining traces of pale yellow RpCl and Rp_2, and then extracting with ether (75 mL) to remove product as a very pale solution. An off-white powder (370 mg) was obtained after evaporating solvent. Reextracting this crude product with 4:1 diethyl ether/nitromethane (2 × 3 mL at −30 °C), washing with hexane (3 × 5 mL), and vacuum drying left a white powder, 263 mg. This was identified as $Cp(CO)_2RuCO_2Zr(Cl)Cp_2$ (**9a**) (60% yield) that retained **11a** (10%) as the only NMR-detectable impurity.

Protonation of $(\eta^5\text{-}C_5H_5)(CO)_2RuCO_2Zr(Cl)(\eta^5\text{-}C_5H_5)_2$ (9a). A THF solution (10 mL) containing $RpCO_2Zr(Cl)Cp_2$ (**9a**) (242 mg, 0.46 mmol) was cooled to −78 °C before adding 0.10 mL of $HBF_4\cdot OEt_2$ (0.6 mmol). A white precipitate formed as the reaction was stirred for 1 h at −78 °C; an IR spectrum of the clear supernatant solution indicated that all **9a** was consumed. The solvent was evaporated under vacuum as it warmed; at room temperature the resulting white residue was extracted with acetonitrile (3 × 4 mL). This solution was filtered into 100 mL of diethyl ether, and the resulting white precipitate was collected, washed with ether, vacuum-dried, and identified as spectroscopically pure $RpCO^+BF_4^-$[22] (122 mg, 78% yield): IR (CH_3NO_2) 2080, 2032 cm^{-1}; ^{1}H NMR (CD_3NO_2) δ 6.13 (CpRu).

Reaction of $(\eta^5\text{-}C_5H_5)(CO)_2RuCO_2^-Na^+$ (7) and $(\eta^5\text{-}C_5H_5)_2TiCl_2$. To a stirred THF solution (−78 °C) containing $RpCO_2^-Na^+$ (**7**) (1.0 mmol, 15.0 mL) was added Cp_2TiCl_2 (250 mg, 1.0 mmol). The reaction did not go to completion between −78° and −50 °C (2 h), as evidenced by the presence of undissolved red-orange Cp_2TiCl_2. Upon warming of this mixture to −40 °C, the titanocene dichloride dissolved (1.5–2.5 h), and IR spectral monitoring of the resulting brown solution indicated a 40% maximum yield of $RpCO_2Ti(Cl)Cp_2$ (**9b**) [ν(CO) 2042, 1975 cm^{-1}; ν(CO_2) 1349, 1284 cm^{-1}]. Other ruthenium carbonyl species that were detected (IR) in the reaction mixture corresponded to variable concentrations of RpCl and RpH and trace amounts of Rp_2.

The product, $RpCO_2Ti(Cl)Cp_2$ (**9b**), is unstable under the reaction conditions. It continuously decomposed above −40 °C (rapidly at room temperature) to give Rp_2, although the amounts of RpH and RpCl did not change appreciably. Solvent was evaporated (−30 to −10 °C), and solutions initially enriched in **9b** were obtained by first washing the orange-brown solid with hexane (to remove Rp_2 and RpH) and then extracting with diethyl ether or toluene (−30 °C to room temperature). Both these solutions and the less soluble residues promptly degraded to Rp_2 at room temperature. Attempts at recording ^{1}H NMR spectra were unsuccessful due to paramagnetic broadening.

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Preparation of (η^5-C_5H_5)(CO)$_2$FeCO$_2$Zr(Cl)(η^5-C_5H_5)$_2$ (10a). A THF solution of Fp^-Na^+[13b] (1.0 mmol/15.0 mL) was transferred to a 50-mL Schlenk flask fitted with a rubber septum and magnetic stirring bar. The solution was cooled to −78 °C, and carbon dioxide (25.0 mL, 1.1 mmol) was introduced by using a 20-mL syringe that was lubricated with THF. The CO_2 was injected slowly (2 min) into the closed system while the syringe needle was kept just above the manually swirled solution. Immediate reaction occurred without any obvious color change to give $FpCO_2^-Na^+$ (**8**)[3b] as a yellow-brown solution; typically small amounts (<5%) of Fp_2 [ν(CO) 1994, 1952, 1785 cm^{-1}] or FpNa [ν(CO) 1881, 1864, 1808, 1770 cm^{-1}] were present. Cp_2ZrCl_2 (292 mg, 1.0 mmol) was added (−78 °C), and it slowly dissolved as the light yellow solution was stirred and warmed to −40 °C (0.5 h). IR spectral monitoring revealed a 3:1 mixture of $FpCO_2Zr(Cl)Cp_2$ (**10a**) [ν(CO) 2037, 1977 cm^{-1}; $\nu(CO_2)$ 1365, 1279 cm^{-1}] and **8**, along with 5% Fp_2. Solvent was evaporated at −10 °C, and the resulting tan solid was washed with cold ether (3 × 12 mL, −40 °C). FpH was the major impurity identified by IR spectral monitoring [ν(CO) 2020, 1958 cm^{-1}] of the combined ether rinses. The remaining ivory solid was washed quickly with ether (3 × 10 mL) at room temperature, which removed FpCl, Fp_2, and a small amount of product **10a** (IR spectrally detected). This left a white solid (420 mg) that contained the cleanest samples of $FpCO_2Zr(Cl)Cp_2$ (**10a**): IR (CH_2Cl_2) 2038, 1981 (CO), 1363, 1268 cm^{-1} (CO_2).

