

## The Coordination and Insertion Chemistry of Carbon Dioxide

Robert J. Morris

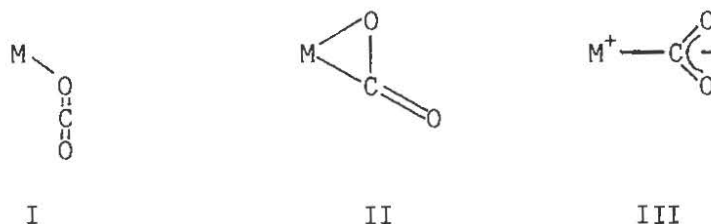
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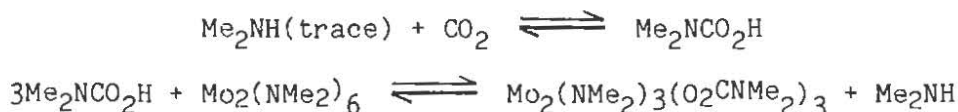
The utilization of carbon dioxide as a carbon feedstock has been an area of great interest for many years. As a source of carbon, the supply of  $\text{CO}_2$  is approximately equal to that of fossil fuels. Consequently, the degree of interest in the use of  $\text{CO}_2$  as a  $\text{C}_1$  starting material has increased exponentially over the past ten years. The principal problem associated with the use of  $\text{CO}_2$  has been overcoming the kinetic activation barrier to reduction. Thus, many investigators have studied the use of transition metals as catalysts for the selective reduction of  $\text{CO}_2$ .

There has been a great deal of work focused on the homogeneous co-oligomerization of  $\text{CO}_2$  with unsaturated organic substrates. For example, Behr has oligomerized  $\text{CO}_2$  with butadiene to produce a series of conjugated lactones [2]. The heterogeneous catalytic reduction of  $\text{CO}_2$  to  $\text{CH}_4$  over alumina-supported metal atoms has been elegantly illustrated by Solymosi [3]. These researchers were able to observe large turnover numbers and very high selectivity for  $\text{CH}_4$  as the final product in this process. Electrocatalytic reduction of  $\text{CO}_2$  to CO with  $\text{Ni}(\text{cyclam})\text{Cl}_2$  as a catalyst has been effectively demonstrated by Sauvage [4]. Similarly, Lehn and co-workers have shown that irradiation of a  $\text{CO}_2$ -saturated solution of  $\text{Re}(\text{bipy})(\text{CO})_3\text{Cl}$  with visible light leads to catalytic reduction of  $\text{CO}_2$  to CO [5]. These catalytic accomplishments have promoted efforts to establish a foundation of mechanistic studies of  $\text{CO}_2$  reactivity.

The initial phase in the study of transition metal- $\text{CO}_2$  catalysis was the investigation of the coordination of  $\text{CO}_2$  to transition metal complexes. The three most likely fashions in which  $\text{CO}_2$  could bind to a transition metal are shown below:



The first transition metal- $\text{CO}_2$  complex was prepared by Aresta and Nobile in 1975 [6]. Since then, only a few transition metal- $\text{CO}_2$  complexes have appeared in the literature [1a]. Complexes of type I have never been isolated and compounds of type II [7a-c] greatly outnumber those of type III [8a-c]. A second aspect of transition metal- $\text{CO}_2$  catalysis was the investigation of the insertion chemistry of  $\text{CO}_2$  into M-E bonds. Virtually all of the examples of  $\text{CO}_2$  insertion have been when  $\text{E} = \text{NR}_2$ , OR, R(Ar), and H [9a-d]. Although direct insertions have been proposed for  $\text{E} = \text{R}$  and H [10,11], Chisholm [12] has shown very clearly that insertion of  $\text{CO}_2$  into M-E bonds with  $\text{E} = \text{NR}_2$  or OR proceed via the mechanism shown below.



Recently, the electrocatalytic reduction of CO<sub>2</sub> to give products such as carbon monoxide has received increasing attention [13] and is likely to become the main area of research in the future. The design of more selective and more efficient catalysts will doubtlessly be assisted by studies directed toward understanding the mechanistic details of metal-mediated CO<sub>2</sub> electroreduction.

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