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Facile Reduction of Carbon Dioxide by Anionic Group 6B Metal Hydrides. Chemistry Relevant to Catalysis of the Water-Gas Shift Reaction

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Little is known about the role of transition metals and their complexes in reactions which effect the reduction of CO_2. Such a deficiency in chemical knowledge is particularly suprising in view of the abundance of work directed toward an understanding of the water-gas shift reaction (eq 1) as homogeneously catalyzed by transition-metal carbonyl complexes.[1] The sequence of re-

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (1)$$

actions pertinent to oxidation of metal-bound CO by hydroxide ion involving the intermediacy of the metallocarboxylic acid species (I) in eq 2 is well established for the group 6B metal hexacarbonyls under both stoichiometric and catalytic reaction conditions.[2] With

$$M{-}C{\equiv}O + OH^- \rightleftharpoons \underset{\text{I}}{\{M{-}COOH^-\}} \rightarrow M{-}H^- + CO_2 \qquad (2)$$

regard to fully understanding the potential of each step of the water-gas shift reaction, it would be worthwhile to examine the nature of the reaction of CO_2 with transition-metal hydrides prominent in such reactions. In this communication we wish to report some preliminary observations on the reaction of CO_2 with the anionic metal carbonyl hydrides, $HM(CO)_5^-$ (M = Cr, Mo, or W).

Reactions of the group 6B metal hexacarbonyls with two equivalents of crypt 222[3] solubilized KOH in aprotic solvents (THF or CH_3CN) were found to afford quantitatively the pentacarbonyl metal hydride anions within minutes at ambient temperature.[4] Identification of the chromium and tungsten pentacarbonyl monohydride species was based on ν(CO) infrared and ^1H NMR spectral comparisons with authentic samples prepared by protonation of the corresponding $M(CO)_5^{2-}$ dianions.[5] Proton decoupled ^{13}C NMR spectra were determined on samples synthesized employing ^{13}CO enriched hexacarbonyls (see Figure 1). Additionally, ^{13}CO enriched samples were obtained by a direct facile ligand exchange (eq 3) of the [K(crypt 222)][$HM(CO)_5$]

$$HM(CO)_5^- + n^{13}CO \rightleftharpoons HM(CO)_{5-n}(^{13}CO)_n^- + n^{12}CO \qquad (3)$$

species with ^{13}CO at ambient temperature, with the relative rates of exchange being W ≥ Mo > Cr.

The pentacarbonyl metal hydride anions were found to readily react with carbon dioxide or carbon disulfide according to eq 4,

$$HM(CO)_5^- + CX_2 \rightleftharpoons HC(X)XM(CO)_5^- \qquad (4)$$
$$(M = Cr, Mo, W; X = O, S)$$

yielding the corresponding pentacarbonyl metal formates or thioformates, respectively. Figure 1 illustrates the ^{13}C NMR spectra observed during the rapid, quantitative conversion of $HW(CO)_5^-$ in 1 atm of CO_2 to $HCO_2W(CO)_5^-$ at ambient temperature. The spectral data (IR and ^{13}C NMR) in the metal carbonyl region for these compounds are given in Table I. In addition, the resonance for the carboxylic carbon atom was observed at 167.3 ppm on a sample of $HCO_2W(CO)_5^-$ prepared from $HW(CO)_5^-$ and ^{13}C–enriched CO_2. This labeling experiment also demonstrated that further reduction of CO_2 to CO was not occurring during reaction 4 in that none of the ^{13}C label appeared in the carbon monoxide ligands. Conversely, no ^{13}C label from the $M(^{13}CO)_5$ moiety was observed in the HCO_2^- ligand. The pentacarbonyl metal formate anions (M = Cr, W) displayed identical ν(CO) infrared and ^{13}C NMR spectral properties with samples prepared by the conventional route described in eq 5.[6]

$$PPN^+M(CO)_5Cl^- + TlOOCH \xrightarrow{CH_2Cl_2} PPN^+M(CO)_5OOCH^- + \mathit{TlCl} \qquad (5)$$

