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Communications

Evidence for the Formation of (*o*-Phenanthroline)dicarbonylmolybdenum(0)[1]

Sir:

Data obtained through isotopic enrichment studies of *fac*-$(CH_3CN)(phen)Mo(CO)_3$ (phen = *o*-phenanthroline) according to

$$fac\text{-}(CH_3CN)(phen)Mo(CO)_3 + {}^{13}CO \rightarrow fac\text{-}({}^{13}CO)(phen)Mo(CO)_3 + CH_3CN \quad (1)$$

have provided evidence that supports the formation of the four-coordinate intermediate $[(phen)Mo(CO)_2]$.

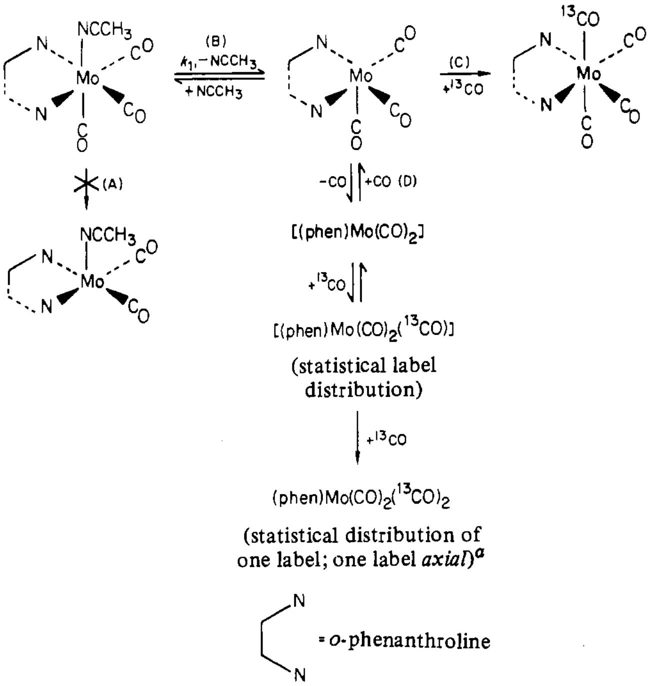
Isotopic enrichment of *fac*-$(CH_3CN)(phen)Mo(CO)_3$ at 0 °C to afford a tetracarbonyl product in which the ^{13}CO label is >95% axial (trans to CO; eq 1) has been reported.[2] This species has also been employed in the delineation of the site of Mo–CO bond breaking in $(phen)Mo(CO)_4$ and the degree of fluxionality in the $[(phen)Mo(CO)_3]$ intermediate thus produced.[2] The data are consistent with 100% axial loss and complete randomization of the carbonyls during the ligand-exchange process.

However, it has not been possible to effect 100% stereoselective labeling of $(phen)Mo(CO)_4$ at the higher temperature of 25 °C. Under the most favorable conditions, ^{13}C FT NMR spectra have indicated that an axial:equatorial ratio of ca. 3:1 was produced. The results contrast dramatically to those observed for $(phen)Cr(CO)_4$, for which 100% stereoselective enrichment was effected at room temperature.[3]

It has also been shown that the principle of microscopic reversibility dictates that, where carbonyl loss is 100% stereoselective, as is true in this case, isotropic enrichment (^{13}CO) will afford a 100% stereoselectively labeled product in which the labeled CO occupies the coordination site created through carbonyl loss, the fluxionality of the intermediate notwithstanding.[4,5] Thus, observed scrambling of the label must take place in a step subsequent to that in which the label is first introduced.

Since in the studies reported here the labeled species were produced under kinetic control, they could not have been produced via a scrambling process in $[(phen)Cr(CO)_3]$ produced subsequently to introduction of the label. It was also demonstrated that no nondissociative scrambling process[6] was accessible under the enrichment conditions employed.

