METALLOCARBOXYLATE CHEMISTRY

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1. Progress report, 1989-90

Work in the past year has concentrated on completing manuscripts describing the synthesis, isolation and characterization of seven metallocarboxylate anions, $M\text{-COOM}'$ ($M = \text{CpFe}(\text{CO})(\text{PPh}_3)$ or $\text{Cp}^*\text{Fe}(\text{CO})(\text{PPh}_3)$; $M' = \text{alkali metal}$) and compounds derived from these anions (see publications list). Four of the anions are hydrated, the others are anhydrous analogs of three of them. The electron-rich metal centers bind CO_2 strongly in all cases; thermolysis occurs through initial hydrolysis to the corresponding metallocarboxylic acid and subsequent decomposition of the latter compound. One of the manuscripts also summarizes an extensive study of the reactions of these anions with electrophiles. With protonating or methylating agents (1:1 stoichiometry) a pattern of competitive C-O and O- M' cleavage has been revealed, according to the following equations:

The more electrophilic counterions promote C-O bond cleavage; the more electron-donating Cp^* ligand also promotes C-O bond cleavage when compared to Cp. Hydration appears to strengthen the O- M' bond slightly. These results are summarized in the attached Table. Consideration of these results allows an alternative interpretation of some results obtained from other metallocarboxylate anions. In particular, N. J. Cooper (JACS, 1987, 109, 2956 and references cited therein) reported that efforts to alkylate $\text{Li}_2\text{W}(\text{CO})_5(\text{CO}_2)$ led only to

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W(CO)_6 . In view of our results, Cooper's observations can be seen simply as involving preferential cleavage of the carboxylate C-O bond by the electrophile which is promoted by the highly oxophilic lithium ion. Also, the increased carbenoid character of the metal-carboxylate carbon bond (due to the dianion nature of this metallocarboxylate) would be expected to facilitate C-O bond breaking, as with our Cp^* system. With this interpretation in mind, the so-called "reductive disproportionation" which the tungsten carboxylate undergoes in reactions with carbon dioxide (leading to lithium carbonate and tungsten carbonyl) becomes predictable.

Also reported in the manuscript are studies of the behavior of the potassium salts of the metallocarboxylate anions toward $\text{Mn(CO)}_5(\text{PPh}_3)^+ \text{BF}_4^-$ which result in oxygen transfer. Reactions of these salts with a further electrophile, Ph_3SnCl , result in bimetallic CO_2 -bridged complexes. The details of the X-ray structure determination of one of the tin complexes is being published separately (see publication list).

In work which has been partly supported by DOE, we completed the synthesis and characterization of several other metal- C_1 complexes which do not involve carbon dioxide (see publications list).

2. Proposed research, 1990-91

The long study of the reactions of the anions with electrophiles made it clear that only the potassium salts of the anhydrous compounds would be useful as synthons for compounds with a CO_2 -containing bridge between two metal centers (compounds which would model catalytic intermediates in various carbon dioxide conversion/activation processes). We have begun what is expected to be a long study of the reactions of the metallocarboxylate anions with cationic complexes which have a weakly coordinated group (e.g., BF_4 , ethylene, etc.). The first reactions have given some very interesting products (not

all characterized at this time). The sequence for the best-characterized product is shown below:

The bimetallic compound (actually a mixture containing two diastereomers) has been characterized by elemental analysis, ^1H , ^{31}P and ^{13}C NMR spectroscopy and IR-DRIFTS. It is formulated as a carboxylate "ester" based on a comparisons of its DRIFTS spectra to that of our other metallocarboxylates (the bimetallic tin derivatives have both carboxylate oxygens bound to the tin atom and show no C=O absorption for the carboxyl group in the IR). There is only one previous example of a $\mu(\eta^1\text{-C}:\eta^1\text{-O})\text{-CO}_2$ complex involving late transition metal centers only; our di-iron compound is the first to involve first transition row elements only. Reactions of the same metallocarboxylate anion with a series of rhenium cations have provided additional new CO_2 -bridged compounds which are being fully characterized; both monodentate and chelating modes of binding to rhenium are represented with these.