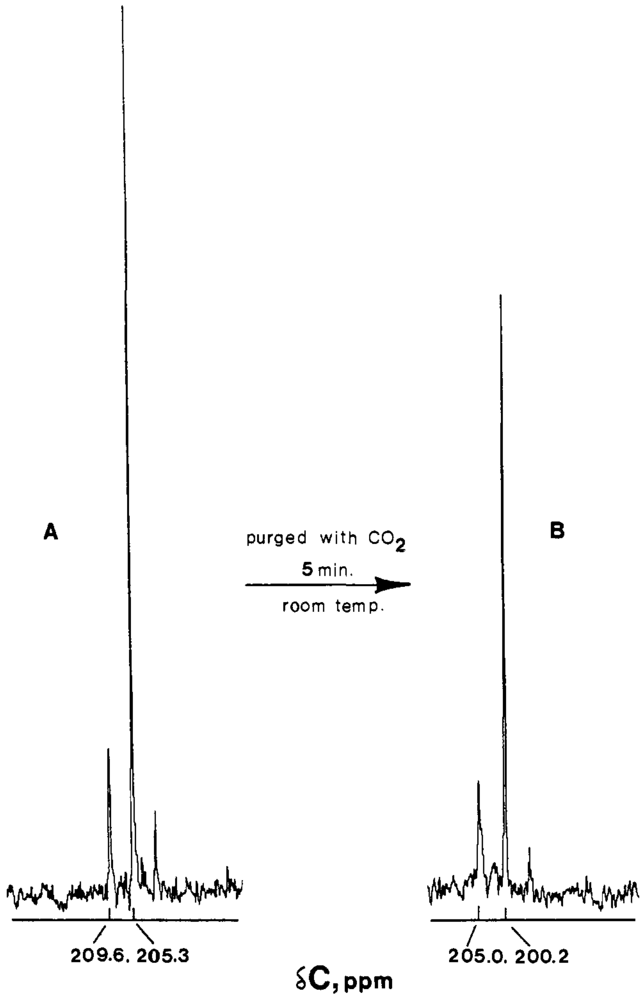

Figure 1. (A) ^{13}C NMR spectrum in CO region of [K(crypt 222)]-[$HW(CO)_5$] in CD_3CN prepared from ^{13}C-enriched $W(CO)_8$ (J_{W-C} = 127.4 Hz). (B) ^{13}C NMR spectrum in CO region of [K(crypt 222)]-[$HCO_2W(CO)_5$] in CD_3CN prepared from sample in A and CO_2 carried out in the NMR tube (J_{W-C} = 130.4 Hz). In both spectra the most downfield peak represents a superposition of the axial CO resonance on one of the W–C_{eq} satellites, with less overlap occurring in B.

Table I. Spectral Data for $HC(X)XM(CO)_5^-$ Anions

		ν(CO), cm$^{-1\,a}$			^{13}C NMR	
M	X	$A_1^{(2)}$	$A_1^{(1)}$	E	δC(eq)	δC(ax)
Cr	O	2056 w	1858 m	1925 s	222.7	216.0
Cr	S	2053 w	1881 m	1927 s	225.4	218.0
Mo	O	2064 w	1853 m	1928 s	205.9	*b*
Mo	S	2059 w	1880 m	1933 s		
W	O	2062 w	1854 m	1917 s	200.2^c	205.0
W	S	2060 w	1873 m	1922 s	199.3	203.3

[a] Frequencies were measured in CH_3CN solution and are accurate to ±2 cm^{-1}. [b] Due to low concentration this peak was not observed (spectra determined in CD_3CN). [c] J_{W-C} = 130.4 Hz.

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(1) Laine, R. M.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 252 and the extensive list of related references in ref 2 and 7.