Scheme I



[a] Two equatorial labels as are observed can arise through a second $[(phen)Mo(CO)_3] \rightarrow [(phen)Mo(CO)_2]$ dissociation step, followed by combination of the four-coordinate species with CO.

These facts force consideration of other means through which an equatorial label in $(phen)Mo(CO)_4$ might be introduced. In this context, it is important to note that carbonyl stretching spectra for the enriched materials produced at 25 °C revealed that at no time was it possible to effect complete introduction of the label, and yet $(phen)Mo(CO)_4$ was produced through 100% conversion of the *fac*-$(CH_3CN)(phen)Mo(CO)_3$ precursor. This observation implies that there is a source of ^{12}CO present in the reaction solution, undoubtedly as the result of the dissociation of CO from some chemical species during the enrichment process.

Scheme I illustrates two possible pathways through which the observed equatorial labeling might take place. Of the two possible initial steps, (A) and (B), step A, involving dissociation of CO from *fac*-$(CH_3CN)(phen)Mo(CO)_3$ can be ruled out

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[1] Octahedral Metal Carbonyls. 52. Part 51: ref 2.
[2] Dobson, G. R.; Asali, K. J. *Inorg. Chem.* **1981**, *20*, 3563.
[3] Dobson, G. R.; Asali, K. J. *J. Am. Chem. Soc.* **1979**, *101*, 5433.
[4] Brown, T. L. *Inorg. Chem.* **1968**, *7*, 2673.
[5] Dobson, G. R. *Inorg. Chem.* **1980**, *19*, 1413. It has been shown in this laboratory that $[(phen)Mo(CO)_3]$ is indiscriminate in its reactivity with various incoming nucleophiles for L = PPh_3, P-*n*-Bu_3: Dobson, G. R.; Binzet, N. S., unpublished results.
[6] See, e.g.: Darensbourg, D. J.; Kudaroski, R.; Schenk, W. *Inorg. Chem.* **1982**, *21*, 2488.

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on the basis of experimental evidence. Studies of the rate of dissociation of CH_3CN from this complex, path B (there is no evidence for the formation of a dicarbonyl product which would result from path A), indicate this process to have a first-order rate constant of ca. 1.8×10^{-2} s^{-1} at 15.5 °C. Moreover, while the expected dicarbonyl products, *cis,trans,cis*-(phen)$(L)_2(CO)_2$Mo, are well-known,[7] they are produced only under reaction conditions far more rigorous (>100 °C) than those employed here. The dissociation of CO in competition with that of CH_3CN in *fac*-(CH_3CN)(phen)Mo$(CO)_3$ also is not expected on the basis of both ground-state[8] and transition-state[9] bonding arguments.

There is evidence, on the other hand, which implicates the competitive pathways (C) and (D) (Scheme I) in these systems.

(a) The stereoselectivity of the introduction of the ^{13}CO label is quite temperature dependent, the labeling being highly stereoselective (>95% axial) at 0 °C, but much less so (ca. 75% axial) at 25 °C. This observation would indicate significant differences in the temperature sensitivity, i.e., in ΔH^*, for the processes leading to each geometrical isomer. For competing associative and dissociative paths such as (C) and (D), the dissociative path, which leads to formation of the species containing the equatorial label, will exhibit greater temperature sensitivity, as is observed.[10]

(b) Enrichment studies using various mixtures of $^{13}CO/N_2$ indicate that the fraction of ^{13}CO label incorporation decreases with decreasing ^{13}CO pressure. This observation is consistent with the decreasing accessibility of the associative path (C) relative to a dissociative path such as (D) as the concentration of ^{13}CO decreases.

