(17) Reisfeld, R. *Struct. Bonding (Berlin)* **1976,** *30*, 65.
(18) Reisfeld, R. *Struct. Bonding (Berlin)* **1975,** *22*, 123.
(19) See ref 20 for an extensive bibliography of early work.
(20) Grant, W. J. C., *Phys. Rev. B.* **1971,** *4*, 648.
(21) Fong, F. K.; Diestler, D. J. *J. Chem. Phys.* **1972,** *56*, 2875.
(22) Matthews, B. W.; Weaver, L. H.; Kester, W. R. *J. Biol. Chem.* **1974,** *249*, 8030.
(23) Kretsinger, R. H.; Nockolds, C. E. *J. Biol. Chem.* **1973,** *248*, 3313.
(24) *n* is taken as 1.35, a value intermediate between that of water (1.33) and that of organic molecules containing only first row atoms (1.39).
(25) Rhee, M.-J.; Sudnick, D. R.; Arkle, V.; Horrocks, W. DeW., Jr., manuscript in preparation.
(26) These facts were ascertained using the laser excitation technique described in ref 10 and will be documented in ref 25.
(27) Snyder, A. P.; Sudnick, D. R.; Arkle, V.; Horrocks, W. DeW., Jr., manuscript in preparation.
(28) Jorgensen, C. K.; Judd, B. R. *Mol. Phys.* **1964,** *8*, 281.
(29) Kretsinger, R. H. *Annu. Rev. Biochem.* **1976,** *45*, 239.
(30) Kretsinger, R. H.; Nelson, D. J. *Coord. Chem. Rev.* **1976,** *18*, 29.
(31) Jack, A.; Ladner, J. E.; Rhodes, D.; Brown, R. S.; Klug, A. *J. Mol. Biol.* **1977,** *111*, 315.
(32) Holbrook, S. R.; Sassman, J. L.; Warrant, R. W.; Church, G. M.; Kim, S. H. *Nucl. Acid Res.* **1977,** *4*, 2811.
(33) Stout, C. D.; Mizuno, H.; Rao, S. T.; Swaminathan, P.; Rubin, J.; Brenan, T.; Sundaralingham, M. *Acta Crystallogr., Sect. B* **1978,** *34*, 1529.

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Approaches to Homogeneous Reduction of Carbon Monoxide. 2. Reactions of $(\eta^5\text{-}C_5H_5)_2NbH_3$ with Metal Carbonyls: Selective Reduction of CO to Ethane

Sir:

A potential route to homogeneous CO reduction involves initial C–H bond formation by attack of a nucleophilic transition metal hydride on an electrophilic metal carbonyl.[1] We have previously reported that the reaction of $(\eta^5\text{-}C_5H_5)_2NbH_3$ (I) with $Fe(CO)_5$ yields an intermediate with a new C–H bond,[2] although the final product, $(\eta^5\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)Fe(CO)_4$ (II),[4] does not contain reduced CO.[5] We have extended this study to include other metal carbonyls and find that, in certain cases, product-selective alkane formation can be observed under very mild conditions.

I reacts with several first-row binary metal carbonyls under Ar in benzene solution to give organometallic products accompanied by hydrogen evolution. The rate depends significantly on the identity of the metal carbonyl, exhibiting an interesting correlation with position in the periodic table. The approximate times for complete reaction[6] and organometallic products for each carbonyl follow: $Cr(CO)_6$, 2 h, 45 °C, $(\eta^5\text{-}C_5H_5)_2NbH(CO)$ (III); $Mn_2(CO)_{10}$, 30 min, 40 °C, III; $Fe(CO)_5$, 20 min, 25 °C, II; $Co_2(CO)_8$, instantaneous, 25 °C, $(\eta^5\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}CO)Co(CO)_3$ (IV).[7] The significance of the trend in reactivity is not clear; IR stretching frequencies for these carbonyls[8] do not indicate any substantial changes in CO electrophilicity (such as in going from III to $Fe(CO)_5$, for example[2]) which would be expected to affect reactivity.[9] No organic products can be detected in solution or in the gaseous phase.

When the reaction of I with $Cr(CO)_6$ is carried out under an atmosphere of H_2 instead of Ar, disappearance of I proceeds at roughly the same rate. However, large amounts of dark precipitates form (only traces are observed under Ar) and the yield of III is lowered considerably. The solids are soluble only in mineral acids and thus appear to consist of metal oxide species. The gas phase, sampled after 3 h or longer, contained ethane in ~10% yield (based on Nb). Only traces ($\leq 1\%$ yields) of methane, ethylene (but see below), and propane could be detected.[10] The reactions of I with $Cr(^{12}CO)_{6-x}(^{13}CO)_x$ leads to ^{13}C-labeled ethane.[11] For all the other metal carbonyls listed above, no difference in reactivity or products was found for reactions under H_2 compared with under Ar.

