Mechanistic and IR Spectroelectrochemical Studies for Alkali Metal Ion Catalyzed Multiple Bond Metathesis Reactions of Carbon Dioxide

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The reaction of the tetrakis(alkyl or aryl isocyanide) complex, $Ni(CNR)_4$ ($R=2,6\text{-}Me_2C_6H_3$, Me), with carbon dioxide in the presence of Li^+ leads to the formation of $Ni(CO)_2(CNR)_2$ and the alkyl- or arylisocyanate, RN=C=O. ^{13}C-labeling studies indicate that the carbonyl ligands of $Ni(CO)_2(CNR)_2$ are produced by multiple bond metatheses between CO_2 and CNR ($R=2,6\text{-}Me_2C_6H_3$, Me) not by deoxygenation of CO_2.

The activation and reduction of CO_2 are of fundamental importance for the eventual chemical utilization of atmospheric CO_2, an increasingly abundant natural carbon resource. The activation of CO_2 by transition metal complexes continues to be the subject of considerable study.[1] In many cases, the activation of CO_2 by transition metal complexes has been achieved by the use of relatively nucleophilic late transition metal complexes.[2-7] As a nucleophile adds to the CO_2 molecule, significant charge redistribution occurs and stabilization of this charge by electrophilic or "oxophilic" early transition metal complexes also may occur.[8-11] The combined requirements of nucleophilic activation at carbon and electrophilic stabilization at oxygen can be met by heterobinuclear complexes; and several heterobimetallic CO_2 complexes have now been reported.[5,12] In the case of Floriani's [Co(pr-salen)K][13] and related alkali metal ion salts of cobalt Schiff base complexes,[14] bifunctional activation of CO_2 by direct involvement of the alkali metal ion with oxygen atoms of CO_2 was observed. Evidence for the importance of hydrogen bonding between protonated amine groups of cobalt macrocycles and CO_2 oxygen atoms in stabilizing the CO_2 to metal macrocycle interaction has been described by Fujita et al.[15]

$$^{*}C{\equiv}NMe + O{=}C{=}O \rightleftarrows {}^{*}C{=}O + O{=}C{=}NMe \qquad (1)$$

$$^{*}C{\equiv}NMe + O{=}C{=}O \rightleftarrows C{=}O + O{=}{}^{*}C{=}NMe \qquad (2)$$

The reaction of the mononuclear tetrakis(aryl isocyanide) complex $Ni(CNAr)_4$ (**1**, $Ar=2,6\text{-}Me_2C_6H_3$) with carbon dioxide in the presence of Li^+ leads to the formation of the dicarbonyl, diiscyanide complex $Ni(CO)_2(CNAr)_2$ (**2**)[16] and two equivalents of the corresponding arylisocyanate in THF, eq. 3.

$$Ni(CNAr)_4 + 2CO_2 \xrightarrow{Li^+} Ni(CO)_2(CNAr)_2 + 2\ O{=}C{=}NAr \qquad (3)$$

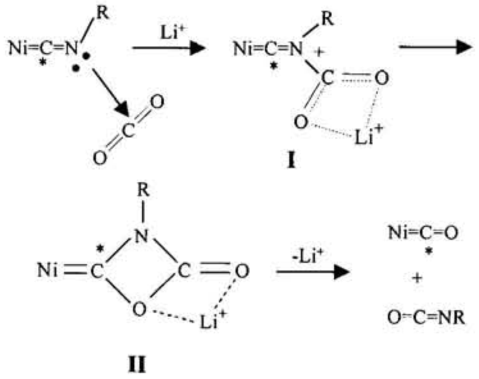
The tetrakis(methyl isocyanide) complex $Ni(CNMe)_4$ (**3**)[17] reacts similarly with carbon dioxide in the presence of Li^+ ($LiBH_4$) to produce the known complex $Ni(CO)_2(CNMe)_2$ (**4**).[16]

The important features of the complexes **2** and **4** are the presence of two CO ligands derived from the reaction with CO_2. The pathway by which these products are formed can be shown to be multiple bond metathesis by isotope labeling studies. When the reaction of **1** is repeated with $^{13}CO_2$, the nickel CO bands are not affected but the aryl isocyanate band shifts from 2275 to 2252 cm^{-1}. A second labeling study using the ^{13}C-methyl isocyanide complex, $Ni(^{13}CNMe)_4$ (**3***), shows that the ν(CO) bands of the product do shift from 2028 and 1994 cm^{-1} to 1992 and 1963 cm^{-1}, consistent with the formation of $Ni(^{13}CO)_2(^{13}CNMe)_2$. The methyl isocyanate formed as the coproduct shows no incorporation of ^{13}C. The results of the ^{13}C-labeling studies are summarized in Table 1. These results establish that the carbon atoms of the CO ligands of complexes **2** and **4** are derived from the isocyanide ligands of complexes **1** and **3**, respectively, not from CO_2.

