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FINAL REPORT: Organometallic Chemistry of Carbon Dioxide

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DOE Patent Clearance Granted
Mark P. Dvorscak
Mark P. Dvorscak
(630) 252-2383
E-mail: mark.dvorscak@ch.doe.gov
Office of Intellectual Property Law
DOE Chicago Operations Office

6-14-04
Date

**Dorothy H. Gibson
Department of Chemistry
University of Louisville
Louisville, KY 40292**

September 26, 2002

I. RESEARCH SUMMARY

Introduction

Since the beginning, research focused on C_1 transition metal complexes that are relevant to CO_2 activation and fixation. At first, June 1986-April 1989, research centered on two highly labile types of organometallic compounds: metallocarboxylic acids, $M-COOH$ (proposed as intermediates in the Water Gas Shift reaction as well as CO_2 fixation reactions) and their corresponding anions, MCO_2^- , which represent sequestered CO_2 . The proposal titles have changed over the years to reflect the evolution of the research program from one involving the synthesis and characterization of compounds that are models for catalytic intermediates (especially CO_2 -bridged bimetallic compounds) to one involving the studies of the chemical reactions of putative catalytic intermediates (rhenium and ruthenium polypyridyl complexes) which are thought to be formed in CO_2 reduction processes and, finally, to the design of compounds and the testing of reaction sequences which could reasonably account for C_2 organic products generated in electrocatalytic reductions of CO_2 promoted by a ruthenium polypyridyl complex. In each case, fundamental information has been sought which could lead to structure/reactivity correlations and, ultimately, to the insights needed to design catalysts capable of converting CO_2 to useful products. The grant titles changed as follows:

1986-89: Synthesis and Properties of Metallocarboxylic Acids

1989-98: Metallocarboxylate Chemistry

1998-2002: Catalytic Intermediates in the Conversion of CO_2 to C_2 Oxygenates

During about the first eight years of the DOE support, funding from the National Science Foundation EPSCoR program supported other research about additional C_1 transition metal complexes. This support allowed us to become expert in metal formyl ($M-CHO$) chemistry and in the chemistry of hydroxymethyl ($M-CH_2OH$) complexes; both areas are relevant to CO_2 fixation since these types of complexes are suggested as catalytic intermediates in CO_2 reduction processes. Where both agencies contributed to the published work, acknowledgement was made to both; this is duly noted in the sections below which profile the research.

For the final report, it is more convenient to divide the research summary into the three sections identified below, together with the time frame appropriate to each subject. The relevant publications resulting from the research in these areas are identified by numbers corresponding to the publications in section II.

A. Synthesis and Characterization of Metallocarboxylic Acids and Metallocarboxylate Anions (1986-1990)

Prototypes for intermediate metallocarboxylates were little known in 1986. We began with iron compounds and later developed a rhenium system also. A good synthesis of the highly labile acid, $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{COOH}$ was achieved followed by good syntheses of related metallocarboxylate anions as their alkali metal salts. The anions are also quite labile, especially in solution. One anion derived from the Cp^* analog was also prepared. The following systems were prepared and characterized:

The initial syntheses generated hydrated metallocarboxylate salts, but anhydrous materials were prepared also. Additionally, methyl ester and triphenyltin derivatives of these metallocarboxylates were prepared and characterized also.

Electrophilic cleavage reactions of the metallocarboxylate anions by HBF_4 , MeI and $\text{Me}_3\text{O}^+\text{BF}_4^-$ were studied to determine the effects of metal ion and ligand environment, as well as the electrophile, on bond-breaking processes. Two competing reaction paths were identified as illustrated below:

Greater cleavage at the C-O bond was seen with the more oxophilic Li^+ than with K^+ ; also, the Cp^* ligand enhanced C-O bond cleavage relative to Cp . Among the electrophiles, H^+ gave the most C-O bond cleavage.

