Correspondence

Octahedral Metal Carbonyls. XXXIV. Ligand Exchange in Monosubstitution Products of Tungsten Hexacarbonyl

AIC400128

Sir:

Equilibrium constants for

$$\mathrm{AW(CO)_5 + L \rightleftharpoons LW(CO)_5 + A} \qquad (1)$$

where A = amine and L = Lewis base coordinating through a P, As, Sb, or Bi donor atom, have been reported by Angelici and Ingemanson (A-I).[1] From data at 35–45° were calculated values of $\Delta H°$ and $\Delta S°$ for A = aniline in toluene solvent. The equilibria exhibited appreciable temperature dependence, K_{eq} increasing with temperature, and thus the calculated changes in enthalpy indicated A–W bonds to be stronger than L–W bonds, although the reported values of K_{eq} indicated the equilibria to favor the formation of products. Consequently, the calculated changes in entropy were highly positive (36–89 cal/deg mol), an unusual result for such a ligand-exchange process. Irreproducibility of data for certain systems was also noted.

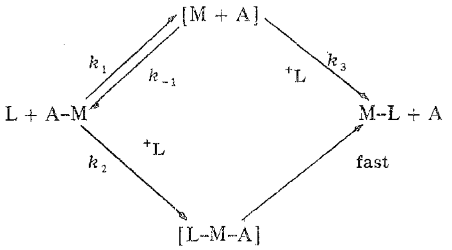
Kinetic studies of reactions of other amine-substituted group VIb metal carbonyl complexes with L

$$\mathrm{A{-}M + L \rightarrow L{-}M + A} \qquad (2)$$

have recently been reported for M = $(C_6H_5)_3PMo(CO)_4$[2] and $Mo(CO)_5$.[3] The reactions proceed *via* a limiting two-term rate law

$$-\mathrm{d[A{-}M]/d}t = k_1\,\mathrm{[A{-}M]} + k_2\,\mathrm{[A{-}M][L]} \qquad (3)$$

consistent with the general overall mechanism (4). For the



(4)

dissociative path of (4), the steady-state rate expression is (5),

$$-\mathrm{d[A{-}M]/d}t = k_1k_3\,\mathrm{[A{-}M][L]}/(k_{-1}\,\mathrm{[A]} + k_3\,\mathrm{[L]}) \qquad (5)$$

which, with L present in large excess and [A] = 0, reduces to the observed term in (3).

Studies of the ability of L and A to compete for intermediate M demonstrated a lack of discrimination of M for A or L, as reflected in the "competition ratios," k_{-1}/k_3, which were found to vary over a narrow range (less than fivefold).[2,3] Further, Covey and Brown, in an attempt to measure K_{eq} for their reactions noted that, after several days, only the $LMo(CO)_5$ product was present in the equilibrating mixtures, even for large ratios of [A] to [L].[3]

Kinetic studies of equilibrium 1 were in progress in this laboratory at the appearance of the definitive study of the analogous Mo system.[3] Since our initial results are markedly similar,[4] the investigation has been terminated. However, one observation is worthy of note: $LW(CO)_5$ complexes fail to react to an observable extent (ir spectral monitor) over several days within the temperature range employed by A-I.[1] Further, kinetic examination of $(C_6H_5)_3Sb{-}W(CO)_5$,[5] in which it is probable that the L–W bond is relatively weak,[6] revealed it to react with loss of CO and/or triphenylstibine *via* a first-order rate law (k_1 = 1.27 (6) × 10^{-4} $\mathrm{sec^{-1}}$) at 140.0°. These results demonstrate that under the conditions employed by A-I, *the reaction 1 must necessarily proceed to completion.*

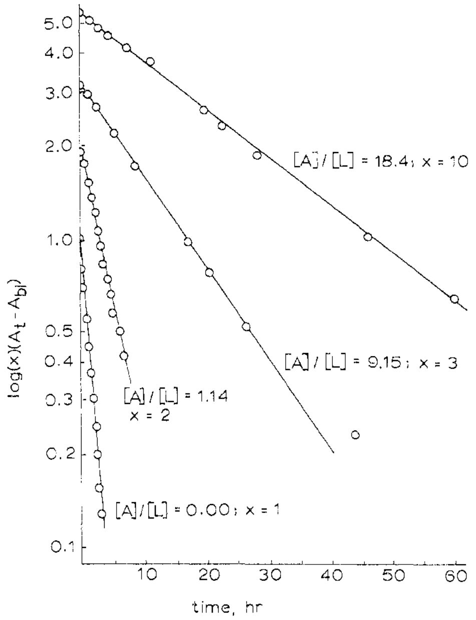


Figure 1. Plots of $(\log x)(A_t - A_{bl})$ *vs. t* for reactions of (aniline)-$W(CO)_5$ with aniline–triphenylphosphine (A–L) in toluene at 35.4°. The ratio [A]/[L] is given. The arbitrary multiplicative constant, *x*, is employed for clarity of the graphical presentation.