Work in the next year will focus on the full characterization of these compounds and is expected to include studies of their reactions with electrophiles, studies of their thermolysis behavior and studies of their behavior toward reducing agents (particularly

hydride transfer agents).

3. Other

The "Summaries of FY 1990 Research in the Chemical Sciences" reported that I received \$94,601 in that period; actually, it was \$78,601 (plus an \$8,000 supplement). If there is extra money floating around up there somewhere, I could use it; the syntheses and studies of the chemistry of the bimetallic complexes are going to be exciting!

On a more personal note, I have been named to the Editorial Advisory Board of Organometallics for three years, beginning January 1, 1991. I wish to thank the Department of Energy for providing the funding which allowed our work to advance and to receive the recognition that prompted this appointment.

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Table. Reactions of Metallocarboxylates with Electrophiles^a

Carboxylate	Electrophiles					
	<u>HCl/H₂O/ acetone</u>	<u>HBF₄/H₂O/ acetone</u>	<u>HBF₄/ether</u>	<u>HBF₄/CH₃CN</u>	<u>CH₃I/CH₃CN</u>	<u>(CH₃)₃O⁺/ CH₃CN</u>
2a	acid (74)	acid (34) cation (19)	acid (37) cation (42)	- cation (90)	ester (92) -	ester (81) cation (7)
2b	acid (81)	acid (22) cation (41)	- cation (71)	- cation (83)	ester (11) cation (69)	ester (50) ^b cation (23) ^b
2c	acid (71)	acid (31) cation (37)	acid (36) cation (53)	- cation (87)	ester (15) cation (71)	ester (43) cation (49)
5	- cation (86)	acid (72) cation (21)	-	- cation (92) ^b	ester (77)	ester (38) ^b cation (43) ^b
3a	-	-	acid (40) cation (41)	acid (57) cation (17)	ester (92) -	ester (80) -
3b	-	-	- cation (94)	- cation (65)	- cation (69)	ester (61) ^b cation (26) ^b
6	-	-	-	- cation (91) ^b	ester (77)	ester (33) ^b cation (45) ^b

^aProduct yields are shown in parentheses. ^bReaction conducted in CD₃CN.

2a-c

a: M = K

b: M = Li

c: M = Na

3a,b

a: M = K

b: M = Li

5

6

Publications Acknowledging DOE Support

a) Published during the past year

Synthesis and Characterization of Manganese and Rhenium Metallacycles, Dorothy H. Gibson, Kathryn Owens, Santosh K. Mandal, William E. Sattich and John F. Richardson, Organometallics, 1990, 9, 424.

Synthesis and Characterization of Secondary Carbene Complexes of Manganese and Rhenium, Dorothy H. Gibson, Santosh K. Mandal, Kathryn Owens and John F. Richardson, Organometallics, 1990, 9, 1936.

b) Accepted for Publication

1-carbonyl-1- η^5 -cyclopentadienyl-2,2,2-triphenyl-1-triphenylphosphine- μ -carboxylate-1kC:2kO:2kO'-irontin, Dorothy H. Gibson, John F. Richardson and Tek-Sing Ong, Acta Cryst. C, in press.

Synthesis of Alkoxymethyl Complexes from Metal Formyls, Dorothy H. Gibson, Kathryn Owens, Santosh K. Mandal, William E. Sattich and Jaime O. Franco, Organometallics, in press.

Synthesis and Characterization of Aminomethyl Complexes of Rhenium, Dorothy H. Gibson and Kathryn Owens, Organometallics, in press.

c) Submitted for Publication

Synthesis and Characterization of Iron Metallocarboxylates, Dorothy H. Gibson, Tek-Sing Ong and Ming Ye, submitted to Organometallics.

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