The triphenyltin derivatives of both metallocarboxylates were prepared from the K^+ salts and $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{CO}_2\text{SnPh}_3$ was structurally characterized. Slightly unequal O-Sn bond distances were observed. The structure helped to confirm our formulation of the metallocarboxylates.

Efforts were then made to extend the metallocarboxylate syntheses to a series of phosphite complexes, but the phosphite ligand, being more electron withdrawing, directed the reaction along a

different pathway. However, a metallocarboxylate anion is believed to be a reaction intermediate in each case. The path for one iron complex is shown below:

Reactions of $\text{CpMo}(\text{CO})_3[\text{P(OEt)}_3]^+$ and *trans*- $\text{Mn}(\text{CO})_4[\text{P(OPh)}_3]_2^+$ with OH^- afforded hydrides; these compounds are most likely formed via intermediate metallocarboxylate anions also.

The oxide transfer capabilities of the metallocarboxylate anions was examined briefly. We chose $\text{Mn}(\text{CO})_5(\text{PPh}_3)^+$ as the electrophile and potential oxide acceptor. Reaction between each anion and the manganese cation, followed by reaction with MeI , afforded the iron cation and $\text{MeMn}(\text{CO})_4(\text{PPh}_3)$. The path for oxide transfer is illustrated for one case:

Loss of CO_2 from the manganese carboxylate followed by alkylation of the resulting anion would yield the methyl manganese product.

Publications: Primarily DOE: 1, 3, 4, 5, 9, 10, 15, 18; NSF/DOE: 2, 6, 7, 8, 11, 12, 13, 14, 16, 17, 19.

B. Synthesis and Characterization of CO₂-bridged and Carboxyethylene-bridged Bimetallic Compounds (1990-1996)

The successful synthesis of the tin complex noted in Section A allowed us to think about the design of synthetic routes to other CO₂-bridged bimetallic compounds (MCO₂M') having the carboxyl carbon bound to one metal and one, or both, carboxylate oxygens bound to a second metal. At the time, few of these compounds were known and none had been structurally characterized to establish bonding modes or to allow structure/reactivity or structure/spectral correlations to be made. In addition to providing fundamental information about CO₂ binding between metal centers, it was thought that these types of complexes would be especially useful as models for carbon dioxide bound at metal surfaces.

Reactions of iron metallocarboxylate anions described in Section A had demonstrated the nucleophilicity of these ions toward metal centers with weakly bound ligands. This strategy was developed, allowing us entry into general synthetic methods for μ_2 - η^2 CO₂-bridged compounds (those having only one carboxyl oxygen bound to M') and from there to μ_2 - η^3 CO₂-bridged compounds. The metallocarboxylate anions used were CpFe(CO)(PPh₃)CO₂⁻, Cp*Fe(CO)(PPh₃)CO₂⁻, and Cp*Re(CO)(NO)CO₂⁻; the M' was varied among late and early transition metals and one main group metal (Sn).

The first compounds were generated as shown below from rhenium complexes bearing weakly coordinated BF₄⁻:

Thermolysis of the products, in the solid state, led to a general synthetic route to μ_2 - η^3 complexes:

At this time, and with the subsequent complexes derived from the rhenium metallocarboxylate, we

began to realize that there were actually two classes of the $\mu_2\text{-}\eta^3$ complexes which differed by having equivalent (type A) or inequivalent (type B) O-M' bond lengths:

Type A complexes were those derived from transition metal complexes and type B complexes were derived from tin complexes.