It appeared probable for $W(CO)_5$, as for $(C_6H_5)_3PMo(CO)_4$[2] and for $Mo(CO)_5$,[3] that $k_{-1} \approx k_3$ (eq 5); in the presence of large excesses of A, the conditions under which the equilibrium studies were carried out,[1] $k_{-1}\,[A] >> k_3\,[L]$, and thus the rate of formation of $LW(CO)_5$ would be reduced substantially. The extent of inhibition of the reaction of (ani-

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[1] R. J. Angelici and C. M. Ingemanson, *Inorg. Chem.*, **8**, 83 (1969).

[2] C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, **12**, 1286 (1973).

[3] W. D. Covey and T. L. Brown, *Inorg. Chem.*, **12**, 2820 (1973).

[4] Kinetic studies were carried out, except as noted, as described in ref 1. The reaction of (aniline)$W(CO)_5$ with triphenylphosphine in toluene proceeds *via* rate law (3), consistent with mechanism (4). The observed rate constants are 10^4k_1 = 1.98 (6) (44.8°), 5.42 (7) (54.8°), 16.9 (4) (65.0°) $\mathrm{sec^{-1}}$; 10^4k_2 = 25.2 (12) (44.8°), 50.7 (14) (54.8°), 136 (6) (65.0°) M^{-1} $\mathrm{sec^{-1}}$. The activation parameters are $\Delta H_1^{\ddagger}$ = 22.1 (14) kcal/mol, $\Delta S_1^{\ddagger}$ = –6.4 (46) cal/deg mol; $\Delta H_2^{\ddagger}$ = 17.2 (28) kcal/mol, $\Delta S_2^{\ddagger}$ = –18.1 (74) cal/deg mol. Limits of error (in parentheses) are one standard deviation.

[5] The reaction of $(C_6H_5)_3Sb{-}W(CO)_5$ with 2,2′-dipyridyl (dipy) in mesitylene, for which the exclusive product is (dipy)$W(CO)_4$, was studied as described by G. R. Dobson and A. J. Rettenmaier, *Inorg. Chim. Acta*, **6**, 507 (1972). The accidentally degenerate (A_1 + E) carbonyl stretching modes of the substrate (*ca.* 1950 $\mathrm{cm^{-1}}$) were monitored.

[6] Available evidence indicates M–L bond strengths in such complexes to vary as M–P > M–As > M–Sb > M–Bi; among relevant references are D. R. Powers, G. C. Faber, and G. R. Dobson, *J. Inorg. Nucl. Chem.*, **31**, 2970 (1969); R. A. Brown and G. R. Dobson, *ibid.*, **33**, 892 (1971).

line)LW$(CO)_5$ with triphenylphosphine in toluene at 35.4° was studied for several ratios of [A] to [L].[7] The resulting plots of (log x)($A_t - A_{\text{blank}}$) *vs.* t, exhibited in Figure 1, indicate reaction 2, M = W$(CO)_5$, to be markedly inhibited by added amine.[8] In the presence of 10-20-fold excesses of amine the reactions *fail to attain equilibrium over the time allowed for equilibration by A-I* (2 days).[1] The activation parameters are readily explicable on this basis: the reactions proceed further toward equilibrium at higher temperature, resulting in the previously discussed temperature sensitivity of "K_{eq}."

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Registry No. (Aniline)W$(CO)_5$, 16969-72-5; triphenylphosphine, 603-35-0.

Supplementary Material Available. A table of all rate observations will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1790.

(7) Specific ratios of [A] to [L] were not given in ref 1. However, from the concentration ranges of amine and L employed in that study ([amine], (100-1600) × 10^{-4} *M*; [L], (2-100) × 10^{-4} *M*) and from the magnitudes of the reported values of K_{eq}, it can be inferred that 10-20-fold excesses of amine relative to triphenylphosphine conservatively represent conditions employed in those studies.

(8) For triphenylstibine at an [A] to [L] ratio of 9.90, $t_{1/2}$ was observed to be 22.2 (2) hr.