^{1}H and ^{13}C NMR spectra were recorded for C_6D_6 or $C_6D_5CD_3$ solutions of weighed portions of the crude reaction mixture (most of the sample dissolved); only **10a** and $[Cp_2(Cl)Zr]_2O$ (**11a**) (8–10% of product) were detected under these conditions. ^{1}H NMR: $FpCO_2Zr(Cl)Cp_2$ (**10a**), δ 6.08 (s, Cp_2Zr), 4.15 (s, CpFe); **11a**, δ 6.01 (s, Cp_2Zr). ^{13}C NMR: **10a** (−30 °C), δ 206.2 ($FeCO_2Zr$), 213.9 (FeCO), 114.2 (Cp_2Zr), 86.1 (CpFe); **11a**, δ 114.1 (Cp_2Zr).

Small quantities of relatively pure **10a** that contained 8–15% $[Cp_2(Cl)Zr]_2O$ (**11a**) as the only detectable impurity were obtained as a white precipitate by immediately cooling the room-temperature ether washings. Attempts to further purify **10a** by extracting it with cold toluene, ether, or THF (−40 to 0 °C) inevitably enhanced μ-oxo **11a** and Fp_2 contaminants. Solutions of **10a** in benzene, THF, or ether rapidly degraded at room temperature (pronounced within 15 min), with **11a** and Fp_2 the major products detected by ^{1}H NMR and IR spectral monitoring.

Decomposition of (η^5-C_5H_5)(CO)$_2$FeCO$_2$Zr(Cl)(η^5-C_5H_5)$_2$ (10a). $FpCO_2^-Li^+$ (**8Li$^+$**)[3b] was generated in THF solution (15 mL) by treating Fp^-Li^+ (1.0 mmol) with carbon dioxide (25.0 mL, 1.1 mmol) at −78 °C. The resulting yellow-brown solution of **8Li$^+$** (IR ν(CO) 2010, 1942 cm^{-1}), containing 10% unreacted FpLi (IR ν(CO) 1884, 1868, 1813, 1750 cm^{-1}), was treated with Cp_2ZrCl_2 (292 mg, 1.0 mmol). IR spectral monitoring of the yellow-brown solution after stirring for 1.0 h at −78 °C and then 0.5 h at −20 °C indicated that **8Li$^+$** had been replaced by a 2:1:1 mixture of $FpCO_2Zr(Cl)Cp_2$ (**10a**), Fp_2, and FpH (ν(CO) 2016, 1952 cm^{-1}). Stirring this mixture for 4 h at room temperature converted it to Fp_2 along with small amounts (5–10%) of FpH and of **10a** as the other species evident by IR spectroscopy.

Solvent was evaporated from the filtered reaction mixture, and the light brown residue was extracted with 4 × 7 mL of diethyl ether. The combined ether filtrates were evaporated and reextracted with 4:1 hexane/ether, which left additional white solid and a brown filtrate. These white solids from the extraction steps were combined (231 mg) and identified by ^{1}H NMR spectroscopy as $[Cp_2(Cl)Zr]_2O$ (**11a**), δ (C_6D_6) 6.01, 87% yield. The ether-containing filtrates afforded Fp_2 (152 mg, 86%) as the only CpFe species detected by ^{1}H NMR spectroscopy.

Degradation of **10a** in C_6D_6 solution (23 °C) was monitored by ^{1}H NMR spectroscopy. Within 1 h, pronounced Cp resonances for FpCl (δ 3.95), Fp_2 (δ 4.21), and $[Cp_2(Cl)Zr]_2O$ (**11a**) (δ 6.01) were evident (in addition to unassigned, less intense signlets in the Cp region at δ 6.20, 6.10, 4.36, 4.21); after 48 h, only Fp_2 and **11a** were detected in the clear brown solutions.

Protonation of (η^5-C_5H_5)(CO)$_2$FeCO$_2$Zr(Cl)(η^5-C_5H_5)$_2$ (10a). A sample of $FpCO_2Zr(Cl)Cp_2$ (**10a**) (120 mg, 0.25 mmol) containing 10% $[Cp_2(Cl)Zr]_2O$ (**12a**) was dissolved in 5 mL of THF, and the solution was cooled to −78 °C and treated with $HBF_4{\cdot}OEt_2$ (0.05 mL, 0.25 mmol). The yellow solution was warmed to room temperature and immediately evaporated. IR spectral analysis of the reaction product after dissolving in nitromethane (3.75 mL) indicated quantitative conversion of **10a** to $FpCO^+BF_4^-$ [ν(CO) 2128, 2080 cm^{-1}]. This solution was concentrated to 2 mL under reduced pressure and diluted with diethyl ether (15 mL). The resulting pale yellow precipitate was filtered out, washed with ether (3 × 5 mL), vacuum-dried, and identified as $FpCO^+BF_4^-$[19] (70 mg, 95% yield): ^{1}H NMR (CD_3NO_2) δ 5.91 (CpFe). The combined ether filtrates were evaporated, and the resulting tan foam (49 mg) was identified as $[Cp(Cl)Zr]_2O$ (**11a**) by ^{1}H NMR spectroscopy, δ ($CDCl_3$) 6.45 (Cp_2Zr) (76% yield), along with trace amounts of other presumed Cp_2Zr complexes.

