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"Transition Organometallic Heterobimetallic
 μ -Carbon Dioxide and μ -Format Complexes in
Homogeneous Carbon Dioxide Fixation"

Alan R. Cutler, Principal Investigator

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New W- and Re-containing bimetallic μ-formate salts $[L_xM]-OCHO-[ML_y]^+$ (L_xM, $L_yM = W(CO)_3Cp$, $Re(NO)(CO)Cp$) were characterized. The Re center is more labile than the corresponding W center. Their reactions with nucleophiles, especially hydride donors, were studied. Attempts to synthesize bimetallic CO_2 complexes $Cp(CO)_2Fe-CO_2-M''L_y$ from $Fp-CO_2^-$ and a variety of organometallic Lewis Acids LyM''^+ were unsuccessful. The stable $(\eta^1-C : \eta^2-S,S')$ CS_2 adduct $Fp-C(S)S-Fp$, prepared from $FpCS_2^-$, was characterized. Early-late bimetallic $\mu-(\eta^1-C : \eta^2-O,O')$ CO_2 complexes $Cp(CO)_2M-CO_2-M'(Cl)Cp_2$ ($M = Fe, Ru$; $M' = Ti, Zr, Hf$) were synthesized (from $FpCO_2^-$ or $RpCO_2^-$) and studied. Cleavage of a C-O bond on the bridging CO_2 is a prevailing trend in (1) thermal decomposition of these bimetallocarboxylates (stability decreases: $RuZr \gg FeZr > RuTi > FeTi$), (2) protonation of the more stable Zr adducts and (3) $Cp_2Zr(H)Cl$ reduction of the fully characterized $RuZr CO_2$ adduct to the $\mu(\eta^1-C : \eta^1-O)$ formaldehyde complex $Rp-CH_2O-Zr(Cl)Cp_2$. CO_2 converts the Fe-Zr and Ru-Zr bimetallics $Cp(CO)_2M-Zr(X)Cp_2$ ($X = Cl, O^tBu$) to their bimetallocarboxylates.					
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Part I

- b. "Carbon Monoxide and Carbon Dioxide Fixation: Relevant C_1 and C_2 Ligand Reactions Emphasizing $(\eta^5-C_5H_5)Fe$ -Containing Complexes", A. R. Cutler, P. K. Hanna, and J. C. Vites, *Chem. Rev.* **1988**, *88*, 1363 (Invited).[‡]
- "Homo- and Hetero-Bimetallic $\mu(\eta^1-O:\eta^1-O')$ Formate Complexes $(M-OCHO-M')^+ PF_6^-$ [$M, M' = (\eta^5-C_5H_5)(CO)(NO)Re, (\eta^5-C_5H_5)(CO)_3W$, and $(\eta^5-C_5H_5)(CO)_2Fe$], Their Synthesis, Solution Lability, and Reactivity Towards Hydride Donors", C. C. Tso and A. R. Cutler, *Inorg. Chem.* **1990**, *29*, 471.*
- "Reactions of Carbon Disulfide and Carbon Dioxide Adducts $(\eta^5-C_5H_5)(CO)_2Fe-CX_2^-$ with Organoiron Electrophiles", M. E. Giuseppetti-Dery, B. E. Landrum, J. L. Shibley, and A. R. Cutler, *J. Organomet. Chem.* **1989**, *378*, 421.*
- "Characterization of the Heterobimetallic $\mu(\eta^1-C:\eta^2-O,O')$ Carbon Dioxide Complexes $Cp(CO)_2M-C(O)O-M'(Cl)Cp_2$ ($M = Fe, Ru; M' = Ti, Zr$)", J. C. Vites, M. E. Giuseppetti-Dery, and A. R. Cutler, *Organometallics* **1991**, *10*, 2827.
- "Reduction of the Heterobimetallic $\mu(\eta^1-C:\eta^2-O,O')$ Carbon Dioxide Complex $Cp(CO)_2Ru-C(O)O-Zr(Cl)Cp_2$ to its $\mu(\eta^1-C:\eta^1-O)$ Formaldehyde Derivative $Cp(CO)_2Ru-CH_2O-Zr(Cl)Cp_2$: Hydride Transfer Occurs at Ligated Carbon Monoxide", B. D. Steffey, J. C. Vites, and A. R. Cutler, *Organometallics* **1991**, *10*, 3432.
- e. ONR Technical Report No. 4: "Characterization of a Family of Heterobimetallic $\mu(\eta^1-C:\eta^2-O,O')$ Carbon Dioxide Complexes $Cp(CO)_2M-C(O)O-M'(Cl)Cp_2$ ($M = Fe, Ru; M' = Ti, Zr$)", J. C. Vites, M. E. Giuseppetti-Dery, and A. R. Cutler
- h. "Catalyzed and Noncatalyzed Hydrosilation of Metal Acyl Complexes," New England Workshop on Organometallic Chemistry, Andover, MA (May 5-7, 1989).[‡]
- Office of Naval Research / Gas Research Institute Conference on Carbon Dioxide Reactivity; Stanford Research Institute (Menlo Park, CA) 1988; "Heterobimetallic Carbon Dioxide Complexes and CO_2 Reduction."
- Second International Conference on Heteroatom Chemistry (SUNY-Albany) 1989
North East Regional ACS meeting, June 20, 1989; "Heterobimetallic Carbon Dioxide Complexes and CO_2 Reduction."
- Miami National ACS meeting, September, 1989, "Heterobimetallic Carbon Dioxide Complexes and CO_2 Reduction."

