OFFICE OF NAVAL RESEARCH

FINAL REPORT

FOR

Contract N00014-87-K-0465

R&T Code 413j006

"Transition Organometallic Heterobimetallic
\( \mu \)-Carbon Dioxide and \( \mu \)-Format Complexes in
Homogeneous Carbon Dioxide Fixation"

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Transition Organometallic Heterobimetallic \( \mu \)-Carbon Dioxide and \( \mu \)-Formate Complexes in Homogeneous Carbon Dioxide Fixation

New W- and Re-containing bimetallic \( \mu \)-formate salts \([L_xM]-OCHO-[ML_y]^+\) (\( L_xM = W(CO)_3Cp \), 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 \( L_yM'^+ \) 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 >> FeZr > RuTi > FeTi), (2) protonation of the more stable Zr adducts and (3) Cp\(_2\)Zr(H)Cl reduction of the fully characterized RuZr CO\(_2\) adduct to the \( \mu-(\eta^1\)-C : \( \eta^1\)-O) formaldehyde complex Rp-CH\(_2\)O-Zr(Cl)Cp\(_2\). CO\(_2\) converts the Fe-Zr and Ru-Zr bimetallics Cp(CO)\(_2\)M-Zr(X)Cp\(_2\) (\( X = Cl, O\text{Bu} \)) to their bimetallocarboxylates.
Part I


"Characterization of the Heterobimetallic μ(η¹-C:η²-O,O') Carbon Dioxide Complexes Cp(CO)₂M-C(O)O-M'(Cl)Cp₂ (M = Fe, Ru; M' = Ti, Zr)", J. C. Vites, M. E. Giuseppetti-Dery, and A. R. Cutler, Organometallics 1991, 10, 2827.


e. ONR Technical Report No. 4: "Characterization of a Family of Heterobimetallic μ(η¹-C:η²-O,O') Carbon Dioxide Complexes Cp(CO)₂M-C(O)O-M'(Cl)Cp₂ (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 CO₂ Reduction."

Second International Conference on Heteroatom Chemistry (SUNY-Albany) 1989 North East Regional ACS meeting, June 20, 1989; "Heterobimetallic Carbon Dioxide Complexes and CO₂ Reduction."

Miami National ACS meeting, September, 1989, "Heterobimetallic Carbon Dioxide Complexes and CO₂ Reduction."
k. two

l. three

* Partial Support, NSF Grant CHE-8305484
* Partial Support, DOE Grant DE-FG02-86ER13167
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Transition Organometallic Heterobimetallic $\mu$-Carbon Dioxide Complexes in Homogeneous Carbon Dioxide Fixation

Project Description

We are establishing the coordinated ligand reactions depicted for reducing CO$_2$ 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 CO$_2$ and uses a third metal system as the reductant (e.g., catalytic hydrosilation). These bimetallic CO$_2$ adducts feature synergistic CO$_2$ binding in which an electron-rich metal system L$_x$M contributes ($\eta^1\cdot C$) metallocarboxylate binding and an oxophilic L$_y$M$'$ system sequesters one or both metallocarboxylate oxygens (2a and 2b, respectively). In addition to stabilizing the CO$_2$ adduct, the resulting electronic "push-pull" also activates the CO$_2$ ligand as a hydride acceptor.

Goals

I. Synthesis and characterization of heterobimetallic CO$_2$ complexes

$$L_xM$-CO$_2^-$ + Cl-M$'$_Ly $\rightarrow$ L$_x$M-CO$_2$-$M'$Ly $\quad 2a/2b$

II. CO$_2$ "insertion" into the metal-metal bond of 1 (step A)

$$L_xM$-M$'$_Ly + CO$_2$ $\rightarrow$ L$_x$M-CO$_2$-$M'$Ly $\quad 2a/2b$

III. Reduction of ligated CO$_2$ to heterobimetallic formaldehyde compounds 4 (step B)

$$L_xM$-CO$_2$-$M'$Ly + reductant $\rightarrow$ L$_x$M-CH$_2$O-$M'$Ly $\quad 2a/2b$

IV. Reaction chemistry of the formaldehyde compounds L$_x$M-CH$_2$O-$M'$Ly (4)

(a) Further reduction : L$_x$M-CH$_2$O-$M'$Ly $\rightarrow$ L$_x$M-CH$_3$,
(b) Formaldehyde extrusion (step C) [formaldehyde + base $\rightarrow$ Formose liquid]

V. Electrochemical studies

(a) Electron-transfer catalysis: enhance lability of L$_x$M-$M'$Ly (1) (step A) and of L$_x$M-CH$_2$O-$M'$Ly (4) (step B)
(b) Electrochemistry of CO$_2$ adducts L$_x$M-CO$_2$-$M'$Ly (2) as model for electrocatalytic CO$_2$ 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 → 2a/2b (step A)