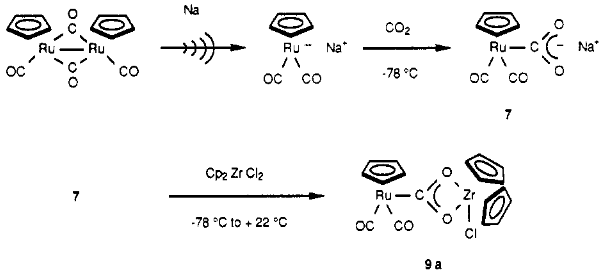
Reaction between (η^5-C_5H_5)(CO)$_2$FeCO$_2^-$Na$^+$ (8) and (η^5-C_5H_5)$_2$TiCl$_2$. A cold (−78 °C) THF solution (15.0 mL) containing $FpCO_2^-Na^+$ (**8**)[3b] (1.0 mmol) was treated with Cp_2TiCl_2 (251 mg, 1.0 mmol). The suspension was warmed to −40 °C (0.5 h) and stirred for another 1.0 h before most of the red titanocene dichloride dissolved to give a brown solution. IR spectral monitoring indicated a 1:1.5:1 mixture of unreacted **8**, Fp_2, and $FpCO_2Ti(Cl)Cp_2$ (**10b**) [ν(CO) 2033, 1970 cm^{-1}; $\nu(CO_2)$ 1379, 1273 cm^{-1}]. At −40 °C, only **10b** was transformed into Fp_2 and FpH (2:1). Evaporation of solvent at −30 °C also decomposed remaining **8** and left a brown solid, which only partially redissolved in THF as a 5:1 mixture of Fp_2 and FpH. A slightly soluble orange solid remained.

In a separate experiment, the reaction mixture was evaporated (room temperature) and extracted with ether (3 × 5 mL). Fp_2 (152 mg, 86% yield) was isolated as a purple crystalline solid after layering the combined ether extracts with hexane and was identified by its IR and ^{1}H NMR spectra. The ether-insoluble reaction residue was extracted with warm dichloromethane (5 × 5 mL) and layered with hexane. An orange precipitate was isolated (291 mg) and identified as a 1:5 mixture of Cp_2TiCl_2/$[Cp_2(Cl)Ti]_2O$ (**11b**)[26] [^{1}H NMR ($CDCl_3$) δ 6.59 and 6.31, respectively].

Results

Synthesis and Characterization of (η^5-C_5H_5)(CO)$_2$RuCO$_2$Zr(Cl)(η^5-C_5H_5)$_2$ (9a).

The starting ruthenium metalate Rp^-Na^+ is available quantitatively in THF solution by sonication of Rp_2 and sodium metal using a standard ultrasonic cleaning bath (eq 2).[13b,25] This procedure offers a significant improvement over other reduction procedures using 2% sodium amalgam[27] or borohydride reagents[28] for cleaving Rp_2 to Rp^-Na^+. The presence of ruthenium byproducts and lower yields that characterize the sodium amalgam route and the need to remove trialkylborane byproducts from the trialkylborohydride procedure are avoided by sonication.



(2)

The resulting yellow-brown solution of Rp^-Na^+ in THF exhibits only two terminal carbonyl IR ν(CO) bands at 1907 and 1825 cm^{-1}. These compare with the ν(CO) 1881- and 1808- cm^{-1} absorptions that are assigned to the ionic

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[26] (a) Döppert, K. *J. Organomet. Chem.* **1979**, *178*, C3. (b) LePage, Y.; McCowan, J. D.; Hunter, B. K.; Heyding, R. D. *J. Organomet. Chem.* **1980**, *793*, 201. See also refs 11a and 23c.

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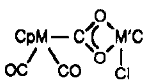
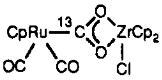
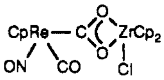
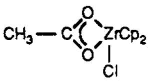
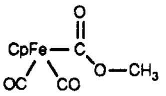
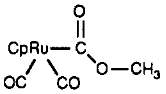
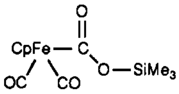
Table I. Selected ^{13}C NMR and IR Spectral Data for Metallocarboxylates

compd	$\delta(CO_2)$ (solvent)	$\nu_{asym}(CO_2)$, cm^{-1}	$\nu_{sym}(CO_2)$, cm^{-1}	medium (ref)
		1344 1348 1349	1285 1290 1291	KBr CH_2Cl_2 THF
M = Ru, M′ = Zr (**9a**)	213.2 (C_6D_6)			
M = Fe, M′ = Zr (**10a**)	206.2 (C_6D_6)	1363 1365	1268 1279	CH_2Cl_2 THF
M = Ru, M′ = Ti (**9b**)		1349	1284	THF
M = Fe, M′ = Ti (**10b**)		1379	1273	THF
		1312	1264	THF
 **5**	212.6 ($CDCl_3$)	1348 1350	1288 1273	KBr (5) CH_2Cl_2 (5)
 **6a**	187.1 ($CDCl_3$)	1528 1751, 1728	1477 *a*	CH_2Cl_2 (7) THF (7)
	200.8 ($CDCl_3$)	1647	*a*	THF (3b)
	184.7 (C_6D_6)	1651	*a*	C_6D_6
	200.7 ($CDCl_3$)	1625	*a*	THF (3b)

[a] $\nu(CO_2)_{sym}$ not assigned because of interfering fingerprint region background and solvent absorptions.

