Table I. Rates of Reaction of B_{12s} with B_{12a}[a]

additives	pH	k/dm^3 mol^{-1} s^{-1}
	4.0	1.5×10^7
CO_2 saturated[b]	~4.0	1.2×10^7
	7.8	1.0×10^7
	8.8	7.8×10^5
10^{-2} M borate buffer	9.1	9.0×10^5
10^{-2} M borate buffer	9.7	1.8×10^5
	10.35	7.7×10^4
	11.1	2.9×10^4

[a] All solutions contained 0.1 M 2-propanol, 6×10^{-5} M B_{12r}, and (0.6–2.4) $\times 10^{-5}$ M B_{12a} and were He saturated; accuracy ± 20%, temperature 22 ± 2 °C. Rates were measured at 390 and 460 nm. [b] CO_2 and not He was used as saturating gas.

although we have no evidence of these; these solutions thus had $\mu \approx 0$.

The results can be summarized as follows. (1) In the acidic range, pH 3.9–4.2, in the presence of 0.1 M 2-propanol, under either He or CO_2, the second-order rate constant is $(1.5 \pm 0.3) \times 10^7$ dm^3 mol^{-1} s^{-1}, in substantial agreement with that reported in the earlier radiolysis study[4] in the acidic range. These results also agree with those from the chemical study when the latter are extrapolated to acidic pH. The rate constant for the term in which eq 3 shows a dependence on $[OH^-]^{-1}$ can, with inclusion[3] of K_a and K_w, be written in the kinetically equivalent form $k[B_{12s}][B_{12a}]$, giving $k = 1 \times 10^8$ dm^3 mol^{-1} s^{-1}. Considering the extrapolations involved and the different ionic strengths, these results too can be considered comparable. (2) At higher pHs, especially pH > pK_a = 7.8, the rate constants decrease markedly as summarized in Table I. In this respect the results agree with the chemical result but not the earlier pulse radiolysis studies. Furthermore, the earlier radiolysis workers[4] who used buffer solutions of nominal pH (5.8–11.0) also saturated them with CO_2; thus they also really worked in comparably acidic solutions (i.e., saturation with excess CO_2 simply caused neutralization of the basic buffering components, and the solutions likely had pHs <7), and all their data refer to conditions where the major species is aquocobalamin, B_{12a}.

Thus these new pulse radiolysis experiments (a) affirm the kinetics results of the chemical study,[2] (b) establish by direct measurement that B_{12s} is much more reactive (by a factor of 10^3) toward B_{12a} than toward B_{12b} (perhaps for the reasons alluded to earlier[2]), in contradiction to the claim[4] that the two react at essentially the same rate, and (c) establish that a simple error in pH control was the likely reason for the published differences.[8]

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Registry No. B_{12s}, 13422-51-0; B_{12a}, 13422-52-1; B_{12b}, 18534-66-2.

References and Notes

(1) (a) Work at both laboratories was supported through the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences program. (b) Visiting scientist at Argonne National Laboratory from the Nuclear Research Centre Negev and the Ben-Gurion University of the Negev, Beer-Sheva, Israel.
(2) E. J. Kaufmann and J. H. Espenson, *J. Am. Chem. Soc.*, **99**, 7051 (1977).
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(5) The radiation chemistry, B_{12r} reductions, and scavenging of $H\dot{O}$ by HCO_2^- and $(CH_3)_2CHOH$ are detailed in the literature.[4,6] The pulse radiolysis experiments were conducted using equipment at Argonne National Laboratory which has been described.[7]
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(8) A. J. Swallow (personal communication) has informed us that he agrees with the acidic nature of solutions used in the original pulse radiolysis experiments and that his laboratory agrees with the findings reported herein.