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Part II

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- e. Significant Resultspage 5
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Transition Organometallic Heterobimetallic μ -Carbon Dioxide Complexes in Homogeneous Carbon Dioxide Fixation

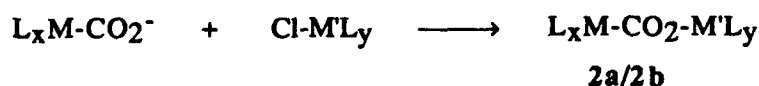
Project Description

We are establishing the coordinated ligand reactions depicted for reducing CO₂ to formaldehyde and methanol; our objective in future studies includes optimizing and combining these ligand reactions into a reaction cycle or a catalytic system.

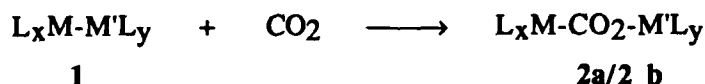
Our approach exploits bimetallic complexation of CO₂ and uses a third metal system as the reductant (e.g., catalytic hydrosilation). These bimetallic CO₂ adducts **2** feature synergistic CO₂ binding in which an electron-rich metal system L_xM contributes (η^1 -C) metallocarboxylate binding and an oxophilic L_yM' system sequesters one or both metallocarboxylate oxygens (**2a** and **2b**, respectively). In addition to stabilizing the CO₂ adduct, the resulting electronic "push-pull" also activates the CO₂ ligand as a hydride acceptor.