(c) Evidence for the presence of *two* labels in some labeled molecules, consistent with the accessibility of path D as that which leads to the equatorial enrichment, comes from the observation of a weak band in the carbonyl stretching spectrum of (phen)Mo$(CO)_4$ prepared from *fac*-(CH_3CN)(phen)Mo$(CO)_3$ (25 °C), at 1788 cm^{-1}. This band is attributable to the antisymmetric stretch of the two equatorial ^{13}CO's (B_2 mode in the C_{2v} local symmetry of the complex).[11] No splitting attributable to $^{13}C-^{13}C$ coupling was observed in the ^{13}C FT NMR spectrum of the complex. Such splitting would be indicative of the presence of two labels in the same molecule, rather than two species each containing an axial or equatorial label. However, such splitting also was not observed for (phen)Mo$(CO)_4$ prepared from $Mo(CO)_6$ containing ca. 30 mol % ^{13}CO, statistically distributed,[12] although this complex is more highly enriched than is that prepared from *fac*-(CH_3CN)(phen)Mo$(CO)_3$.

It would appear probable that the dissociation of the second carbonyl is from the apical position of the five-coordinate, square-pyramidal intermediate on the basis both of "cis labilization" arguments[13] and strong π-bonding in the equatorial plane, which should inhibit carbonyl dissociation from such a position.

The proposed mechanism is of interest in its relationship to decomposition of substituted metal carbonyls. For example, it has been suggested that (amine)M$(CO)_5$ complexes decompose via initial amine dissociation, followed by a bimolecular interaction of $[M(CO)_5]$ and (amine)M$(CO)_5$.[14] A successive dissociation mechanism such as is indicated here would also seem reasonable.

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Registry No. *fac*-(CH_3CN)(phen)Mo$(CO)_3$, 15492-80-5; [(phen)Mo$(CO)_2$], 85735-65-5; CH_3CN, 75-05-8; CO, 630-08-0.

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(7) See, e.g.: Houk, L. W.; Dobson, G. R. *Inorg. Chem.* **1966**, *5*, 2119.

(8) See, e.g.: Stolz, I. W.; Sheline, R. K.; Dobson, G. R. *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 1.

(9) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3190.

(10) For competing pathways (similar ΔG^*), ΔH^* is greater for the path with the more positive ΔS^*, i.e., for the dissociative path. See, e.g.: Angelici, R. J.; Graham, J. R. *J. Am. Chem. Soc.* **1966**, *88*, 3659.

(11) Cohen, M. A.; Brown, T. L. *Inorg. Chem.* **1976**, *15*, 1417.

(12) Prepared, in turn, through displacement of tmpa from (tmpa)Mo$(CO)_4$ (tmpa = *N,N,N',N'*-tetramethyl-1,3-diaminopropane) by ^{13}CO: Asali, K. J. Ph.D. Dissertation, 1979.

(13) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380.

(14) Darensbourg, D. J.; Brown, T. L. *Inorg. Chem.* **1968**, *7*, 1679.

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Articles

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Nonadiabaticity in Ruthenium(III)-Titanium(III) Outer-Sphere Electron-Transfer Reactions

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$Ru_2(OAc)_4^+$ is reduced by Ti(III) (at 25 °C, in 1 M $LiCF_3SO_3-HCF_3SO_3$) by a two-term rate law, indicating that both Ti^{3+} and $TiOH^{2+}$ are effective reductants for this oxidant. Rate constants are 2.3×10^2 and 3.4×10^3 M^{-1} s^{-1}, respectively. Tris(pentane-2,4-dionato)ruthenium(III) is reduced by Ti(III), in 1 M LiCl-HCl at 25 °C, by the same general rate law with rate constants of 0.08 M^{-1} s^{-1} for Ti^{3+} and 0.7 M^{-1} s^{-1} for $TiOH^{2+}$. Ti^{3+} is *not* an effective reductant for Ru(III) oxidants that lack delocalized π electrons: we take this as indicating that such reactions would be nonadiabatic.

Previous papers from this laboratory have demonstrated that Ru(III)-Ti(III) redox reactions proceed by both outer-sphere[1] and inner-sphere (bridged)[2] electron-transfer (ET) mechanisms, depending on the ligand coordinated to Ru(III). In the