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Base Catalysis of Ligand Substitution in Metal Carbonyls[1,2]

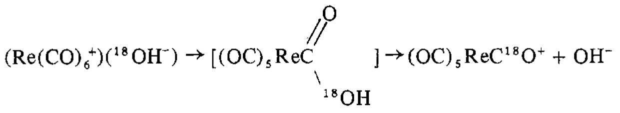
Sir:

Nucleophilic attack at carbon in metal carbonyls has been demonstrated in several different chemical situations. Examples include reaction of metal carbonyls with organolithium compounds[3,4] or Grignard reagents,[5] with amines to form carbamoyl compounds,[6,7] and with azide[8] and ^{18}O exchange of metal carbonyl cations with aqueous base.[9,10] The formation of hydridometal carbonyl species via hydroxide attack at carbonyl carbon is apparently an important pathway in homogeneous Reppe-type catalysis.[11] Nucleophilic attack of hydrides at carbon leads to formation of formyl complexes.[12]

In earlier work we have described the evidence that many ligands, L, in six-coordinate metal carbonyl compounds are capable of labilizing the metal center toward dissociative loss of CO as compared with L = CO.[13,14] This labilization is, for most ligands, specific to the cis position. The purpose of this correspondence is to point out that the ideas of cis labilization and nucleophilic attack at carbon together account for several interesting and important aspects of metal carbonyl reactivities.

As an illustration of the concept involved, consider Scheme I. The parent $Mn(CO)_6^+$ is, from all indications, quite inert with respect to CO dissociation.[13] The attack of CH_3^- at the carbonyl carbon to form the stable compound $Mn(CO)_5C(O)CH_3$ converts the relatively inert metal carbonyl species into one in which the rate of CO dissociation is increased by many orders of magnitude. That is, acetyl is a cis-labilizing ligand relative to CO.

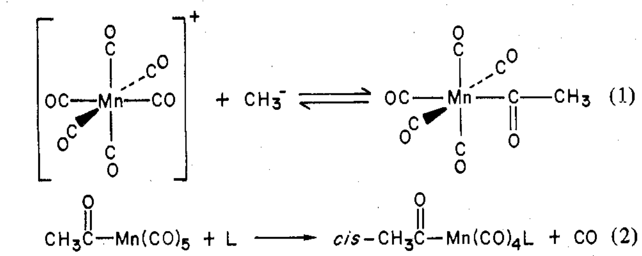
Bases might interact with the carbon atoms of a metal carbonyl to form weak acid–base adducts, without forming a stable product. Such an interaction is presumably involved in the base-catalyzed exchange of ^{18}O between water and metal carbonyls.[9,10]



$$(Re(CO)_6^+)(^{18}OH^-) \rightarrow [(OC)_5ReC(=O)(^{18}OH)] \rightarrow (OC)_5ReC^{18}O^+ + OH^-$$

There are several indications from literature reports that base interaction with metal carbonyls may play a role in ligand substitution processes. The second-order term in the rate law for substitution of CO by another ligand L could be interpreted in terms of an associative interaction between L and carbonyl carbon.[15] In a somewhat different vein, Morris and Basolo interpreted the effect of bases on ligand substitution reactions of $Fe(CO)_2(NO)_2$ in terms of base interaction at carbon.[16] Drew, Darensbourg, and Darensbourg[7] report that $CH_3CNMn(CO)_5^+$ reacts with pyridine to give *fac*-$Mn(CO)_3(py)_3^+$ in several minutes at room temperature, whereas

Scheme I

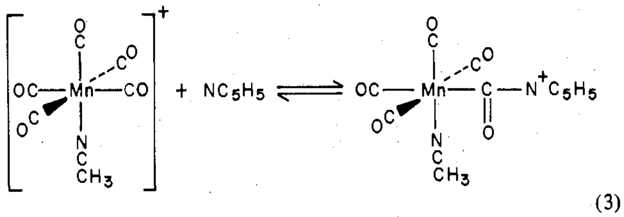


$CH_3C(O){-}Mn(CO)_5 + L \longrightarrow cis\text{-}CH_3C(O){-}Mn(CO)_4L + CO$ (2)

reaction with triphenylphosphine requires 18 h at 30 °C to give $Mn(CO)_5PPh_3^+$.