Table 1. IR spectral data for the reaction of complex **1** with $^{13}CO_2$ and the reaction of ^{13}C isotopically labeled complex **3** with CO_2

Reaction	Products	
	$Ni(CO)_2(CNR)_2$ ν (CN), cm^{-1} ν (CO), cm^{-1}	RN=C=O ν (NCO), cm^{-1}
$Ni(CNAr)_4$ (**1**) + CO_2	2147, 2124 2011, 1974	2275
$Ni(CNAr)_4$ (**1**) + $^{13}CO_2$	2147, 2124 2011, 1974	2252
$Ni(CNMe)_4$ (**3**) + CO_2	2176, 2142 2028, 1994	2273
$Ni(^{13}CNMe)_4$ (**3***) + CO_2	2135, 2105 1992, 1963	2273

A key finding in this study is that the multiple bond metathesis chemistry between complexes **1** or **3** and CO_2 is catalytic in Li^+. As little as 1% or as much as 1 equivalent of Li^+ has been used to catalyze the reaction. Rates of the reaction based on the initial rates of disappearance of **1** are clearly first order in $[Li^+]$.[18] The rate constant, k_1, is estimated to 1.20×10^{-8}. Addition of the lithium ion specific crown ether 12-crown-4 in a 1:1 ratio with respect to $[Li^+]$ results in rate inhibition by over a factor of 50. Kinetic studies, based on initial rates of disappearance of **1**, were also undertaken to show that the rate of the reaction of **1** with CO_2 in the presence of Li^+ also depends to first order on $[CO_2]$.[18] The rate constant, k_2, is estimated to 1.05×10^{-8}. A mechanism which is consistent with the isotope labeling and kinetic studies is summarized by the following scheme (Scheme 1). Our observations suggest that Li^+ ions may catalyze the multiple bond metathesis reaction by stabilizing the development of negative charge on the CO_2 oxygen atoms in the interaction between a non-bonded electron pair on the isocyanide N-atoms and CO_2, structure **I**. However, we have not yet spectroscopically obtained direct evidence of intermediates of this type. The isotope labeling studies indicate a mechanism whereby a CO_2 O-atom and isocyanide RN-group are interchanged. This interchange is perhaps best accommodated by a four-membered transition state, similar to structure **II**. We suggest that the catalytic role of Li^+ ions lies in the ability to promote the interchange between a CO_2 O-atom and isocyanide RN-group, resulting in the formation of multiple bond methathesis products in accord with eq. 2.



Scheme 1. Proposed mechanism of the formation of alkyl- or arylisocyanate.

The alkali metal ion catalyzed metathesis of the multiple bonds of CO_2 and isocyanides is rather general. The only other reported multiple bond metathesis chemistry between CO_2 and isocyanides[19,20] proceeded from a reactive μ-CNMe ligand of the binuclear $[Ni_2(\mu\text{-CNMe})(CNMe)_2(dppm)_2]$ complex under photochemical conditions or in the presence of liquid CO_2, eq. 4.

$$[Ni_2(\mu\text{-*CNMe})(\text{*CNMe})_2(dppm)_2] + 3\ CO_2 \rightarrow\rightarrow\rightarrow \\ [Ni_2(\mu\text{-*CO})(\text{*CO})_2(dppm)_2] + 3\ O{=}C{=}NMe \qquad (4)$$

An isotope labeling study with ^{13}CNMe indicated that all three carbonyl carbon atoms in the product, $[Ni_2(\mu\text{-*CO})(\text{*CO})_2(dppm)_2]$, originated as isocyanide carbon atoms in the starting material, $[Ni_2(\mu\text{-*CNMe})(\text{*CNMe})_2(dppm)_2]$. We now find that the multiple bond metatheses of $[Ni_2(\mu\text{-CNMe})(CNMe)_2(dppm)_2]$ and the related isocyanide complexes, $[Ni_2(\mu\text{-CNR})(CNR)_2(dppm)_2]$ (R = n-C_4H_9, t-C_4H_9, C_6H_{11}, $CH_2C_6H_5$, C_6H_5, 2,6-CH_3-C_6H_3), are also alkali metal ion catalyzed. We will describe IR spectroelectrochemical and kinetic studies of the mechanism of these potentially important oxygen atom transfer reactions of CO_2 in the near future.

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