(ion-paired) $Cp(CO)_2Fe^-Na^+$ structure predominating in THF solutions.[29] Lower energy ν(CO) bands analogous to those observed for the isocarbonyl Cp(CO)FeCONa and covalently bound $Cp(CO)_2FeNa$ species[29b] are not detected for Rp^-Na^+.

The ruthenium metalate Rp^-Na^+ in THF rapidly and quantitatively consumes 1 equiv of CO_2 at −78 °C. We obtained identical results independent of whether the dried CO_2 was added by syringe at −78 °C or it was condensed into the reaction apparatus on a vacuum line at −196 °C. (A typical experimental using the former procedure is given for $FpCO_2^-Na^+$ (**8**).) Limited attempts at characterizing the ruthenium species in this yellow-brown solution as $RpCO_2^-Na^+$ (**7**) proved unsuccessful, since only RpH was detected by IR spectroscopy as the solution warmed. We presume that this solution contains the unstable metallocarboxylate **7** because of its subsequent reaction chemistry.

Treating **7** with zirconocene dichloride, Cp_2ZrCl_2, affords the heterobimetallic CO_2 complex $RpCO_2Zr(Cl)Cp_2$ (**9a**) in excess of 90% yield, as judged by IR spectral monitoring. The terminal carbonyl absorptions of **9a** [ν(CO) 2041, 1983 cm^{-1}] are particularly diagnostic; only trace amounts of RpH [ν(CO) 2022, 1958 cm^{-1}] and Rp_2 [ν(CO) 1996, 1964, 1953, 1936 cm^{-1}] are detected. We obtained analytically pure $RpCO_2Zr(Cl)Cp_2$ (**9a**) as a thermally stable white solid, albeit in low yield, after washing with diethyl ether and extracting with benzene. The presence of the zirconocene μ-oxo complex $[Cp_2(Cl)Zr]_2O$ (**11a**)[23] complicates the workup procedure; both **11a** and **9a** have very similar solubility properties, and **9a** is unstable upon attempted column chromatography. Larger quantities of **9a** (60% yield) are available that are contaminated only with **11a** (10–15%).

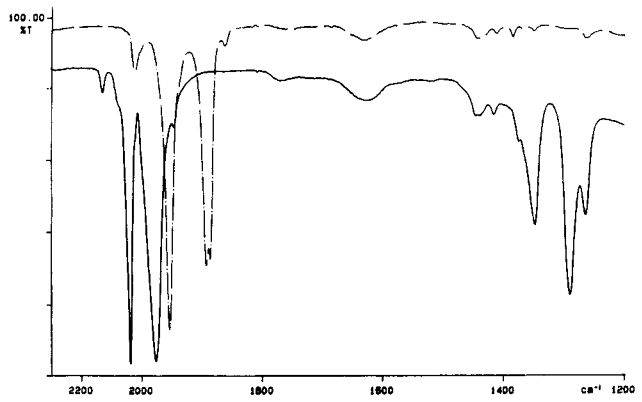


Figure 1. Infrared spectra of $Cp(CO)_2RuZr(Cl)Cp_2$ (**12**) (upper scan) and $Cp(CO)_2RuCO_2Zr(Cl)Cp_2$ (**9a**) in pressed KBr disks.

IR and ^{1}H NMR spectra of **9a** are consistent with the presence of $CpRu(CO)_2$ and $Cp_2(Cl)Zr$ moieties (1:1). Its ^{13}C NMR spectrum additionally has terminal carbonyl and carboxylate absorptions (δ 198 and 215, respectively) that compare favorably with those of the analogous ReZr μ-CO_2 adduct **5** (δ 201 and 213).[9] Similar assignments for the corresponding terminal carbonyl and acyl carbon centers on $RpCOCH_3$[30] (δ 200 and 238, $CDCl_3$), on $RpC(O)OCH_3$[22]

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(29) (a) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263. Pannell, K. H.; Jackson, D. *J. Am. Chem. Soc.* **1976**, *98*, 4443. Nitay, M.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *136*, C23. (b) Darensbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221.

(30) Green, M. L. H.; Mitchard, L. C.; Swanwick, M. G. *J. Chem. Soc. A* **1971**, 794.

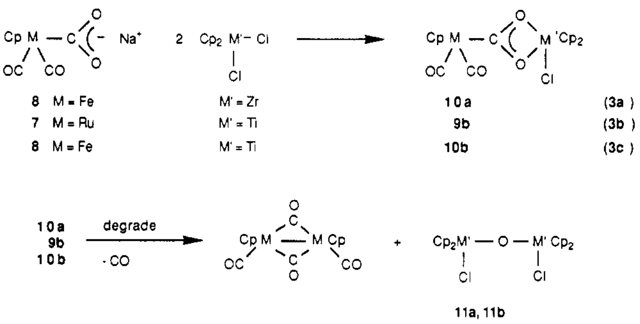
(δ 199 and 185), and on Geoffroy's FeW and RuW μ-(η^1-C:η^2-O,O′) metallocarboxylates[7] $[Cp(CO)_2Fe{=}CO_2WCp_2]^+$ (δ 212 and 260) and $[Cp^*(CO)_2Ru{=}CO_2WCp_2]^+$ (δ 199 and 252) are worth noting. The higher values for the carboxylate carbons on Geoffroy's FeW and RuW metallocarboxylates agree with their formulation as dimetalated dioxocarbene ligands.[7]