The selective formation of a C_2 hydrocarbon is highly significant; with few exceptions, hydrocarbon formation from CO is generally selective for methane or else not very selective at all. It is notable that the reaction of AlH_3 with group 6 metal carbonyls is selective for C_2, but the major product is ethylene (C_2H_4:C_2H_6 ~ 95:5). A mechanism involving a carbenoid intermediate was proposed.[13] The observation here of a C_2 product with a group 6 metal suggests possible mechanistic similarity: i.e., that C_2H_4 is the initial product (either free or complexed) which is efficiently hydrogenated by the system involving I but *not* by AlH_3. In fact, when the gas phase is monitored during the course of the reaction,[14] ethylene comprises a substantial fraction of the C_2 product during early stages. (In a typical run, the ratio of C_2H_4/C_2H_6 was 0.23 after 1 h, 0.09 after 2 h, 0.006 after 5 h.) Similarly, if 1 equiv of C_2H_4 is added to the original reaction atmosphere, it is gradually hydrogenated during the reaction. The fact that hydrogenation continues after all starting material is consumed indicates that the reaction byproducts are responsible for catalytic hydrogenation.[15] Furthermore, when I and $Cr(CO)_6$ are reacted under D_2 the ethane contains zero, one or two deuterium atoms per molecule;[10] this would be consistent with a mechanism where in C_2H_4 is formed initially using only hydrogen derived from I, while hydride derived from atmospheric D_2 becomes involved only in the subsequent hydrogenation.[17]

Reaction of I with $Cr(CO)_6$ under a mixed H_2–CO atmosphere does not lead to any catalysis; instead (as with H_2–C_2H_4)[15] formation of ethane and insoluble metal oxides are both suppressed, and III is formed nearly quantitatively.[17] I reacts with $Mo(CO)_6$ and $W(CO)_6$ in similar fashion (comparable rates and precipitate formation), but with notable differences: the gaseous products (in trace amounts only) are methane for Mo and a mixture of methane and ethane for W; the soluble organometallic product in each case is clearly not III but appears to be a bimetallic species.[20]

Catalytic CO reduction does not appear to be possible with this combination of reagents, because of both the tendency to form unreactive III and the formation of metal oxides rather than free H_2O from the O atom. However, the selective formation of ethane under conditions where the metal hydride species is potentially stable to CO reduction products[1] offers encouragement for further studies along these lines.

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References and Notes

(1) Labinger, J. A. *Adv. Chem. Ser.* **1978,** No. 167, 149–59, and references therein.
(2) Labinger, J. A.; Wong, K. S.; Scheidt, W. R. *J. Am. Chem. Soc.* **1978,** *100*, 3254–5. We suggested this intermediate might be a form of $(HCO)Fe(CO)_4^-$ bonded through the acyl oxygen to Nb, i.e., $(\eta^5\text{-}C_5H_5)_2H_2Nb(\mu\text{-}OCH)Fe(CO)_4$. It is notable that stable complexes incorporating this structural feature, $(\eta^5\text{-}C_5Me_5)_2HZr(\mu\text{-}OCH)ML_n$ (where $ML_n = Cp_2W$, Cp_2NbH), have recently been prepared by attack of a nucleophilic metal hydride on a metal carbonyl.[3]
(3) Wolczanski, P. T.; Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1979,** *101,* 218–20.
(4) Wong, K. S.; Scheidt, W. R.; Labinger, J. A. *Inorg. Chem.* **1979,** *18*, 136–40.
(5) Thermolysis of II (~70 °C under H_2) leads to formation of small amounts of CH_4, C_2H_6, and C_3H_8; as with III, ^{13}CO labeling shows that only the CH_4 comes from CO.[2] The only identifiable metal-containing product is $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, resulting from C_5H_5-ring migration from Nb to Fe.
(6) Reactions in benzene solution, ~0.2 M in each reagent; disappearance of ^1H NMR signals of I used to monitor reaction.
(7) Wong, K. S.; Scheidt, W. R.; Labinger, J. A. *Inorg. Chem.* **1979,** *18,* 1709–12.
(8) Braterman, P. S. "Metal Carbonyl Spectra", Academic Press: New York, 1975; pp 179–198.
(9) It should be noted that the intermediate assigned to C–H bond formation

has only been observed from I and $Fe(CO)_5$. This may result from relative rates of various steps making the steady-state concentration of the corresponding species too low to detect for other metal carbonyls, but it is also conceivable that one or more of these reactions involve a different mechanism.