(2) Darensbourg, D. J.; Rokicki, A. *ACS Symp. Ser.*, in press.

(3) 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt 222, Kryptofix 222). Supplied by Parish Chemicals, Provo, UT 84601.

(4) The solids which precipitated from the solution during this reaction consisted of potassium bicarbonate (main component), potassium formate, and potassium carbonate as established by ^{13}C NMR spectroscopy of their solutions in D_2O/2-ethoxyethanol mixture.

(5) Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.*, in press. Darensbourg, M. Y.; Slater, S., unpublished results.

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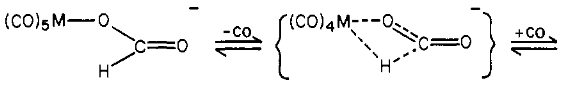
The reverse of CO_2 reduction as depicted in eq 4 proceeded under mild conditions (25-50 °C) for the case where M = Cr, i.e., $HCO_2Cr(CO)_5^-$ readily undergoes decarboxylation to $HCr(CO)_5^-$ and CO_2. Consistent with this finding it was possible to alternate between metalloformate and metallodithioformate derivatives by introducing CO_2 or CS_2 (eq 6). On the other hand,

$$HCO_2Cr(CO)_5^- + CS_2 \rightleftharpoons HCS_2Cr(CO)_5^- + CO_2 \qquad (6)$$

decarboxylation of $HCO_2W(CO)_5^-$ occurred sluggishly at elevated temperatures (>80 °C). Moreover, it was found that the chromium pentacarbonyl formate derivative exchanges CO ligands with free ^{13}CO in solution much faster (~80% in 10 min) than the tungsten analogue (~50% in 3 h) at ambient temperature and in advance of the decarboxylation process. Hence CO lability appears to be a requisite step in the mechanism for rupture of the C-H bond in the formate ligand in systems involving coordinatively saturated metal centers (eq 7).[7-10] As required by the



II

$$(CO)_5MH^- + CO_2 \qquad (7)$$

principle of microscopic reversibility, the reverse process, addition of CO_2 to $HM(CO)_5^-$ to afford $HCO_2M(CO)_5^-$(II), would also entail CO dissociation, a property indeed exhibited by $HM(CO)_5^-$ anions.

Both metalloformate (**II**) and metallocarboxylic acid (**I**) species are significant to a complete discussion of the water-gas shift reaction as catalyzed by metal carbonyls in alkaline solution. Carbon-13 labeling studies (vide supra) have established that the two structural isomers do not interconvert in an *intramolecular* manner. As demonstrated in this report the most prominent intermediate in the WGSR, $HM(CO)_5^-$, can react with a product of this reaction, CO_2, to provide $HCO_2M(CO)_5^-$. Although the concentration of CO_2 should be reduced due to trapping by $OH^- \rightarrow HCO_3^-$, the great facility with which $HM(CO)_5^-$ reacts with CO_2 suggests the latter to be competitive with bicarbonate formation. There are additional routes to formation of the $HCO_2M(CO)_5^-$ anions during catalysis of the WGSR. The reaction of $HM(CO)_5^-$ with a proton source affords H_2 and the unsaturated $[M(CO)_5]$ species which can be scavenged by HCO_2^- (from $OH^- + CO \rightleftharpoons HCO_2^-$) to yield $HCO_2M(CO)_5^-$. This latter derivative can also be obtained from reaction of formate ion with the $[M(CO)_5]$ intermediate resulting from CO dissociation in $M(CO)_5$ at elevated temperatures.[11] We have shown that both chromium and tungsten metalloformates are unstable toward decarboxylation, with the latter, however, being much more resistant and probably inhibitory to H_2 production. In any instance, of the two intermediates capable of affording H_2 and CO_2, the metallocarboxylic acid pathway is energetically more favorable, i.e., the process described in eq 2 was determined to occur under milder reaction conditions than the reversal of reaction 4. Similar observations have been reported for the decarboxylation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2COOH$.[7] These comments are totally consistent with the greater thermodynamic and kinetic stability of metal formates vs. metal carboxylic acid derivatives. Investigations aimed at providing more quantitative definitions of the various energy barriers are in progress.