Complex **9a** is assigned as a μ-(η^1-C:η^2-O,O′) carboxylate structure on the basis of its IR spectrum, which shows carboxylate $\nu(CO_2)$ bands[31,32] at 1350 and 1290 cm^{-1} in solution (dichloromethane and THF) and in a KBr pellet (Table I). We also synthesized the ^{13}C-labeled **9a** (using 99% ^{13}C-labeled CO$_2$) in order to confirm these $\nu_{asym}(CO_2)$ and ν_{sym} (CO$_2$) assignments (Table I). IR spectra of KBr pellets for **9a** and for Casey's heterobimetallic compound RpZr(Cl)Cp$_2$ (**12**) are compared in Figure 1. The broad, medium-intensity carboxylate absorptions for **9a** closely resemble in appearance those of the analogous ReZr μ-carboxylate **5**, with the 60-cm^{-1} separation, ν_{asym} (CO$_2$) − ν_{sym}(CO$_2$), for **9a** (and for **5**) indicating chelating (η^2-O,O′) metallocarboxylate structures.

The RuZr bridging carboxylate complex **9a** is stable at room temperature either as a solid or as a benzene solution for at least 24 h. Thermal stability of **9a** was further assessed by monitoring ^{1}H NMR spectra of its thoroughly degassed C$_6$D$_6$ solutions in sealed NMR tubes. Under these conditions, **9a** slowly degrades above 40 °C, and at 80 °C it decomposes 40% within 4 h to give clear brown solutions. The zirconocene μ-oxo compound **11a** accounts for perhaps 85% of the Cp$_2$(Cl)Zr complexes observed (δ 5.85–6.20 region), with small amounts of Cp$_2$ZrCl$_2$ and several unidentified Cp$_2$Zr complexes also evident. Rp$_2$ is the major ruthenium-containing species detected in the CpRu region (δ 4.30–4.90), although we note that RpCl appears during initial stages of the reaction.

In THF solution, however, **9a** only has a half-life ($\tau_{1/2}$) at room temperature of 12 h, as it smoothly degrades to RpH and **11a**. This reaction appears messy after the first half-life and ultimately affords a 1:1 mixture of RpH/RpCl (36 h). These stability studies were conducted by distilling the THF on a vacuum line (from sodium benzophenone ketyl) directly into the reaction vessel and monitoring the degradation of **9a** by IR and (after changing solvent) by ^{1}H NMR spectroscopy. It is important to note that under these conditions both Rp$^-$Na$^+$ and RpZr(Cl)Cp$_2$ (**12**) are stable and that the qualitative order of their moisture sensitivity (as gauged by the relative difficulty of obtaining IR spectra free of contaminating RpH) is **12** > Rp$^-$Na$^+$ ≫ **9a**. Exposure of RpZr(Cl)Cp$_2$ (**12**) to trace concentrations of moisture immediately and quantitatively provides RpH and **11a**.

Less Stable Bimetallocarboxylates (η^5-C$_5$H$_5$)(CO)$_2$MCO$_2$M′(Cl)(η^5-C$_5$H$_5$)$_2$ (MM′ = FeZr (10a), RuTi (9b), FeTi (10b)). The reaction between FpCO$_2^-$Li$^+$ or FpCO$_2^-$Na$^+$ (**8**) and Cp$_2$ZrCl$_2$ (eq 3a) is sluggish at −78 °C; however, warming the cold reaction mixture to −40 °C over 0.5 h and then evaporating the solvent at −10 °C affords crude FpCO$_2$Zr(Cl)Cp$_2$ (**10a**) as a light tan solid. Under these conditions, any remaining FpCO$_2^-$Na$^+$ (**8**) degrades to Fp$_2$ and FpH,[2a,3b] which are extracted by diethyl ether. The remaining white powder contains **10a** plus 8–10% of the zirconocene μ-oxo complex **11a** as the only organometallic contaminant that is detected by ^{1}H NMR spectroscopy. Cooling and concentrating the ether extracts deposits small amounts of **10a**, although these fractions also retain 8–10% of the **11a**.



We could not further purify **10a** for two reasons. First, synthesis of **10a** between −40 and −10 °C approximates a point of diminishing returns at which its rate of formation balances its rate of decomposition into dimeric Fp$_2$ and μ-oxo complex **11a**. In these reaction mixtures **10a** remains intact between −40 °C and −30 °C for at least 2 h, and attempts to extract and precipitate **10a** by using THF/diethyl ether/toluene solvent mixtures between −40 °C and room temperature inevitably increase the concentrations of Fp$_2$ and [Cp$_2$(Cl)Zr]$_2$O (**11a**). The second reason is that **10a** and **11a** have very similar solubility properties. Although washing the crude reaction product with hexane and ether removes Fp$_2$, FpCl, and other minor organoiron and -zirconium contaminants, attempts at completely separating **10a** from **11a** by extraction and fractional crystallization or precipitation procedures at lower temperatures repeatedly failed.

Solution instability of FpCO$_2$Zr(Cl)Cp$_2$ (**10a**) is pronounced at room temperature. As a crude reaction product, **10a** has a $\tau_{1/2}$ of 1 h in THF, and maintaining this reaction mixture at room temperature for 4 h affords both Fp$_2$ and μ-oxo **11a** in over 85% isolated yields (eq 3a). In contrast, **10a** remains intact as a solid at room temperature for several hours, and partially purified samples are spectroscopically characterized as benzene or toluene solutions. Such solutions in C$_6$D$_6$ are somewhat more stable ($\tau_{1/2}$ = 3 h), although ^{1}H NMR spectral monitoring indicates degradation to Fp$_2$ and μ-oxo **11a** along with smaller concentrations of FpCl and several unidentified Cp$_2$Zr species. Only Fp$_2$ and μ-oxo **11a** remain after 48 h.