$(\eta^5\text{-}C_5H_5)Mn(CO)_2NO^+$ reacts rapidly with pyridine to form $(\eta^5\text{-}C_5H_5)Mn(CO)(NO)C_5H_5N^+$, in contrast to a much slower reaction with PPh_3.[17] Pyridine is similarly more reactive in replacing amino-coordinated alanine in *cis*-$BrRe(CO)_3(NH_2CH(CH_3)CO_2H)_2$.[18]

These results can be accounted for by assuming that the nitrogen base interacts with the carbon atom of a cis carbonyl group, forming a weak complex, as in eq 3. There are three possible fates of a complex of this type: (1) A stable carbamoyl complex could be formed by loss of a proton, a reaction known to occur when the nitrogen base is methylamine[6,7] but impossible with the bases used here. (2) There could be dissociative loss of the attacked CO as implied by Morris and Basolo.[16] A reaction of this kind is observed when the base is trimethylamine oxide,[19] which reacts to convert the attacked CO to CO_2, liberating $N(CH_3)_3$. This possibility is excluded in the example at hand by the evidence for $Mn(CO)_5py^+$ as a product in the reaction with pyridine in dilute solution.[7] (3) A ligand remote from the site of attack is labilized; the weak CO–base adduct acts as a strongly cis-labilizing ligand.



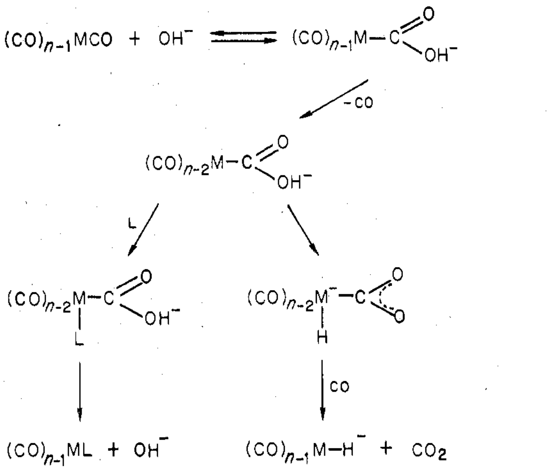
(3)

The proposed mechanism is as follows: The base attacks the carbon atom of a carbonyl cis to acetonitrile, and a rapid equilibrium is established. The CO with bound base becomes a cis-labilizing ligand, leading to rapid dissociation of a ligand cis to it, either CO or acetonitrile (but most likely acetonitrile). The five-coordinate unsaturated intermediate which is formed rapidly adds base. Attack at a carbonyl could occur again, leading to a cis-disubstituted product which, since the base would be expected to be a cis-labilizing ligand in its own right, would lead to loss of the mutually cis CO and incorporation of another molecule of base, giving the observed *fac*-$Mn(CO)_3L_3^+$ product.

A very wide range of cis-labilizing abilities, covering a range of perhaps 10^8 or more, is observed for various ligands.[13] Thus, it is not unreasonable to suppose that ligand dissociation from the transient acid–base adduct of eq 3 is several orders of magnitude faster than in the parent compound. As a result, even though the acid–base formation constant may be too small for the adduct to be observed, the interaction has a substantial effect on the observed kinetics.

Similar mechanisms may operate in other systems. The interaction of metal carbonyls with aqueous base has been of interest in connection with metal hydride formation[11,20] and in applications of phase-transfer catalysis to metal carbonyl substitution processes (Scheme II).[21] Transient formation of a –COOH moiety has the effect, as indicated above, of producing a cis-labilizing ligand. Following CO loss there may be uptake of a ligand present in excess, or elimination of CO_2, forming a metal carbonyl hydride. This elimination should in general be facilitated by—indeed may require—the presence of a coordination vacancy at the metal. The β elimination of butene from di-*n*-butylbis(triphenylphosphine)platinum(II)[22] or from $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(n\text{-}C_4H_9)$[23] is strongly inhibited by excess PPh_3, suggesting that dissociation of this ligand precedes the elimination step in both cases.

Scheme II



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(1) This is part 6 in the series, "Cis Labilization of Ligand Dissociation". For the previous paper, see ref 14.

(2) This research was supported by the National Science Foundation via Research Grant NSF CHE76-17570.

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