Rate (lability) as a function of M (X on Zr = Cl, OCMe₃):

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 \( \mu \)-Carbon Dioxide and \( \mu \)-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-

\[
\begin{align*}
\text{HBF}_4 & \quad \rightarrow \quad L_x M & - CH_3 & \quad \rightarrow \quad L_y M^{+} \quad \text{(7)}
\end{align*}
\]

and rhenium-containing \( \eta^1 \)-O formates 14a and 14b and their bimetallic \( \mu \)-formate salts 16a-16d were synthesized and were fully characterized. The reactions of nucleophiles, especially hydride honors, with 16a-16d received considerable emphasis.

Rhenium- and tungsten-containing \( \eta \)-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 that the corresponding tungsten center on 16a and 16c.

\[
[\text{Re}]-\text{OCHO-}[\text{Re}]^+ + \text{Fp-OC(O)H} \quad \rightarrow \quad [\text{Re}]-\text{OCHO-Fp}^+ + [\text{Re}]-\text{OC(O)H} \quad (8)
\]

Both \( \mu \)-formates 16a and 16b react identically with one equivalent of LiHBEt3 or KHB(Oi-Pr)3 and immediately release a formate complex (14a or 14b, respectively) (eq. 8).

B. Bimetallic \( \text{CO}_2 \) Complexes

1. Late-Late Bimetal Combinations

We attempted to synthesize examples of bimetallocarboxylates 28a and 28b by treating Fp-CO\(_2\)\(^-\) (24) with organometallic Lewis Acid \( \text{LyM}^+/ \text{LyM-X} \). Lewis acids such as
Fp(THF)+PF6-, Cp(L)(CO)FeI (L = CO, PPh3, P(OPh)3), FpX (X = Cl, I, OSO2CF3, HgCl), and etc.

Although these attempts proved unsuccessful, we did highlight the dramatic differences between FpCO2- (24) and FpCS2- (29) in their reactions with organoiron electrophiles. No examples of bis-iron μ(η1-C : η1-O) CO2 complexes 31 were observed, in contrast to the thermally stable (η1-C : η1-S) CS2 adduct Fp-C(S)S-Fp (30). Treatment of 29 with Cp(CO)Fe(NCCH3)2 PF6- (32) affords the stable, fully characterized (η1-C : η2-S,S') CS2 complex 34, whereas the analogous reaction using FpCO2-Na+ (24) decomposes.

2. Early-Late Bimetallic μ-CO2 Compounds

Our study on using the new metallocarboxylate Cp(CO)2Ru-CO2-Na+ (RpCO2-Na+) (36) and its known iron congener FpCO2-Na+ (24) to generate the family of RuZr, RuTi, FeZr, and FeTi bimetallic CO2 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 13C NMR and IR spectral data. We also find that cleavage of a carbon-oxygen bond on the bridging CO2 is a prevailing trend in (1) the thermal decomposition of these bimetalcarboxylates, (2) the protonation of the more stable zirconium adducts 37a and 37c, and (3) the Cp2Zr(H)Cl reduction of 37a. This RuZr CO2 adduct 37a is the first heterobimetallic CO2 complex that has been prepared using CO2.

Conversion of RpCO2- (36) to its bimetalcarboxylate Rp-CO2-Zr(Cl)Cp2 (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 CO2. Second, the bimetalcarboxylate structure activates the ligated CO2 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 Cp2Zr(H)Cl (17). This reduction cleanly affords the μ(η1-C:η1-O) formaldehyde complex Rp-CH2O-Zr(Cl)Cp2.

We were particularly interested in understanding how varying the metal centers M and M' in bimetallic CO2 complexes Cp(CO)2M-CO-Zr(X)Cp2 (37) (eq. 9) and related systems affects their stability as well as their subsequent reactivity. Both zirconocene and titanocene dichlorides Cp2M'C12 readily transform the iron and ruthenium CO2 complexes Cp(CO)2MCO (24, M = Fe; 36, M = Ru) in THF above -40°C to bimetallic μ(η1-C:η2-O,O') CO2 adducts 37a-d (eq. 9). Stability of these bimatellcarboxylates, indicated by their relative ease of synthesis and purification, decreases in the order: RuZr (37a) >> FeZr (37c) > RuTi (37b) > 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 Cp(CO)2M-Zr(X)Cp2 (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 FpCO2- (24) and Cp2(Me3CO)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(OCH₃)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 bimetalliccarboxylates 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.