Spectroscopic data for **10a** are entirely consistent with a μ-(η^1-C:η^2-O,O′) bimetallocarboxylate structure that is analogous to its RuZr congener **9a**. IR spectra of **10a** (Table I), in particular, show Fp group terminal carbonyl ν(CO) and a chelating carboxylate group $\nu(CO_2)$ absorptions[31] [$\Delta\nu(CO_2)$ = 86–95 cm^{-1}]. ^{1}H and ^{13}C NMR spectra

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(31) IR spectral correlations involving absorptions for ligated carboxylate (MOC(O)R), $\nu(CO_2)_{asym}$ and $\nu(CO_2)_{sym}$, are well established. See ref 32. Monodentate (η^1-O) carboxylates typically exhibit a medium-intensity $\nu(CO_2)_{asym}$ band in the region 1600–1750 cm^{-1} and have a carboxylate peak separation, $\Delta\nu = \nu(CO_2)_{asymm} - \nu(CO_2)_{sym}$, greater than 250 cm^{-1}. Bridging (η^1-O:η^1-O′) MOC(R)OM and chelating (η^2-O,O′) MOCOR carboxylate ligands both usually show the higher energy $\nu(CO_2)_{asym}$ bands below 1550 cm^{-1} and have a much smaller carboxylate peak separation ($\Delta\nu < 100$ cm^{-1}). Recent examples of these IR spectral correlations for well-characterized carboxylate complexes are available. (a) FpOCOR and FpOC(R)O-Fp$^+$; Tso, C. T.; Cutler, A. R. *Organometallics* **1985**, *4*, 1242. (b) Cp(CO)$_3$WOC(O)R and Cp(CO)$_2$WOC(O)R: Werner, H.; Roll, J.; Zolk, R.; Thometzek, P.; Linse, K.; Ziegler, M. *Chem. Ber.* **1987**, *120*, 1553. (c) (PPh$_3$)$_2$(CO)$_2$(NO)WOC(O)R and (PPh$_3$)$_2$(CO)(NO)WOC(O)R: Hillhouse, G. L.; Haymore, B. L. *Inorg. Chem.* **1987**, *26*, 1876. Holl, M. M.; Hillhouse, G. L.; Folting, K.; Huffman, J. C. *Organometallics* **1987**, *6*, 1522. (d) (PR$_3$)$_2$(CO)$_2$[RC(O)O]MoOC(O)R: Brower, D. C.; Winston, P. B.; Tonker, T. L.; Templeton, J. L. *Inorg. Chem.* **1986**, *25*, 2883. Riera, V.; Arnaiz, F. J.; Herbosa, G. G. *J. Organomet. Chem.* **1986**, *315*, 51. (e) Cp$_2$(Cl)ZrOC(O)R and Cp$_2$(Cl)(THF)ZrOC(O)R: see ref 10. (f) (PMe$_3$)$_3$PhOC(O)R and (PMe$_3$)$_2$RhOC(O)R: Darensbourg, D. J.; Grötsch, G.; Wiegreffe, P.; Rheingold, A. *Inorg. Chem.* **1987**, *26*, 3827. (g) (PPh$_3$)$_3$CuOC(O)H, (PPh$_3$)$_3$CuOC(H)OCu(PPh$_3$)$_2^+$, and (PPh$_3$)$_2$CuOC(O)H: Bianchini, C.; Ghilardi, C. A.; Meli, A.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1985**, *24*, 924.

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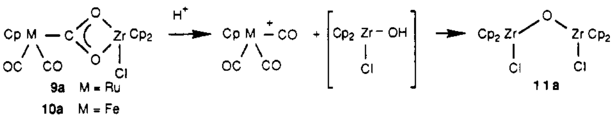
further support the presence of Fp and $Cp_2(Cl)Zr$ moieties, with the carboxylate carbon appearing at δ 206 in the ^{13}C NMR spectrum.

In agreement with its assigned bimetallocarboxylate structure, **10a** cleaves to form $FpCO^+BF_4^-$ and the zirconocene μ-oxo complex **11a** (isolated yields 95% and 76%, respectively) upon treating with 1 equiv of HBF_4 (eq 4).



(4)

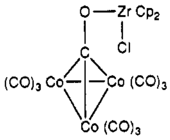
We independently established that protonating Fp_2 under similar conditions does not give $FpCO^+$ but instead produces the known[33] bridging hydride compound $Fp_2H^+BF_4^-$. Protonation of the RuZr μ-CO_2 complex **9a** also gives its metal carbonyl salt, $RpCO^+BF_4$ (78% yield). These protonation reactions represent additional examples of the general electrophilic cleavage of metalloester compounds to their metal carbonyls,[3a,6,22b,34] reactions that are documented for protonating $Cp(CO)_2MCO_2Et$ (M = Fe,[19a] Ru[22]), $FpCO_2SiMe_3$,[3b] and the ReZr bimetallocarboxylate **5**.[9]

