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**"Transition Metal-Mediated Thermal and Photochemical Carbon Dioxide
Activation"**

Progress Report

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A. Project Summary: The focus of this project is the study of the thermal (dark) and photochemical reactivity of carbon dioxide coordinated to transition metal centers. Our efforts are centered on defining the fundamental reactivity patterns of selected, structurally characterized η^2 -mononuclear CO_2 complexes: a) under thermal (dark) conditions towards external reagents including electrophiles, nucleophiles and radical reagents and b) under photolytic conditions. Among the CO_2 complexes to be examined are $\text{Cp}_2\text{M}(\eta^2\text{-CO}_2)\text{L}_n$ [$\text{M}=\text{Mo}, \text{W}, \text{Cr}, \text{V}$ ($n=0$); Ti ($\text{L}=\text{PR}_3$) and Nb ($\text{L}=\text{CH}_2\text{SiR}_3$)]; b) $(\text{R}_3\text{P})_2(\text{RNC})\text{Mo}(\text{CO}_2)_2$; c) $(\text{R}_3\text{P})_2\text{Ni}(\text{CO}_2)$; and relatives of these. These studies will model and may eventually lead to catalytic processes for carbon dioxide reduction and/or splitting.

B. Progress:

We have continued our ground-breaking reactivity studies of the $\eta^2\text{-CO}_2$ complex, $\text{Cp}_2\text{Mo}(\eta^2\text{-CO}_2)$ (**1**). Following our discovery of the remarkably facile reactions of **1** with various electrophilic reagents (E-Nu) which afford cationic carbonyl complexes according to eq. 1 [1], we have examined the reactions of **1** with several main group and transition metal hydrides with the objective of modeling reductions of the coordinated CO_2 molecule.

Complex **1** has been found to react with strongly acidic $\text{HCo}(\text{CO})_4$ rapidly at $<-78^\circ\text{C}$ to produce $[\text{Cp}_2\text{MoH}(\text{CO})]\text{Co}(\text{CO})_4$ (**2**) according to eq. 2 [2].

Labeling experiments (with $^{13}\text{CO}_2$) indicate that the original CO_2 is converted to coordinated CO in **2**. Product **2** slowly converts to a novel unsymmetrically-bridged hydrido complex $[\text{Cp}_2\text{Mo}(\mu\text{-H})(\mu\text{-CO})\text{Co}(\text{CO})_3]$ (**3**) whose structure was established crystallographically. The structure of **3** features an unsaturated 34 electron count and the hydride (accurately located) position significantly closer to the larger Mo atom [1.64(3) Å vs. 1.88(3) Å to Co]. In collaboration with my colleague Prof. Ralph Wheeler the bonding in **3** has been analyzed using extended Huckel calculations [3]. From this study we conclude that there is only a very weak Mo-Co bonding interaction in **3** and that the metals bond to the bridging hydride and carbonyl ligands primarily through a delocalized

four center-four electron bond. The CO₂ complex **1** also reacts, albeit more slowly, with the weaker acid H₂Fe(CO)₄, resulting in reduction of coordinated CO₂ according to eq. 3.

The capability of the hydrides HCo(CO)₄ and H₂Fe(CO)₄ to be produced from molecular hydrogen raises the attractive possibility of their serving as agents for *catalytic* CO₂ reduction. Trial reactions of **1** with HMCP(CO)₃ (M=Cr, Mo) indicates that its reactivity with transition metal hydrides roughly follows the trend of the metal hydride's acidity, i.e. HCo(CO)₄ > H₂Fe(CO)₄ >> HMCP(CO)₃, Cp₂MoH₂.

We have also initiated studies directed towards modeling CO₂ insertion reactions into M-C bonds using (MeC₅H₄)₂Nb(η²-CO₂)CH₂SiMe₃ (**4**), the only established example of a complex containing both coordinated CO₂ and alkyl ligands. To our surprise **4** undergoes *decarbonylation* rather than *insertion* when heated at 60 °C, efficiently producing (MeC₅H₄)₂Nb(O)CH₂SiMe₃ (**5**) (eq. 4) which has been structurally characterized [4].

Even more remarkable is the finding that the **4** → **5** conversion is dramatically accelerated by ultraviolet irradiation (minutes at -20 °C, I ≥ 17%). Very recent efforts to promote insertion reactions of **4** have involved reactions with Lewis acids. Indeed, **1** reacts cleanly and rapidly with BF₃, LiPF₆ and ZnCl₂; characterization of the products is underway.

A number of new systems are also under investigation. Our interest in establishing metal-dependent effects on coordinated CO₂ reactivity has led us to attempt to prepare new Cp₂M(CO₂) complexes where M=Cr, W, and V. To date these efforts have met with limited success. Cp₂W(CO₂) appears to be produced according to the method used for the Mo species **1** but in poor yield. Interaction of chromocene and vanadocene with CO₂ under a variety of conditions results in the production of sparingly soluble metal-oxide clusters but we have been unable to detect intermediate CO₂ adducts in these reactions. In a different vein we have recently prepared the only known monometallic *bis*-CO₂ complex trans-Mo(CO₂)₂(PMe₃)₄ and are currently investigating its photochemistry with the hopes of inducing intramolecular CO₂-coupling to produce an oxalato complex.

Finally, in what may prove to be our most exciting discovery to date we have found that the cationic Rh-phosphine complex **6** *catalyzes* the reduction of CO₂ to formic acid under very mild conditions (20 °C/50 atm 1:1 H₂:CO₂) with turnover numbers in excess of 80 (eq. 5).

