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METALLOCARBOXYLATE CHEMISTRY

Progress Report/Continuation Proposal

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METALLOCARBOXYLATE CHEMISTRY

1. Progress report, 1992-93

Our research is presently focused on bimetallic compounds of late transition metals with carbon dioxide or CO₂-containing bridging ligands. The compounds represent models for catalytic intermediates in CO₂ fixation/activation processes. With a moderate number of compounds now characterized, we are beginning to make structure-activity correlations.

In the last report, we outlined some initial observations on the thermolysis behavior of a newly characterized μ_2 - η^2 -CO₂-bridged complex, CpFe(CO)(PPh₃)(CO₂)Re(CO)₄[P(OEt₃)] (A). We now know that thermolysis of A at low temperatures, in solution, gives the carbene complex B (see attached scheme); B has been crystallographically characterized (see attached figure). B is stable to further thermolysis unless CO is available; with CO, B gives the same thermolysis products as those obtained from A in high temperature reactions (C-E). At room temperature, B in the presence of CO slowly reverts to A. The final product of thermolysis is E which has been isolated and characterized by elemental analysis and spectral data. Cleavage of E by HBF₄ gives CpFe(CO)₂[P(OEt₃)⁺ BF₄⁻], confirming that E (and its precursor D) result from phosphorus ligand exchange on the iron and rhenium centers. Throughout the rearrangements, the CO₂ bridging group remains intact! How the ligand exchange takes place will require further work (which is in progress).

Structure work on the indenyl iron complex, (η^5 -C₉H₇)Fe(CO)(PPh₃)(CO₂)SnPh₃, has been completed (and published; see

Proposed Thermolysis Pathway

attachment); it shows severe distortions of the CO₂ bonding parameters as compared to other similar compounds, resulting from the steric demands of the indenyl ligand. Unfortunately we have not been able to make other CO₂ bridged complexes from this system since we can generate it in aqueous solution only.

We have synthesized and characterized a new metallocarboxylic acid, Cp*Re(CO)(NO)COOH, and we have found that it can be used directly with other reagents to generate CO₂-bridged complexes as shown below:

Both bimetallic products have been characterized fully, including their X-ray crystal structures (see attachments). Most interesting is the fact that the rhenium-rhenium complex is of the $\mu_2\text{-}\eta^3$ type, formed without an observable $\mu_2\text{-}\eta^2$ precursor; enhanced nucleophilicity of the carboxylate intermediate is believed to be responsible.

After trying unsuccessfully to extend our work on iron-iron carboxyethylene bridged complexes (reported earlier: *Organometallics*, **11**, 1993, **1992**) to systems containing alkyne or diene groups, we have chosen to probe reactions of the new rhenium metallocarboxylate as outlined below:

Figure 1. ORTEP drawing of **3** with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and bond angles (deg) are as follows: Re–C(1), 2.100(9); C(1)–O(1), 1.322(9); C(1)–O(2), 1.24(1); O(1)–Sn, 2.092(3); O(2)–Sn, 2.399(1); O(1)–C(1)–O(2), 114.6(7); Re–C(1)–O(1), 119.4(6); Re–C(1)–O(2), 126.0(6); O(1)–Sn–O(2), 56.79(5)

Figure 2. ORTEP drawing of **4** with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and bond angles (deg) are as follows:
Re(1)–C(1), 2.089(6); C(1)–O(1), 1.296(6); C(1)–O(2), 1.289(8); O(1)–Re(2), 2.165(4);
O(2)–Re(2), 2.175(3); O(1)–C(1)–O(2), 113.2(5); Re(1)–C(1)–O(1), 122.0(4);
Re(1)–C(1)–O(2), 124.8(3); O(1)–Re(2)–O(2), 59.6(1)

The bridged compound has been isolated and spectrally characterized.

Interestingly, it undergoes thermolysis with loss of ethylene but with apparent retention of the carboxyl group. Efforts are in progress to fully characterize both compounds. Compounds in this series promise to be more interesting than those in the previous series.

2. Plans for 1993-94

Clearly there is much work in progress which will require additional effort for completion. The new rhenium metallocarboxylate has provided some interesting new compounds and its derivatives are frequently crystalline. This will be very helpful in expanding structure-activity correlations. Efforts will be made to prepare other CO_2 -bridged complexes derived from this system and to alter conditions in hopes of observing $\mu_2\text{-}\eta^2$ complexes as well.

Compounds having chelating organic carboxylato ligands [e.g., to $\text{Re}(\text{I})$ centers] are known to exchange one type of carboxylato ligand for another. We intend to probe the reactions of some of these with metallocarboxylates in hopes that we can access some types of $\mu_2\text{-}\eta^3$ bridging compounds which cannot be made by our current methods. For example, reaction of $\text{HRe}(\text{CO})_2(\text{PPh}_3)_3$ with acetic acid yields $\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{O}_2\text{CCH}_3)$. Reaction of this product with chloroacetic acid provides the chloroacetate-chelated product. We will try to do similar exchange reactions with our iron and rhenium metallocarboxylates as a means of generating new $\mu_2\text{-}\eta^3$ products.

Publications and Presentations

Publications

a) published

Synthesis and Characterization of μ_2 - μ^2 and μ_2 - η^3 -CO₂ complexes of Iron and Rhenium, Dorothy H. Gibson, Ming Ye and John F. Richardson, *J. Am. Chem. Soc.*, 1992, 114, 9716.

Reactions of *cis*- and *trans*-(η^5 -C₅H₅)Mo(CO)₂-[P(OPh)₃]CH₂OCH₃ with Electrophiles, Dorothy H. Gibson, Jaime O. Franco and John F. Richardson, *Organometallics*, 1993, 12, 860.

1-Carbonyl- μ -carboxylato-1KC:2KO:2KO'- η^5 -indenyl-2,2,2-triphenyl-1-1-(triphenylphosphine) irontin, Dorothy H. Gibson, John F. Richardson and Okey P. Mbadike, *Acta Cryst.*, 1993, B49, 784.

b) in preparation

Synthesis and Characterization of Rhenium Metallocarboxylates, Dorothy H. Gibson, Jayesh M. Mehta, John F. Richardson and Mark S. Mashuta.

Synthesis and Thermolysis Reactions of CO₂-Bridged Bimetallic Complexes, Dorothy H. Gibson, Ming Ye, and John F. Richardson.

Presentations

CO₂-Bridged Bimetallic Complexes, Dorothy H. Gibson, Ming Ye, Michael T. Harris, Jaime O. Franco, Okey P. Mbadike, Jayesh M. Mehta and John F. Richardson, presented at the International Conference on Carbon Dioxide Utilization, September 28, 1993 in Bari, Italy.

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