Goals

I. Synthesis and characterization of heterobimetallic CO₂ complexes



II. CO₂ "insertion" into the metal-metal bond of **1** (step A)



III. Reduction of ligated CO₂ to heterobimetallic formaldehyde compounds **4** (step B)



IV. Reaction chemistry of the formaldehyde compounds L_xM-CH₂O-M'L_y (**4**)

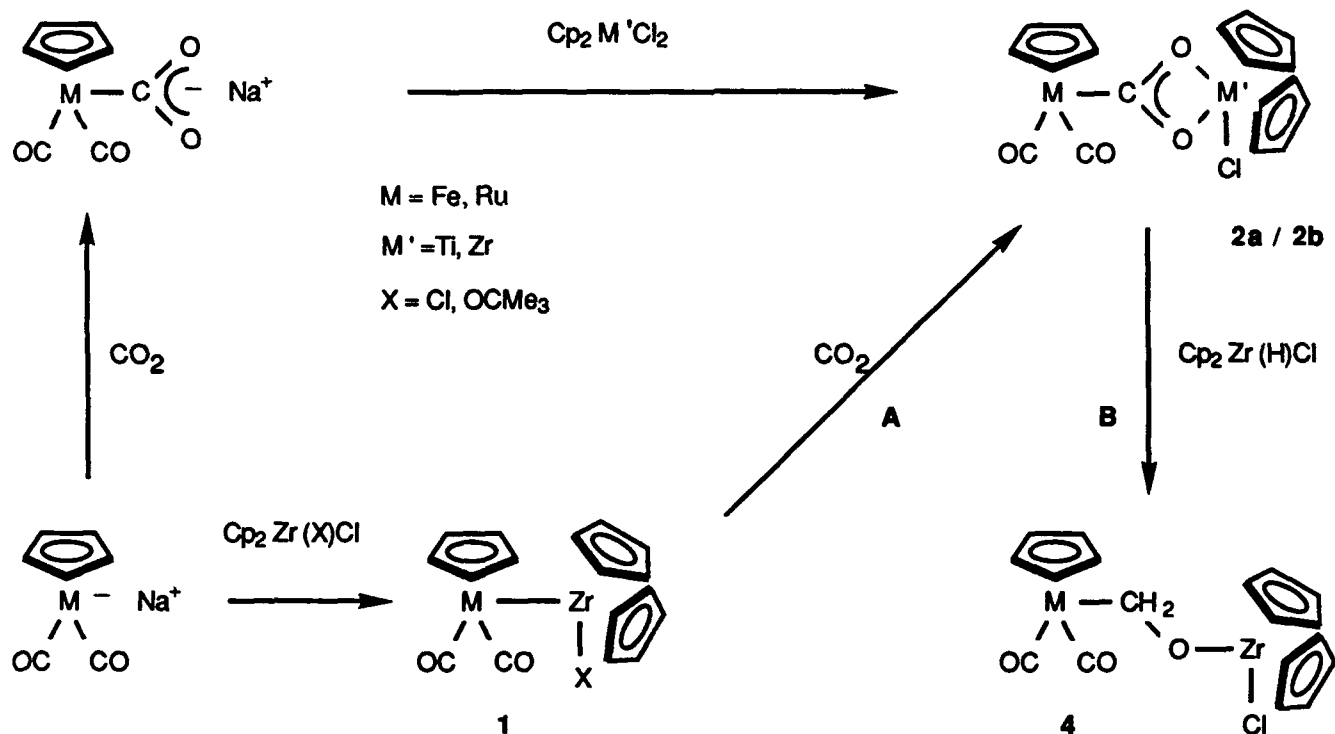
- (a) Further reduction : L_xM-CH₂O-M'L_y $\longrightarrow$ L_xM-CH₃,
- (b) Formaldehyde extrusion (step C) [formaldehyde + base $\rightarrow$ Formose liquid]

V. Electrochemical studies

- (a) Electron-transfer catalysis: enhance lability of L_xM-M'L_y (**1**) (step A) and of L_xM-CH₂O-M'L_y (**4**) (step B)
- (b) Electrochemistry of CO₂ adducts L_xM-CO₂-M'L_y (**2**) as model for electro-catalytic CO₂ reduction on electrode surface

Transition Organometallic Heterobimetallic μ -Carbon Dioxide Complexes in Homogeneous Carbon Dioxide Fixation

RESULTS



I. Stability of these heterobimetallic CO₂ complexes 2a/2b as a function of M and M':

RuZr >> FeZr > RuTi > FeTi (relative ease of synthesis & purification)

Equilibrium 2a and 2b : established for Cp(CO)₂Ru-CO₂-Zr(OCMe₃)Cp₂

and Cp(CO)₂Ru-CO₂-Zr(Cl)(C₅Me₂)₂

II. CO₂ "insertion" into the metal-metal bond, 1 $\longrightarrow$ 2a/2b (step A)

Rate (lability) as a function of M (X on Zr = Cl, OCM₃):

Cp(CO)₂Fe-CO₂-Zr(Cl)Cp₂ >> Cp(CO)₂Ru-CO₂-Zr(X)Cp₂

III. Reduced ligated CO₂ to yield heterobimetallic formaldehyde compounds 4 (step B)

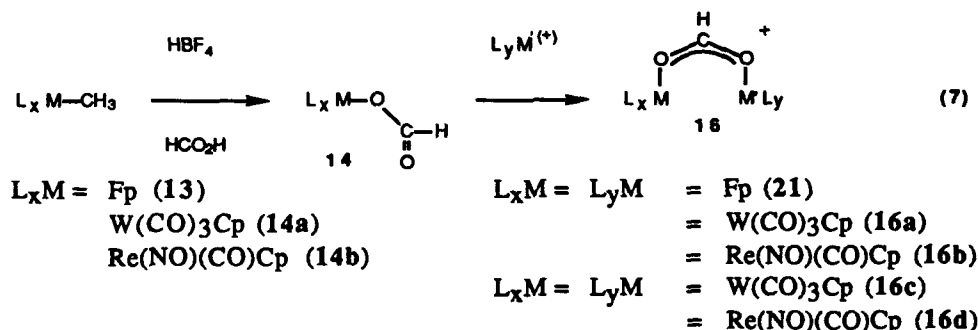
Characterized Cp(CO)₂M-CH₂O-Zr(Cl)Cp₂ (4) M = Fe, Zr