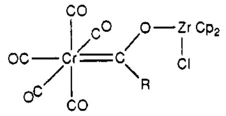
Both $RpCO_2^-Na^+$ (**8**) and $FpCO_2^-Na^+$ (**7**) react with titanocene dichloride, Cp_2TiCl_2, under conditions used to prepare **10a** and generate the corresponding RuTi (**9b**) and FeTi (**10b**) bimetallocarboxylates, albeit as unstable products, (eq 4b,c). A maximum 40% yield of $RpCO_2Ti(Cl)Cp_2$ (**9b**) accumulates at −40 °C, a temperature at which **9b** steadily degrades ($\tau_{1/2}$ = 2 h). During attempted workup (between −10 and +20 °C), the product quickly converts to Rp_2 (15 min at 22 °C), as ascertained by IR spectral monitoring. The decomposition of crude reaction mixtures containing $FpCO_2Ti(Cl)Cp_2$ (**10b**) is even more rapid, since **10b** smoothly decomposes to Fp_2 and $[Cp_2(Cl)Ti]_2O$[26] (**11b**) between −40 and −30 °C (2 h). The FpH initially detected in these reaction mixtures (above −40 °C) can be ascribed to decomposition of unreacted $FpCO_2^-Na^+$ (**8**).

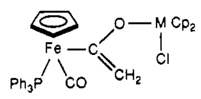
For structural assignment of the RuTi (**9b**) and FeTi (**10b**) bimetallocarboxylates, we rely exclusively on IR spectral data. Both sets of terminal carbonyl ν(CO) and carboxylate $\nu(CO_2)$ absorptions for **10b** and **9b** are assigned. The medium-intensity carboxylate absorptions, in particular, appear very similar in band shape to those of their RuZr (**9a**) and FeZr (**10a**) congeners. Values for $\Delta\nu(CO_2)$ of 65 $cm^{-}11$ (**9b**) and 106 cm^{-1} (**10b**), as compared to 61 cm^{-1} (**9a**) and 86 cm^{-1} (**10a**) (Table I), indicate the presence of chelating (η^2-O,O′) carboxylate to the Ti centers.

Discussion

Heterobimetallic complexes, particularly those pairing early and late transition metals, may engender synergistic interactions as these oxophilic (early) and electron-rich (late) metal centers either stabilize a connecting ligand or mediate its subsequent reactions.[35] One synthetic approach to heterobimetallic complexes entails displacing chloride from titanocene or zirconocene dichloride with anionic organometallic complexes that form Ti–O and Zr–O bonds.[36] Examples include using Cp_2ZrCl_2 to derivatize $Co_3(CO)_{10}^-$ as a zirconoxymethylidyne compound $(CO)_9Co_3COZr(Cl)Cp_2$[37] and chromium acyl complexes $(CO)_5CrC(O)R^-$ as zirconoxycarbene compounds $(CO)_5Cr{=}C(R)OZr(Cl)Cp_2$.[38] Floriani recently reported that the unstable iron acetyl enolate $Cp(PPh_3)(CO)FeC(O){=}CH_2^-$ intercepts Cp_2MCl_2 to provide stable FeTi and FeZr μ-enolates **13**.[39] These heterobimetallic μ-enolate compounds **13** are particularly relevant, since the (η^1-C) ketene complexes $Cp(L)(CO)FeC(O){=}CH_2^-$ (L = CO, PPh_3) also resemble the corresponding (η^1-C) metallocarboxylates $Cp(L)(CO)FeCO_2^-$ in their reactivity toward electrophiles.[3a,40]

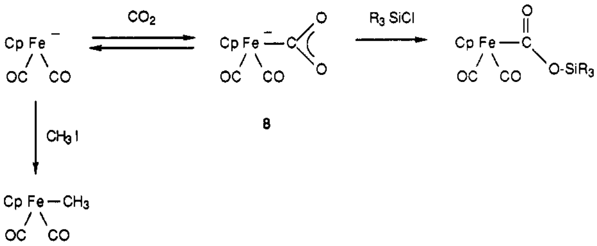






13 (M = Ti, Zr)

The metallocarboxylate $FpCO_2^-Na^+$ (**8**) undergoes several different reactions with Lewis acids. The products obtained from treating **8** with methyl iodide[2a,3c,13a] and with the oxophilic trimethylsilyl chloride[3b] (eq 5) illustrate two



(5)

of these pathways. Methyl iodide quantitatively converts **8** to $FpCH_3$ by intercepting a dissociative equilibrium between **8** and Fp^-Na^+, whereas trimethylsilyl chloride traps **8** as the metalloester $FpC(O)OSiMe_3$. Another pathway involving electron-transfer and odd-electron organoiron intermediates apparently operates upon treating **8** with $Cp(L)(CO)FeX$ (L = CO, PPh_3, $P(OPh)_3$; X = Cl, I, triflate); these reactions uniformly produce only Fp_2 but no traces of the bis(iron) metallocarboxylates, $FpC(O)OFe(CO)(L)Cp$.[40]

We now find that zirconocene and titanocene dichlorides readily react with both iron and ruthenium CO_2 complexes $Cp(CO)_2MCO_2^-$ (M = Ru (**7**) and Fe (**8**)) in THF and afford bimetallic adducts $Cp(CO)_2MCO_2M'(Cl)Cp_2$ (**9a**,**b**, M = Ru, M′ = Zr and Ti; **10a**,**b**, M = Fe, M′ = Zr and Ti); see eq 1. Stability of these bimetallocarboxylates, as in-

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dicated by their relative ease of synthesis and purification, decreases in the order RuZr (**9a**) $\gg$ FeZr (**10a**) > RuTi (**9b**) > FeTi (**10b**). The RuZr adduct **9a** is stable at room temperature, and the FeZr complex **10a** has a $\tau_{1/2}$ in THF solution of 1 h. Hence both are isolated, **9a** analytically pure and **10a** partially purified, and are characterized by IR, ^{1}H, and ^{13}C NMR spectroscopy. Their titanium cogeners RuTi (**9b**) and FeTi (**10b**), on the other hand, are unstable above −30 °C, which thwarted purifying them and collecting definitive NMR spectral data. Attempts to purify **9b** at −30 °C affords enriched solutions, although it promptly degrades upon warming above 0 °C. The FeTi adduct **10b** rapidly decomposes between −40 and −30 °C.