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(7) Darensbourg, D. J.; Fischer, M. B.; Schmidt, R. E., Jr.; Baldwin, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 1297.

(8) In order to firmly establish the requirement for CO dissociation prior to decarboxylation in saturated metal centers, CO concentration dependence rate studies of decarboxylation are necessary and are under way.

(9) The solid-state structures of the acetatopentacarbonylmetalates of the group 6B metals,[10] as well as that of $(\eta^5\text{-}C_5H_5)Fe(CO)_2O_2CH$,[7] show the uncoordinated oxygen atom to be located in the direction of the carbonyl ligands. Hence, the initial species depicted in eq 7 would result from a 180° rotation about the metal-bound oxygen atom and formate carbon atom bond. Since this bond has been shown to have multibonding character in the $RCO_2M(CO)_5^-$ species,[10] the rotational barrier is expected to be of significance in these cases.

(10) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398.

(11) King, R. B.; King, A. D., Jr.; Yang, D. B. *ACS Symp. Series*, in press.

Diels-Alder Reactions Involving Cross-Conjugated Dienones. Effects of Substitution on Reactivity

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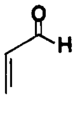
Unsaturated ketones are among the most commonly used dienophiles in Diels-Alder reactions.[1] As a general rule, the dienophilicity of enones is increasingly diminished as (a) the number of alkyl substituents attached to the double bond increases, (b) conformational effects become more severe, and (c) the hindrance afforded by remote substituents increases in the transition state of the reaction. Thus, while acrolein (**1**) is a moderately reactive dienophile, 3-methylcyclohexenone (**2**) fails to undergo Diels-Alder reactions under either thermal or Lewis acid-catalyzed conditions.[2,3]



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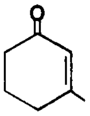

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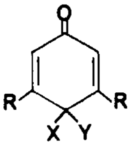

3

In principle, cross-conjugated cyclohexadienones **3** should be more reactive dienophiles than their corresponding cyclohexanone derivatives. Sterically, cyclohexadienones exist as shallow boats and, with the exception of the hindrance provided by the geminal substitution at C-4, are quite accessible to an approaching diene. Electronically, species such as **3** have lower lying LUMO's than their enone counterparts and are therefore predicted to be more reactive in Diels-Alder reactions.[4] For these reasons, we recently undertook a general study which examined the scope and limitations of Diels-Alder reactions involving cross-conjugated dienones. In particular, we have examined (a) the effects of double bond substitution on the reactivity of the dienone and (b) the effects of differential geminal substitution at C-4 with regard to "face selectivity" in Diels-Alder reactions. The preliminary results of our study are reported below.[5]

Formyl dienone **4a**[6] reacts with excess piperylene (**5**) slowly at room temperature and rapidly at 70 °C to yield a single adduct **6a**. Since we were unable to unequivocally assign the stereo-

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† Fellow of the Alfred P. Sloan Foundation, 1980-1984.

(1) (a) Sauer, J. *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 211. (b) *Ibid.* **1967**, *6*, 16. (c) Hamer, J. "1,4-Cycloaddition Reactions"; Academic Press: New York, 1967. (d) Seltzer, S. *Adv. Alicycl. Chem.* **1968**, *2*, 1. (e) Opplozer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10.

(2) Butz, L. W.; Rytina, A. W. *Org. React.* **1949**, *5*, 136.

(3) The inertness of **2** in Diels-Alder reactions is probably the result of both electronic factors (relatively high-lying LUMO) and steric factors.

(4) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361.

(5) Satisfactory spectral data and elemental analyses were obtained for all new compounds.

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