Other strategies were developed to prepare complexes with Zr as M'. In one, the sensitivity of alkyl or alkoxy groups bound to Zr toward protonic acids was exploited; in another, transmetalation of Zr for Sn was used:

Thermolysis of carboxyethylene-bridged compounds (a group to be discussed below) was also effective in providing a new route to some $\mu_2\text{-}\eta^3$ complexes:

After characterizing a large number of the type A (symmetrical) $\mu_2\text{-}\eta^3$ complexes by IR spectroscopy (DRIFTS) and by X-ray crystallography, we found that the ν_{asym} carboxyl band in the IR was dependent upon the coordination geometry at M'. The table below presents part of our data supporting these observations:

Dependence of Carboxylate ν_{asym} on Coordination Geometry				
entry no.	symmetrical $\mu_2\text{-}\eta^3$ complex $\text{M}=\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{M}'$	IR (cm^{-1})		geometry at M'
		ν_{asym}	ν_{sym}	
1	$\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{CO}_2)\text{Re}(\text{CO})_5[\text{P}(\text{OEt})_3]$	1435	1252	octahedral
2	$\text{Cp}^*\text{Re}(\text{CO})(\text{NO})(\text{CO}_2)\text{Re}(\text{CO})_5(\text{PPh}_3)$	1437	1282	octahedral
3	$\text{Cp}^*\text{Re}(\text{CO})(\text{NO})(\text{CO}_2)\text{Re}(\text{CO})_5(\text{PPh}_3)_2$	1435	1278	octahedral
4	$\text{Cp}^*\text{Re}(\text{CO})(\text{NO})(\text{CO}_2)\text{Zr}(\text{Cl})\text{Cp}_2$	1348	1288	edge-capped tetrahedral
5	$\text{Cp}^*\text{Re}(\text{CO})(\text{NO})(\text{CO}_2)\text{Zr}(\text{CH}_3)\text{Cp}_2$	1340	1288	not determined
6	$\text{Cp}^*\text{Ru}(\text{CO})_2(\text{CO}_2)\text{Zr}(\text{Cl})\text{Cp}_2$	1339	1287	edge-capped tetrahedral
7	$\text{Cp}^*\text{Ru}(\text{CO})_2(\text{CO}_2)\text{Zr}(\text{CH}_3)\text{Cp}_2$	1341	1285	not determined
8	$\text{Cp}^*\text{Re}(\text{CO})(\text{NO})(\text{CO}_2)\text{Mo}(\text{CO})_2\text{Cp}'$	1319	1285	square-based pyramidal
9	$\text{Cp}^*\text{Re}(\text{CO})(\text{NO})(\text{CO}_2)\text{W}(\text{CO})_2\text{Cp}'$	1321	1287	not determined

One particularly interesting $\mu_2\text{-}\eta^2$ complex, $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{CO}_2\text{Re}(\text{CO})_5[\text{P}(\text{OEt})_3]$, was prepared and its thermolysis reactions studied. As illustrated Scheme 1 below, conversion of this initial complex, A, to compound B took place in solution at 60 °C.; compound B was structurally characterized. However, solid-state thermolysis of A gave a totally different product. Several other solution and solid-state thermolyses were conducted before a complete profile could be obtained. The transformations which took place resulted in exchange of the two phosphorus ligands between the two metal centers (conversion of A to E). The intermediate species were spectroscopically observable; the suggested pathway is shown in Scheme 1. Remarkably, the CO_2 bridging ligand remained intact through these rearrangements, demonstrating the strength of the binding of the carboxyl carbon to these electron-rich iron centers.

Thermolysis reactions of a series of new $\text{M-CO}_2\text{-SnR}_3$ complexes (ten) were also examined to determine the effects of bonding type and the presence of electron-withdrawing or electron-donating ligands on M and Sn. In general, compounds which are primarily in the $\mu_2\text{-}\eta^2$ bonding state decarboxylate most readily; ligands on both metal centers influence whether the $\mu_2\text{-}\eta^2$ form or the $\mu_2\text{-}\eta^3$ form is predominant. With a good donor ligand on the carboxyl side and an electron-withdrawing group on Sn, the $\mu_2\text{-}\eta^3$ form is favored, but if the group on Sn is electron-donating, then the $\mu_2\text{-}\eta^2$ form is predominant. The effects of ligands was further seen on a $\text{Re-CO}_2\text{-Sn}$ complex having a Cl and two methyl groups bound to Sn. The effect of the chloride ligand is powerful; unlike other Sn complexes studied, this one adopts nearly symmetrical $\mu_2\text{-}\eta^3$ bonding of the CO_2 and edge-capped tetrahedral geometry about the tin atom.