Another major organic product is produced as well which we have tentatively identified as γ -butyrolactone, the apparent result of THF *oxidation*. Studies to confirm, elucidate, and expand these novel initial results are underway (vide infra).

References

1. J.-C. Tsai, M.A. Khan and K.M. Nicholas, *Organometallics*, **1989**, *8*, 2967.
2. "Reduction of Coordinated Carbon Dioxide by Transition Metal Hydrides", J.-C. Tsai, M.A. Khan and K.M. Nicholas, *Organometallics*, **1991**, 000 (in press).
3. "Structure and Bonding in the Unsymmetrically Hydrido-Bridged Heterobimetallic Complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\mu\text{-H})(\mu\text{-CO})\text{Co}(\text{CO})_3$ ", J.-C. Tsai, R.A. Wheeler and K.M. Nicholas, *Organometallics*, **1991**, 000 (in press).
4. "Thermal and Photochemical Decarbonylation of $(\eta^5\text{-MeC}_5\text{H}_4)_2\text{Nb}(\eta^2\text{-CO}_2)\text{-CH}_2\text{SiMe}_3$ ", P.-F. Fu, M.A. Khan and K.M. Nicholas, *Organometallics*, **1991**, 000 (in press).

Continuation Application for "Transition Metal-Mediated Thermal and Photochemical Carbon Dioxide Activation" (D.O.E. FGO5 80ER 13997)

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for 3/15/91-3/14/92

Plans for FY 1991

Our efforts during the next year will be directed towards: 1) expanding the thermal and photochemical reactivity studies of $\text{Cp}_2\text{Nb}(\text{CO}_2)\text{R}$ and $\text{Cp}_2\text{Mo}(\text{CO}_2)$; 2) examining the photochemistry of $(\text{R}_3\text{P})_4\text{Mo}(\text{CO}_2)_2$; 3) exploring the chemistry of the known CO_2 complexes: $\text{Cp}_2\text{Ti}(\text{CO}_2)(\text{PMe}_3)$ and $(\text{Cy}_3)_2\text{Ni}(\text{CO}_2)$; and 4) studying further the intriguing Rh-catalyzed redox chemistry of CO_2 with H_2 and (apparently) tetrahydrofuran.

To further elucidate the novel and photochemical decarbonylation reaction of $\text{Cp}_2\text{Nb}(\text{CO}_2)\text{R}$ (**4**), we plan to probe the nature of the electronic transition involved via: 1) Fenske-Hall M.O. calculations; 2) solvent and substituent effects on electronic spectra and quantum yield; 3) the emission spectrum of **4**; and 4) its flash photolysis with UV/VIS and possibly IR transient monitoring (in collaboration with G. Dobson at U. North Texas). We will also further characterize the Lewis acid-derived products from **4** with the hope of finding conditions for effecting migratory insertions of CO_2 into the Nb-C. A new tack will be to utilize Lewis-acid promotion in the presence of added ligands (e.g. CO , $\text{P}(\text{OMe})_3$) to fill the incipient coordination site. Of particular interest are the issues of orientation (i.e. to form Nb-OC(=O)R vs. Nb-C(=O)OR) and of the conditions which promote insertion.

In exploring the prospects for photoinduced reductive C-C coupling of CO_2 with $\text{trans-Mo}(\text{CO}_2)_2(\text{PMe}_3)_4$, we will be examining the electronic spectrum, M.O. scheme, and irradiating wavelength dependency of the product identity since both $\text{trans} \rightarrow \text{cis}$ isomerization followed by $\text{M} \rightarrow \text{L}$ charge transfer excitation would appear to be necessary to effect the desired reaction. Synthesis of an authentic sample of $\text{Mo}(\text{C}_2\text{O}_4)(\text{PMe}_3)_4$ via the reaction of oxalate with $\text{Mo}(\text{PMe}_3)_4\text{Cl}_2$ may also prove valuable.

Expansion of these exploratory studies of thermal and photochemical reactions of CO_2 complexes to include new systems will provide additional insight into the available reaction pathways for coordinated CO_2 . The complexes $\text{Cp}_2\text{Ti}(\text{CO}_2)(\text{PMe}_3)$ and $(\text{Cy}_3)_2\text{Ni}(\text{CO}_2)$ are both known but their reactivity has received very little attention. As with our studies of the Mo- and Nb- CO_2 complexes, we plan to examine basic reactivity patterns when thermolyzed, with polar reagents (including metal hydrides), and photochemically. We anticipate rather different reaction pathways for these very early and very late metal complexes.

Finally, our studies of the catalytic $\text{CO}_2/\text{H}_2/\text{THF}$ reaction promoted by $[\text{Rh}(\text{PMe}_2\text{Ph})_2(\text{NBD})]^+$ will seek to: 1) complete the characterization and quantization of the major organic products (also are CO and/or H_2O as produced); 2) establish the origin of the products (i.e. where does the added O- in the lactone come from?) via labeling experiments; 3) probe the mechanisms by examining the pressure dependencies on the product ratio and rate (to determine the reaction order); and 4) optimize the conversion and yields via temperature, pressure and solvent manipulation. If our initial observations are confirmed and optimized, this Rh-catalyzed reaction could represent the first, truly useful homogeneous catalytic reaction of carbon dioxide (other than enzymatic processes).

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