Transition Organometallic Heterobimetallic μ -Carbon Dioxide and μ -Formate Complexes in Homogeneous Carbon Dioxide Fixation

Progress Report (final) 6/1/87 - 9/30/90

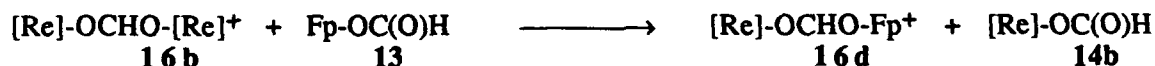
A. Bridging Formate Chemistry

We finished our studies on the synthesis and characterization of homo- and heterobimetallic bridging formates and on their reductive chemistry. New tungsten-

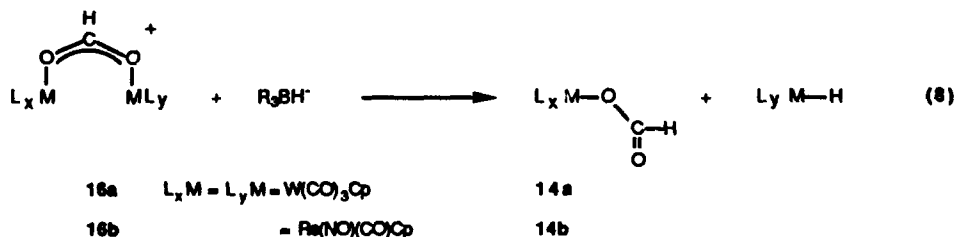


and rhenium-containing η^1 -O formates **14a** and **14b** and their bimetallic μ -formate salts **16a-16d** were synthesized and were fully characterized. The reactions of nucleophiles, especially hydride donors, with **16a-16d** received considerable emphasis.

Rhenium- and tungsten-containing μ -formate compounds differ greatly in their solution chemistry. Bis-Re **16b**, in particular, proves to be unusually labile: a rhenium center on the bimetallic formates **16b** and **16d** is considerably more labile than the corresponding tungsten center on **16a** and **16c**.



Both μ -formates **16a** and **16b** react identically with one equivalent of LiHBEt_3 or KHB(Oi-Pr)_3 and immediately release a formate complex (**14a** or **14b**, respectively) (eq. 8). Hydride transfer to **16a** with LiDBEt_3 eliminated only $\text{Cp(CO)}_3\text{W-OC(O)H}$ (**14a**)

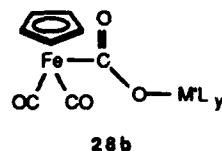
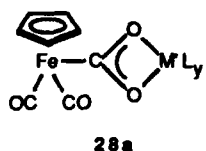


B. Bimetallic CO₂ Complexes

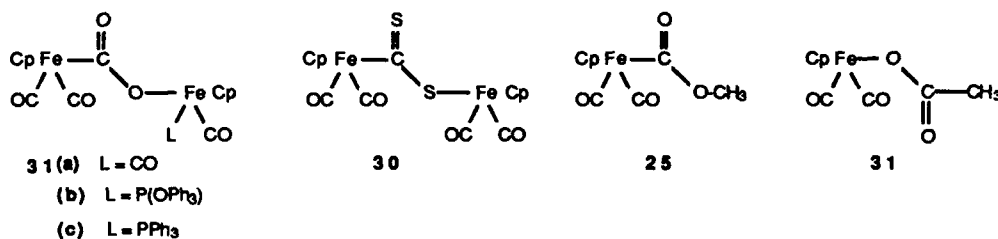
1. Late-Late Bimetal Combinations

We attempted to synthesize examples of bimetalloxy-carboxylates **28a** and **28b** by treating Fp-CO_2^- (**24**) with organometallic Lewis Acid $\text{LyM}^+ / \text{LyM-X}$. Lewis acids such as

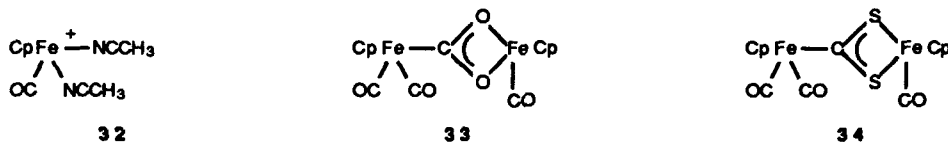
$\text{Fp}(\text{THF})^+\text{PF}_6^-$, $\text{Cp}(\text{L})(\text{CO})\text{FeI}$ ($\text{L} = \text{CO}$, PPh_3 , $\text{P}(\text{OPh})_3$), FpX ($\text{X} = \text{Cl}$, I , OSO_2CF_3 , HgCl), and etc.