Scheme 1

Again probing the reactivity of the metallocarboxylate anions toward electrophiles, we showed that the anions would add to coordinated ethylene to yield new compounds with carboxyethylene bridging ligands, $-\text{COOCH}_2\text{CH}_2-$, between metal centers and new oxygen-carbon bonds. These results contrast with work done by others showing that CO_2 will insert into electron-rich metal-olefin bonds to generate new carbon-carbon bonds. The generality of our reactions is limited by the ease of displacement of ethylene vs addition to it. Displacement is favored in instances where electron-withdrawing (or π -acceptor) ligands are bound to the metal center bearing the ethylene ligand. Additionally, the third-row metal tungsten binds ethylene better than molybdenum.

Publications: DOE: 20, 21, 23-31, 34; DOE/NSF: 22

C. Synthesis and Characterization of Reactive Intermediates Related to Catalysis of CO₂ Reduction by Ruthenium and Rhenium Polypyridyl Complexes (1995-2002)

As the result of a number of factors: attendance at national and international conferences related to CO₂ activation/fixation, broader reading of the literature in these areas and discussions with other researchers, it became clear that a void existed in the homogeneous catalysis areas of electrocatalysis and photocatalysis. Most of the earlier research efforts had focused on establishing the activity of compounds for their catalytic behavior and very little information was available about the nature of possible catalytic intermediates. In early 1995, we started to address this problem which had been given new emphasis because of a report by the Tanaka group in Japan (*Inorg. Chem.*, 1994) that electrocatalytic reduction of CO₂ by Ru(bpy)(tpy)(CO)⁺² 2PF₆⁻ afforded a variety of organic products: HCOOH, CH₂O, CH₃OH, and glycolic and glyoxylic acids. Although a possible "catalytic cycle" was proposed, there was little support for it. Both ruthenium and rhenium polypyridyl complexes had been used as electro- or photocatalysts for reductions of CO₂ to CO, H₂ and/or formate for several years by this time, but the Tanaka system was clearly more versatile and a system that might involve organometallic compounds with C₁ ligands other than the metallocarboxylates thought to precede CO. Also, organometallic rhenium polypyridyl chemistry relevant to CO₂ fixation had not been investigated.

1. Ruthenium polypyridyl chemistry

Our first efforts, in early 1995, were to synthesize a formyl complex, Ru(bpy)₂(CO)₂⁺ PF₆⁻, from Ru(bpy)₂(CO)₂⁺² 2PF₆⁻, a well-known electrocatalyst for CO₂ reduction. We were interested in determining the stability/reactivity of this formyl complex in relation to the many others we had characterized (NSF-supported) by that time. The desired formyl complex was synthesized in good yield using methanol as solvent. A few months later, the Tanaka group reported the same compound in the literature, but they reported that the compound "*reacted with methanol with liberation of hydrogen*"! This was clearly contrary to our experience with the compound and we began to study its behavior in order to try to understand the report from the Tanaka group. Eventually, we determined that the reaction with methanol required either photoassistance or the presence of O₂; with neither available, the compound was stable in solution in methanol. This was an exciting result because it linked the activity of the C₁ ligand to photoactivation of the complex. We determined that the formyl complex would also react with water; this reaction required O₂ and gave a CO₂-bridged compound as the final product. Our proposed routes to these products were developed after a number of probe experiments were conducted with other possible intermediate species and are shown in Scheme 2.

Later, we studied the related phenanthroline formyl complex, Ru(phen)₂(CO)(CHO)⁺ PF₆⁻,

to determine any effects of the more rigid phenanthroline ligand on the reactions. This one also required photoassistance for the methanol reaction, but proceeded at about the same rate. However,

Scheme 2.

the reaction with water was much slower than that of the bipyridine analog; the proposed metallocarboxylic acid intermediate could actually be observed here. Competition experiments indicated that the slowness could be attributed to lowered acidity of the phenanthroline acid as compared to the corresponding bpy complex.

