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Transition Metal-Mediated Thermal and Photochemical Carbon Dioxide Conversion

Final Report

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Progress Report

The primary objectives of this project are 1) to define the fundamental reactivity patterns of transition metal-coordinated CO_2 ; and 2) to discover and elucidate new transition metal-mediated reactions of CO_2 , including both stoichiometric and catalytic variants. Plans during the current project period will be concentrated along two lines. Firstly, we will conduct *followup/continuation* studies of the thermal and photochemical reactivity of $\eta^2\text{-CO}_2$ complexes and the oxygenation of metal-carbonyl complexes. Specific systems of interest include: a) C-centered reactions of $\eta^2\text{-CO}_2$ complexes with ambiphilic metal hydrides and alkylidenes; b) O-transfer reactions of CO_2 complexes with redox active oxophilic metal derivatives; c) photoinduced O-transfer and C-C bond forming reactions; and d) synthetic and mechanistic studies of the oxygenation reactions of metal-CO, alkylmetal-CO, and hydridometal-CO complexes. Secondly, we plan *groundbreaking* stoichiometric and catalytic studies of metal-mediated *hydrocarbon carboxylations* via metal-mediated insertion into C-H and C-C bonds, including the use of supercritical CO_2 . These will include, in the case of the C-H insertion strategy, reactions of CO_2 with selected low oxidation state R-M-H species and reductive eliminations of $\text{RCO}_2\text{-M-H}$ complexes. Approaches to C-C carboxylation will focus on systems known to oxidatively add cyclopropanes, with emphasis on the reactions of CO_2 with metallacyclobutanes and induced reductive eliminations of the insertion products to form lactones.

Progress towards these objectives during the past 9 months has been somewhat limited by the initiation of new lines of investigation and unexpected and unavoidable difficulties (visa problems) associated with securing a replacement postdoctoral fellow for the project. Our efforts over the last several months have been concentrated in the following areas: 1) attempted preparation of *cis*-(tetraphos)Mo(CO_2)₂ (1), the first *cis-bis-CO}_2 complex; and 2) initial investigations of the interaction of CO_2 with metallacyclobutane complexes (2) and hydrido-metal-alkyl complexes (3).*

Our interest in **1** was based on its potential to serve as a precursor for novel C-C coupling to oxalate (eq. 1). Numerous attempts to generate **1** under a variety of reducing conditions (via N_2 , CO complexes) have produced equivocal results. In several experiments (with $R=Ph$) an unstable compound ($IR: 1700, 1620\text{ cm}^{-1}$), believed to be the desired CO_2 adduct has been isolated [1], but we have been unable to obtain it in pure form; further attempts have been given a low priority.

We have initiated CO_2 reactivity studies of a few metallacyclobutane complexes [$L_nM = L_2Cl_2Pt, L_2Ni, Cp^*Rh(PMe_3)$], derivable from cyclopropanes, to model prospective systems for catalytic cyclopropane carboxylation (eq. 2). While several Pt derivatives failed to react with CO_2 [2], insertion appears to occur with some of the Ni- and Rh- derivatives [1].

On the C-H carboxylation side (eq. 3) we have initiated investigations of three known C-H activating systems: $(olefin)_2Mo(PR_3)_4$, $\{HB(pyrz)_3\}Rh(CO)_2$, and $(R_3P)_2Rh(CO)Cl$. The former is known to stoichiometrically insert CO_2 (to produce acrylate derivatives) and the latter weakly catalyzes arene

carbonylation. $\{HB(pyrz)_3\}Rh(CO)(Ph)H$, derived photochemically from $\{HB(pyrz)_3\}Rh(CO)_2$, apparently reacts with CO_2 ; product characterization is underway [3].

We have also submitted a full paper for publication (accepted in *J. Organomet. Chem.*) describing our reactivity and mechanistic studies of the thermal decarbonylation of a set of $Cp'_2Nb(CO)_2R$ complexes, the first systematic reactivity study of a set of related CO_2 complexes [4].

Plans for '95-96

Our efforts during the next year will be concentrated primarily on followup and new exploratory studies of metal-mediated C-H and C-C carboxylation. Secondary attention will be given either to: 1) continuing efforts to develop systems for metal-mediated O-transfer oxidation by CO₂ (eq. 4) or 2) mechanistic studies of our earlier discovered metal-promoted oxygenation of CO to CO₂ (eq. 5).

Specific systems of interest with respect to carboxylation are given in the progress report (above) and in our '94 renewal proposal (p. 16-22). A detailed plan of action and complexes of interest for study of reactions 4 and 5 is also provided in the renewal proposal (p. 12-16).

References

- [1] F. Antwi-Nsiah and K.M. Nicholas, unpublished results, 1995.
- [2] J.M. Kessler and K.M. Nicholas, unpublished results, 1995.
- [3] F.A.K. Rahman and K.M. Nicholas, unpublished results, 1995.
- [4] P.-F. Fu, M.A. Khan and K.M. Nicholas, "Thermolysis of (MeCp)₂Nb(h²-CO₂)R Complexes: Decarbonylation vs. Insertion", *J. Organomet. Chem.* 1995, in press.

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Project Summary

Carbon dioxide, the earth's most abundant carbon resource, is remarkably little used as a chemical feedstock. As the output of CO₂ from combustion into the environment continues to rise, threatening a global environmental crisis, the search for practical methods for regenerating organic compounds from CO₂ has assumed increased importance. The development of such processes will be assisted by an improved understanding of the chemistry of metal-carbon dioxide complexes, potential intermediates in metal-catalyzed transformations of CO₂. The initial stage of this project has focused on the thermal and photochemical reactions of discrete CO₂ complexes, including Cp₂Mo(η^2 -CO₂) and Cp₂Nb(η^2 -CO₂)R, resulting in the elucidation of several new CO₂-splitting reactions. These studies, in turn, have lead to the semi-serendipitous discovery of a number of other novel/important transformations, including: 1) the *catalytic hydrogenation* of CO₂ to formic acid by [H₂Rh(PR₃)₃L]⁺ complexes; 2) the CO₂-mediated, [Rh(PR₃)₂(diene)]⁺-*catalyzed* aerobic oxidation of ethers to esters with co-production of formic acid; and 3) the aerobic oxygenation of electron rich metal-carbonyls and metal-carbonyl-hydrides, forming metal-CO₂ and metal-formate complexes respectively. Plans during the next project period will be concentrated along two lines. Firstly, we will conduct *followup/continuation* studies of the thermal and photochemical reactivity of η^2 -CO₂ complexes and the oxygenation of metal-carbonyl complexes. Specific systems of interest include: a) C-centered reactions of η^2 -CO₂ complexes with ambiphilic metal hydrides and alkylidenes; b) O-transfer reactions of CO₂ complexes with redox active oxophilic metal derivatives; c) photoinduced O-transfer and C-C bond forming reactions; and d) synthetic and mechanistic studies of the oxygenation reactions of metal-CO, alkylmetal-CO, and hydridometal-CO complexes. Secondly, we plan *groundbreaking* stoichiometric and catalytic studies of metal-mediated *hydrocarbon carboxylations* via metal-mediated insertion into C-H and C-C bonds, including the use of supercritical CO₂. These will include, in the case of the C-H insertion strategy, reactions of CO₂ with selected low oxidation state R-M-H species and reductive eliminations of RCO₂-M-H complexes. Approaches to C-C carboxylation will focus on systems known to oxidatively add cyclopropanes, with emphasis on the reactions of CO₂ with metallocyclobutanes and induced reductive eliminations of the insertion products to form lactones.