Although these attempts proved unsuccessful, we did highlight the dramatic differences between FpCO_2^- (24) and FpCS_2^- (29) in their reactions with organoiron electrophiles. No examples of bis-iron $\mu(\eta^1\text{-C} : \eta^1\text{-O}) \text{CO}_2$ complexes 31 were observed, in contrast to the

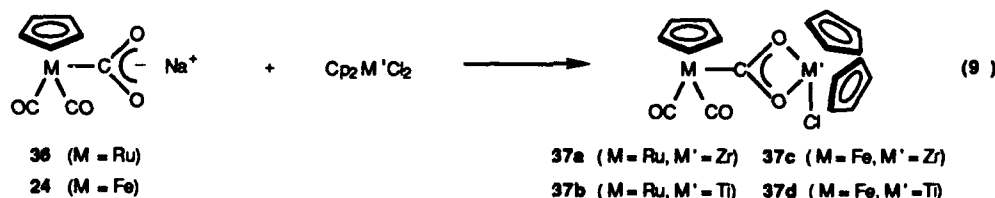


thermally stable $(\eta^1\text{-C} : \eta^1\text{-S}) \text{CS}_2$ adduct Fp-C(S)S-Fp (30). Treatment of 29 with $\text{Cp}(\text{CO})\text{Fe}(\text{NCCH}_3)_2^+ \text{PF}_6^-$ (32) affords the stable, fully characterized $(\eta^1\text{-C} : \eta^2\text{-S,S'}) \text{CS}_2$ complex 34, whereas the analogous reaction using $\text{FpCO}_2^-\text{Na}^+$ (24) decomposes.



2. Early-Late Bimetallic $\mu\text{-CO}_2$ Compounds

Our study on using the new metallocarboxylate $\text{Cp}(\text{CO})_2\text{Ru-CO}_2^-\text{Na}^+$ ($\text{RpCO}_2^-\text{Na}^+$) (36) and its known iron congener $\text{FpCO}_2^-\text{Na}^+$ (24) to generate the family of RuZr , RuTi , FeZr , and FeTi bimetallic CO_2 adducts 37a-37d (eq. 9) is complete. This work emphasizes the relative ease of synthesis and stability of 37a-37d, as well as deduction of their structures from ^1H and ^{13}C NMR and IR spectral data. We also find that cleavage of a carbon-oxygen

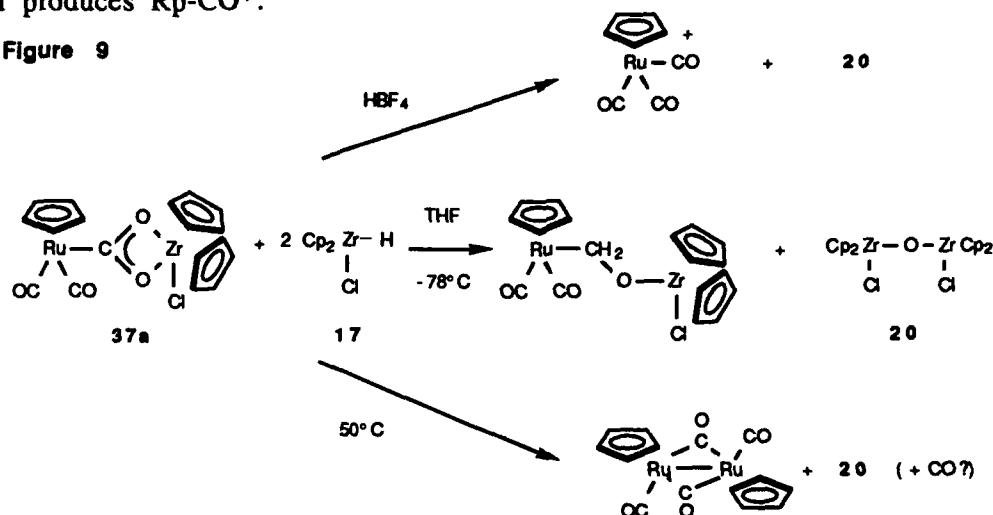


bond on the bridging CO_2 is a prevailing trend in (1) the thermal decomposition of these bimetallocarboxylates, (2) the protonation of the more stable zirconium adducts 37a and 37c, and (3) the $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ reduction of 37a. This RuZr CO_2 adduct 37a is the first heterobimetallic CO_2 complex that has been prepared using CO_2 .