Now convinced that the organometallic chemistry of C_1 ligands bound to ruthenium polypyridyl moieties showed significant differences from systems without these ligands, we started to focus attention on the Tanaka catalyst system and began to try to understand why it differed from other ruthenium polypyridyl catalysts. From the beginning, we had many reservations about the

proposed catalytic cycle since there were several steps in it which had no precedents in organometallic chemistry. After reviewing the literature about the characteristics of other terpyridine complexes and the known ability of this ligand to change, reversibly, between η^2 and η^3 bonding modes, we began to formulate alternate paths to the C_1 and C_2 products that required a different set of intermediates than those suggested by the Tanaka group. We concluded that the actual precursors to the C_2 products, and possibly the C_1 products as well, were formyl and hydroxymethyl complexes derived from the isomeric cations, $\text{Ru}(\text{bpy})(\eta^2\text{-tpy})(\text{CO})_2^{+2} 2\text{PF}_6^-$ which could be generated in the electrocatalytic reactions by reverse Water Gas Shift chemistry from a metalloacid. One of these cations had been characterized previously, the second one was not known. We worked out efficient synthetic routes to both isomers and to the formyl and hydroxymethyl derivatives of both cations as well as their 4,4'-dimethyl-2,2'-bipyridyl analogs. We structurally characterized both bpy cations, one of the dmbpy cations and one hydroxymethyl complex; the formyl complexes (as is typical) are too labile in solution to provide crystals. We also structurally characterized one metallocarboxylic acid in this series. We determined that one of the formyl complexes in the bpy series undergoes rearrangement to the other isomer in solution (even at low temperatures) and does so through a third formyl complex. We concluded that this may be key to explaining the results from the Tanaka catalyst (which is effective only at low temperature) and began studying the reactions in detail.

Since we felt that the ability to change between bidentate and terdentate coordination was necessary to the catalytic chemistry, we also started developing synthetic routes to compounds having other hemilabile ligands. A proposal to continue work in all these areas was "not selected for funding because of the lack of progress!"

Publications: DOE: 33, 36, 37, 40, 43, 44, 45, 46, 47, 49, 50; NSF/DOE: 39

2. Rhenium polypyridyl chemistry

In reviewing the literature about CO_2 reductions catalyzed by rhenium polypyridyl complexes, it became clear that there was no information about expected organometallic intermediates in these reactions either, not even a synthesis of the key intermediate, $\text{Re}(\text{N-N})(\text{CO})_3\text{COOH}$ (N-N= polypyridyl ligand), which was thought to be responsible for CO and had been proposed in 1986! Also, the reaction path leading to formate in these reactions was not understood either.

About two years after beginning the ruthenium polypyridyl chemistry, we began efforts to prepare C_1 complexes (M-COOH , M-CHO and $\text{M-CH}_2\text{OH}$) of rhenium bearing polypyridyl

ligands. The first compound synthesized was *fac*-Re(bpy)(CO)₃CH₂OH. Although stable thermally, photolysis of the compound in methanol afforded *fac*-Re(bpy)(CO)₃(OCH₃) and formaldehyde (present as the hemiacetal). The results of probe reactions suggested a non-radical path for the reaction involving β -hydride elimination and loss of formaldehyde as show below and again demonstrating the photoactivity of the complexes with polypyridyl ligands:

We then synthesized the metalloacids, *fac*-Re(N-N)(CO)₃COOH (N-N=2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine) in order to answer fundamental questions about the nature of the long-proposed catalytic intermediate thought to be the precursor to CO in photocatalytic reductions of CO₂ involving *fac*-Re(N-N)(CO)₃Cl (N-N=bipyridyl ligand). The proposed cycle is shown below:

Additionally, sources of the minor catalytic product, formate, had not been identified although addition of a proton to intermediate anion c, followed by CO₂ insertion could yield this product. Initially, we showed that the thermolysis of the dmbpy acid (chosen because of solubility

characteristics) occurred readily at room temperature and led to the CO₂-bridged bimetallic compound, *fac, fac*-[Re(dmbpy)(CO)(CO₂)Re(dmbpy)(CO)₃]; formate was not a product. The conversion to the bimetallic compound could be photoassisted also. As expected, the metalloacid can be cleaved by strong acid and, under photolysis and in the presence of Cl⁻, the resulting cation liberates CO and yields the chloride complex (a in the above diagram) thus providing support for parts of the proposed cycle. In the presence of CO₂, the metalloacid is readily converted to the bicarbonato complex. Neither metalloacid is crystalline, but the methyl ester of the bpy acid is and was structurally characterized.

Since questions remained about the origin of formate in the photocatalytic reactions, we prepared the formyl complex, *fac*-Re(dmbpy)(CO)₃CHO in order to probe its behavior and determine its viability as an intermediate. Many formyl complexes are readily transformed to hydrides; thus the conversion of this formyl complex to hydride, followed by CO₂ insertion, could provide another pathway leading to formate. Also, it appeared that the reaction conditions involved in the photocatalytic reactions would be conducive to synthesis of the formyl complex. We prepared the formyl complex and determined that it quickly reacts with CO₂ to yield *fac*-Re(dmbpy)(CO)OCHO primarily; this is the formate produced in the catalytic reaction. The reaction occurs in two stages and can be followed by low temperature ¹H NMR. The first reaction results in direct hydride transfer to CO₂ (the first unambiguous demonstration that a formyl complex is capable of hydride transfer to CO₂) and yields Re(dmbpy)(CO)₄⁺ OCHO⁻. This ionic formate rapidly converts to the covalent compound with loss of CO.

After determining that the formyl complex could be a viable intermediate in the photocatalytic reactions, we chose to explore reactions of the metalloacid together with the formyl complex as well as reactions of the acid with other intermediates which might be present under catalytic conditions. These experiments were completed, with NSF support, after termination of the DOE grant.

Publications: DOE: 35, 38, 41, 42, 48; DOE/NSF: 51

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III. RESEARCH STUDENTS SUPERVISED, 1986-2002

(1) Undergraduates

Angela Darnell, Summer 1989
Bradley Sleadd, Spring, Summer 1992
Eric Osterrieder, Spring 1992
Rebecca Miller, Spring 1995
Angela Bastian, Spring 1996
Jose Andino, Spring 1996- Summer 1997

(2) Graduate students

(a) Master's

Michael Harris, August 1990
Hui Li, May 1994
Win Naing, May 1994
Renaud Bardon, August 1994
Rebecca Miller, 1995-96, no degree
Sabrina Cark, 1996-97, no degree

(b) Ph.D.

Yekhlef Elomrani, May 1987
Santosh Mandal, May 1988
Kathryn Owens, May 1988
William Sattich, December 1989
Jaime Franco, May 1990
Chris Onyeso, December 1990
Ming Ye, December 1992
Michael Harris, May 1995
Jayesh M. Mehta, May 1997
Bradley A. Sleadd, May 1997
Brian Nieman, 1998-1999, no degree
Jose Andino, 1998-

(3) Post-doctoral trainees

Xiaolong Yin, December 2001-April 2002
Haiyang He, June 1999-April 2002
Bhamidi Srinivas, August 1999-June 2001
Tanya Lubner, June 1999-May 2000
Xiaolong Yin, October 1997-September 1998
Bradley A. Sleadd, February 1997- August 1998
Jayesh M. Mehta, April 1997-August 1997
Yan Ding, May 1994 -March 1997 (partial)
Ming Ye, December 1992 - October 1994
Jaime O. Franco, May 1990 -October 1995 (partial)
Kathryn Owens, May 1988 - August 1990 (partial)
Tek-Sing Ong, August 1986 - November 1990