(10) Reactions under H_2 and mixed atmospheres were carried out in a Fischer–Porter pressure bottle at slightly above 1 atm; gas samples were removed by gas-tight syringe and analyzed using a Hewlett-Packard 5790 gas chromatograph, with a 4-ft, ⅛-in. Porapak P (50–80 mesh) column and flame ionization detector. Isotopic labeling studies were achieved using a Du Pont DP-101 gas chromatograph–mass spectrometer, with a 5-ft, ¼-in Porapak Q (80–100 mesh) glass column, as well as an AEI MS-9 high-resolution mass spectrometer.

(11) Labeled chromium carbonyl (~70–80% ^{13}C by mass spectrometry) was prepared using the procedure recently reported by Darensbourg, wherein CO exchange is catalyzed by tributylphosphine oxide.[12] The mass spectrum of the gas phase after reaction of this labeled compound with I shows clearly that ^{13}CO has been reduced to ethane (peaks at *m/e* 32, 31; exact mass of former, 32.054; calcd for $^{13}C_2H_6^+$, 32.0535). Because the mass spectrum contains peaks at *m/e* 30, 29, . . . resulting from fragmentation of benzene (the solvent in the reaction; small amounts are present in the vapor phase) as well as fragments from the variously labeled ethanes, it is not possible to determine conclusively that *all* the ethane produced comes from CO reduction (note the formation of ethane from an alternate source in II, at higher temperature[5]); however, by making approximate corrections for the benzene-derived peaks we estimate that *at least* 75% of the ethane originates from CO.

(12) Darensbourg, D. J.; Walker, N.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1980,** *102,* 1213–4.

(13) Masters, C.; van der Woude, C.; van Doorn, J. A. *J. Am. Chem. Soc.* **1979,** *101,* 1633–4. Another mechanistic possibility is provided by the recent report (Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979,** *101,* 5421–2) that reaction of CO with $(\eta^5\text{-}C_5Me_5)TaMe_4$ gives $[(\eta^5\text{-}C_5Me_5)MeTaO(OCMeCMe_2)]_x$ via intermediate formation of an acetone complex. The similarities of this system (group 5 metal; exactly two carbons from CO in product; formation of metal oxide species) to that studied here are suggestive.

(14) These reactions were carried out in a vessel connected directly, via a bellows-type gas circulating pump and a gas sampling valve, to a Carle AGC-311 gas chromatograph, using an 8-ft, ⅛-in Porapak column and FID.

(15) Under an atmosphere of 1:1 H_2-C_2H_4, CO reduction is inhibited: only traces of ethane and III, and *no* insoluble material, are formed; instead a clear solution of $(\eta^5\text{-}C_5H_5)_2Nb(C_2H_5)(C_2H_4)$[16] results. This also indicates that hydrogenation of C_2H_4 is not catalyzed by I under reaction conditions.

(16) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974,** 96, 5420-7.

(17) The possibility that these low levels of deuterium incorporation arise from prior exchange of I with D_2 is excluded by the observation (also reported previously[18]) that very little *reversible* exchange occurs at such mild temperatures; rather some decomposition of I with loss of H_2 is found. This may well be a partial cause of the relatively low yields of C_2H_6, since the reaction of I with $Cr(CO)_6$ is fairly slow. Similarly, the direct reaction of I with CO to give III[19] is too slow at these temperatures to account for the observed inhibition of ethane formation or the formation of III in good yield.

(18) Klabunde, U.; Parshall, G. W. *J. Am. Chem. Soc.* **1972,** *94,* 9081-7.

(19) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971,** *93,* 3793-5.

(20) ^1H NMR, IR and mass spectroscopy are consistent with the product from I and $Mo(CO)_6$ being $(\eta^5\text{-}C_5H_5)_2NbHMo(CO)_6$, isoelectronic (and presumably with a similar structure) to II.