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Crystal and Molecular Structure of Tris(ethyl thioxanthato)cobalt(III). A Reinvestigation

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Sir:

There has been considerable interest in transition metal 1,1-dithiolate complexes, especially tris-chelate compounds.[1-3] Attention has focused on iron(III) complexes of the kind $Fe(S_2CY)_3$ (Y = NR_2, OR, SR) largely because of temperature- and pressure-dependent magnetic studies that have been interpreted[4,5] in terms of a spin equilibrium between two energetically similar ground states of symmetries ^6A and ^2T.[6] There is, morever, firm structural evidence correlating the Fe-S bond lengths in these compounds with their magnetic moments,[3] both of which depend not only upon temperature and pressure but also upon the substituent Y.[5] The mean Fe-S distance in $Fe(S_2CY)_3$ compounds can vary from ~2.29 to 2.42 Å depending upon the magnetic moment. Low-spin ($\mu_{250°} \approx 2.4$-3.0 BM) compounds with bond lengths of 2.297-2.316 Å occur for Y = SR,[7] OR,[8] and NMePh[9] whereas high-spin ($\mu_{250°} \approx 6$ BM) molecules having Fe-S distances of 2.40 Å or larger occur for Y = $N(CH_2)_4$[9] and N(*t*-Bu)$_2$.[10] The analogous cobalt(III) complexes, $Co(S_2CY)_3$, which are all spin paired (^1A ground state), have metal-sulfur bond lengths of ~2.26-2.27 Å,[11] slightly shorter than low-spin iron(III) compounds. It was therefore surprising when the structure of "$Co(S_2CSEt)_3$" was reported to have a mean Co-S bond length of 2.398 (1) Å.[12] This distance is nearly 0.1 Å larger than the value found for $Fe(S_2CS$-*t*-$Bu)_3$,[7] which has an isomorphous cobalt(III) analog with nearly identical unit cell parameters (Table I), raising the possibility that a substantial metal-ligand bond length change might occur without a concomitant change in spin state. Since this possiblity seemed most unlikely to us, and in view of our previous work on $Co(S_2CSR)_3$ and related compounds,[13] we have reinvestigated the structure of tris(ethyl thioxanthato)cobalt(III).

Dark green-black crystals of $Co(S_2CSEt)_3$ were prepared as described earlier[13] and examined by precession photography. The triclinic lattice[12] was confirmed. Using several high-angle reflections centered about the Kα_1 line on a Picker FACS-I-DOS diffractometer, the lattice parameters were refined by a least-squares method. The discrepancy (Table I) between our results and those reported previously[12] encouraged us to collect a full set of intensity data with Mo Kα radiation. The data were obtained and reduced in the usual manner[14] except that the diffractometer was newly equipped with a highly oriented single-crystal graphite monochromator. Using the atomic parameters published originally,[12] the structure was refined by full-matrix anisotropic least-squares methods.[14] Hydrogen atoms were assigned isotropic thermal parameters. The final agreement factors are $R_1 = 0.037$ and $R_2 = 0.044$ based on 6514 observed ($F^2 > 3\sigma(F^2)$) reflections. Tables of the final atomic parameters, selected bond lengths and angles, and a list of observed and calculated structure factor amplitudes are available.[15]

The structure of $Co(S_2CSC_2H_5)_3$ is very similar to that reported previously[12] with two major differences. The cobalt-sulfur distances range from 2.257 (1) to 2.276 (1) Å with a mean (σ mean) of 2.266 (7) Å, and the mean S-Co-S angle is 76.2 (1)°. These results are in close agreement with structural parameters for other tris(1,1-dithiolato)cobalt(III) complexes[11] but differ significantly from the mean

(1) D. Coucouvanis, *Progr. Inorg. Chem.*, 11, 233 (1970).

(2) R. Eisenberg, *Progr. Inorg. Chem.*, 12, 295 (1970).

(3) J. G. Leipoldt and P. Coppens, *Inorg. Chem.*, 12, 2269 (1973), and references cited therein.

(4) A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc., Ser. A*, 280, 235 (1964).

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(6) There has been some discussion about this interpretation, as mentioned in ref 3.

(7) D. F. Lewis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, 11, 823 (1972).

(8) B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 45 (1970).

(9) P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1163 (1972).

(10) B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 1517 (1968).

(11) (a) T. Brennan and I. Bernal, *J. Phys. Chem.*, 73, 443 (1969); (b) S. Merlino, *Acta Crystallogr., Sect. B*, 24, 1441 (1968); (c) S. Merlino, *ibid.*, 25, 2270 (1969).

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(13) D. F. Lewis, S. J. Lippard, and J. A. Zubieta, *J. Amer. Chem. Soc.*, 94, 1563 (1972).

(14) K. M. Melmed, T. Li, J. J. Mayerle, and S. J. Lippard, *J. Amer. Chem. Soc.*, 96, 69 (1974).

(15) See paragraph at end of paper regarding supplementary material.