IR spectral data for all four adducts and for Rp^{13}CO$_2$Zr(Cl)Cp$_2$ (**9a**-^{13}-*C*) define similar μ-(η^1-C:η^2-O,O′) chelating bimetallocarboxylate structures (Table I). The absence of a $\nu(\mathrm{CO_2})_{\mathrm{asym}}$ absorption above 1600 cm^{-1}, even for concentrated THF solutions, precludes the presence of nonchelating μ-(η^1-C:η^1-O) carboxylate complexes Cp(CO)$_2$MC(=O)OM′(Cl)Cp$_2$ (i.e., **4**) in any significant concentration.[31,32] Analogous ruthenium and iron (η^1-C) metalloester species Cp(CO)$_2$MC(O)OCH$_3$ and Cp(CO)$_2$MC(O)OSiMe$_3$ exhibit medium-intensity $\nu(\mathrm{CO_2})_{\mathrm{asym}}$ absorptions between 1625 and 1650 cm^{-1}. The chlorozirconocene acetate **6a** in THF solution produces a carboxylate $\nu(\mathrm{CO_2})_{\mathrm{asym}}$ band above 1720 cm^{-1} (Table I) that we attribute to THF-ligated (η^1-O) acetate Cp$_2$(Cl)(THF)ZrOC(O)CH$_3$.[10a]

All four bimetallocarboxylates Cp(CO)$_2$MCO$_2$M′(Cl)Cp$_2$ (**9a**,**b** and **10a**,**b**) also have similar thermal degradation products, dimeric Cp$_2$M$_2$(CO)$_4$ and μ-oxo compounds [Cp$_2$(Cl)M′]$_2$O (M′ = Zr (**11a**), Ti (**11b**)), that indicate partial deoxygenation of CO$_2$ (eq 3). This deoxygenation occurs rapidly for **10a** and **10b** in THF, but it is relatively slow for **9b** in THF and very slow for **9a** in benzene or toluene. We ruled out the presence of adventitious water as the cause of these deoxygenation reactions. Indeed, both **9a** and **9b** are much less air- and moisture-sensitive than are their corresponding hetereobimetallic systems RpZr(Cl)Cp$_2$ (**12**) and FpZr(O^{t}Bu)Cp$_2$[24] or are their metalates Cp(CO)$_2$M$^-$, compounds that were routinely handled during the course of these studies. Similar deoxygenation of ligated CO$_2$ on mononuclear complexes to give either metal oxo or oxide complexes is well established.[41,42]

We never observed RpZr(Cl)Cp$_2$ (**12**) as an intermediate or byproduct during our studies involving RpCO$_2$Zr(Cl)Cp$_2$ (**9a**). In particular, **9a** evidently does not extrude CO$_2$ between room temperature and 80 °C to generate **12**, a product that would have been easily detected by its distinctive IR spectral ν(CO) band at 1914 cm^{-1} (THF).

Conclusions

Derivatizing an (η^1-C) metallocarboxylate or CO$_2$ adduct **2** as a bimetallocarboxylate can afford more enduring metal–CO$_2$ interactions with appropriate choice of metal systems. Although the metallocarboxylate RpCO$_2^-$Na$^+$ (**7**) in the presence of excess CO$_2$ is unstable above −50 °C (as also observed for its iron congener **8**[3b]), incorporating a zirconium center affords RpCO$_2$Zr(Cl)Cp$_2$ (**9a**), a persistent bimetallic CO$_2$ adduct. Even its iron congener FpCO$_2$Zr(Cl)Cp$_2$ (**10a**) is more stable than its precursor, FpCO$_2^-$Na$^+$ (**7**).

Ligating CO$_2$ as a bimetallocarboxylate Cp(CO)$_2$MCO$_2$M′(Cl)Cp$_2$ also provides a vehicle for facile cleavage of one of its two C–O bonds. All four bimetallocarboxylates degrade in solution (for RuZr (**9a**), heating above 40 °C is required) to the same pair of products, dimeric Cp$_2$M$_2$(CO)$_4$ and μ-oxo [Cp$_2$(Cl)M′]$_2$O (**11**). In a more straightforward deoxygenation of the bridging carboxylate ligand, protonating the RuZr (**9a**) and FeZr (**10a**) CO$_2$ adducts eliminates the zirconocene μ-oxo **11a** and precipitates the cationic metal carbonyls CpM(CO)$_3^+$ (M = Ru, Fe). Studies in progress address further synthesis and characterization of RuZr bimetallocarboxylates, direct CO$_2$ insertion into metal–metal bonds of related heterobimetallic compounds Cp(CO)$_2$MM′(X)Cp$_2$, and the reactivity of heterobimetallic carboxylates toward a variety of reducing media.

Acknowledgment. We thank Dr. Bruce Landrum of this laboratory for sharing results of related experiments and R. S. Pilato and G. L. Geoffroy for a preprint of ref 5. Support from the Office of Naval Research and from the National Science Foundation, Grant CHE-8305484, is gratefully acknowledged.

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