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Evidence for an Intermediate in Nucleophilic Substitution of a Thiamin Analogue. Change from First- to Second-Order Kinetics in Sulfite Ion

Sir:

A hallmark reaction of thiamin (I) is nucleophilic substitution by sulfite ion. We recently provided kinetic evidence to show that this process takes place not by an S_N2 but rather by a multistep process:[1] sulfite ion adds to protonated substrate which then eliminates the leaving group (L = a thiazole) to give a resonance stabilized carbocation intermediate III.[2] Addition of a second sulfite ion to III followed by expulsion of the first gives product. For thiamin this sequence is first order in sulfite ion, reactions of the intermediate taking place after the rate limiting step (Scheme I).

Scheme I

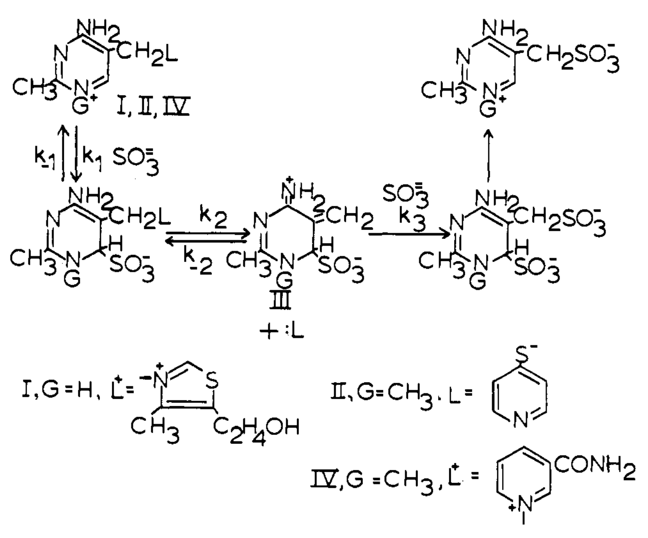

Table I. Apparent Second-Order Rate Constants for Substitution of II by Sulfite Ion at 25.0 °C and 1.0 Ionic Strength[a]

$10^4[II]_0$, M	$10^2[SO_3^{2-}]_{free}$,[b] M	10^4[4-thiopyridone]$_{tot.}$[c] M	10^3k, M^{-1} s^{-1}[d]
0.18	9.80	—	8.50
1.87	9.53	3.66	3.99
1.85	9.40	7.24	2.79
2.00	4.86	8.10	1.65

[a] At pH 9.41 ± 0.02. Reactions followed at 260 nm. [b] Calculated using $pK_a = 6.59$ (1.0 ionic strength). [c] May be converted into the concentration of anion using $pK_a = 8.66$ (1.0 ionic strength). [d] $k_{obsd}/[SO_3^{2-}]_{free}$.

Now we provide evidence to show that an analogue of thiamin undergoes nucleophilic substitution by a similar pathway and that reaction of the second sulfite ion may be rate limiting.

Substrate II has a methyl group bonded to nitrogen (G = CH_3) instead of a proton.[3] The leaving group is the anion of 4-thiopyridone. At low substrate concentration (Table I), the rate of substitution is first order both in substrate and in sulfite ion. Either at high substrate concentrations or when leaving group is added at the start, the rate is retarded.[4] Adding more thiolate ion at the start leads to progressively larger retardations, as much as a 5.2-fold reduction in the apparent second-order rate constant, $k_{obsd}/[SO_3^{2-}]_{free}$ (Table I).[5]

The hetarenethiolate ion leaving group is a powerful nucleophile and competes with sulfite ion for intermediate. That is, formation of intermediate becomes reversible and its capture by a second sulfite ion becomes rate limiting. The equation expressing the pseudo-first-order rate constant for such a sequence may be rearranged to produce eq 1 which is linear.

$$\frac{[SO_3^{2-}]_f}{k_{obsd}} = \frac{k_{-1}k_{-2}[L]_f}{k_1k_2k_3[SO_3^{2-}]_f} + \frac{k_{-1} + k_2}{k_1k_2} \qquad (1)$$

Figure 1 shows a plot of the results in Table I in the form of eq 1. As required by our mechanism, this plot indeed is linear. Moreover, the slope to intercept ratio is a quantity of some significance, being the ratio of the rate constants expressing the ability of thiolate and sulfite ions to compete for intermediate III. Thus, the anion of 4-thiopyridone traps intermediate 250 times faster than sulfite ion.[6]

The good fit of our results to eq 1 allows us to reach another conclusion: thiolate ion does not add in significant amounts to C_6 of II. Hence, thiolate ion successfully competes with sulfite ion for intermediate but not for aromatic substrate, reflecting a difference in kinetic and equilibrium affinities. Such an

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