Conversion of RpCO_2^- (36) to its bimetallocarboxylate $\text{Rp-CO}_2\text{-Zr}(\text{Cl})\text{Cp}_2$ (37a) accomplishes two objectives. First, the relatively high thermal stability of 37a vs 36 confirms the obvious advantage of using two appropriate metals for more effective binding of CO_2 . Second, the bimetallocarboxylate structure activates the ligated CO_2 to C-O

cleavage. Warming 37a deoxygenates the CO₂ (Figure 9); we found no evidence for 37a deinserting CO₂ and producing stable Rp-Zr(Cl)Cp₂ (38a). Protonation of 37a also releases μ -oxo 20 and produces Rp-CO⁺.

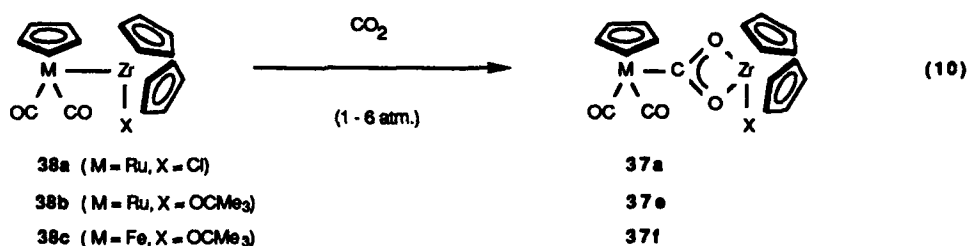
Figure 9



Finally, deoxygenation of 37a occurs upon treating with $\text{Cp}_2\text{Zr(H)Cl}$ (17). This reduction cleanly affords the $\mu(\eta^1\text{-C} : \eta^1\text{-O})$ formaldehyde complex $\text{Rp-CH}_2\text{O-Zr(Cl)Cp}_2$.

We were particularly interested in understanding how varying the metal centers M and M' in bimetallic CO₂ complexes $\text{Cp(CO)}_2\text{M-CO}_2\text{-M'(X)Cp}_2$ (37) (eq. 9) and related systems affects their stability as well as their subsequent reactivity. Both zirconocene and titanocene dichlorides $\text{Cp}_2\text{M'Cl}_2$ readily transform the iron and ruthenium CO₂ complexes $\text{Cp(CO)}_2\text{MCO}_2^-$ (24, M = Fe; 36, M = Ru) in THF above -40°C to bimetallic $\mu(\eta^1\text{-C} : \eta^2\text{-O,O'})$ CO₂ adducts 37a-d (eq. 9). Stability of these bimetallocarboxylates, indicated by their relative ease of synthesis and purification, decreases in the order: $\text{RuZr (37a)} \gg \text{FeZr (37c)} > \text{RuTi (37b)} > \text{FeTi (37d)}$.

3. Insertion of CO₂ into Metal-Metal Bonds



Results of preliminary studies established the differing reactivity of Fe-Zr and Ru-Zr bimetallic complexes $\text{Cp(CO)}_2\text{M-Zr(X)Cp}_2$ (38a-38c) towards CO₂ insertion (eq. 10). The FeZr bimetallic 38c quantitatively reacts within 20 minutes with CO₂ (1 atm.) in THF to generate the μ -CO₂ adduct 37f. Unfortunately, 37f decomposes nearly as fast as it forms, although quenching these reactions with HBF₄ affords FpCO^+ in 25-30% yields (cf. Figure 9). Spectroscopic data for 37f, whether it originates from CO₂ insertion into 38c or from metathesis of FpCO_2^- (24) and $\text{Cp}_2(\text{Me}_3\text{CO})\text{ZrCl}$, resembles that of 37a and 37c.

Both Ru-Zr bimetallics **38a** and **38b** also insert CO₂, but at much slower rates. With Rp-(t-butoxy)zirconocene **38b**, for example, CO₂ (6 atm.) converts 85% of it in THF over 3 days to a 3:1 mixture of Rp-CO₂-Zr(OCMe₃)Cp₂ (**37e**) and RpH, and one-half of it in toluene over 12 days to a 1:4 mixture. This RpH evidently originates from trace amounts of water in the CO₂. The formation of stable, fully characterized RuZr bimetalloxy-carboxylates **37a** and **37f** in these CO₂ insertion reactions more than compensates for the relatively low reactivity of the starting Ru-Zr bimetallics. This reaction chemistry is unprecedented.