reducing agents capable of reducing up to 3.33 mol of gold(III) to the elemental state. This is in striking contrast to the previously reported reduction of gold(III) to gold(I) by 3 mol of cysteine.[7] The apparent thermodynamic discrepancy that cystine is a better reducing agent results from the ability of cysteine to stabilize the resulting gold(I) complex and remove it from solution. The oxidation of colloidal gold and $KAu(CN)_2$ to gold(III) by oxygen in the presence of penicillamine was recently demonstrated by Brown et al.[6] However, the reactions reported here are thermodynamically favorable and kinetically facile in the reverse direction. It is becoming clear that the redox reactions of gold compounds containing sulfur ligands comprise a rich chemistry and that careful monitoring of the oxidation states of sulfur as well as gold is necessary to define such systems.

Although the oxidation of disulfides by $KAuBr_4$ is not unexpected from a thermodynamic standpoint, given the strong oxidizing ability of gold(III) halides,[1,14] the possibility has surprisingly not been considered in the context of the biological chemistry of gold.[1] Ironically, purple deposits of colloidal gold on the skin, a keratinous tissue rich in disulfides, are quite common among gold chemists and probably result from the reaction described here. More significantly, this reaction may play an important role in the toxicity of gold(III) which precludes its use as in chrysotherapy.[2,3] The oxidation of protein disulfides by gold(III) will disrupt the secondary and tertiary structure of a protein, altering and probably preventing its normal biological function. In fact, a recent survey of enzyme inhibition by gold complexes show gold(III) to be a much more potent inhibitor than gold(I) at equimolar concentrations.[1] Oxidized glutathione, a hexapeptide containing a disulfide moiety and insulin, and a protein with three disulfides but no methionine or free sulfhydryl groups both rapidly reduce $AuCl_4^-$ and $AuBr_4^-$. The structural consequences of these reactions are being investigated and will be reported elsewhere.

Registry No. CySSCy, 56-89-3; (hCy)SS(hCy), 870-93-9; PaSSPa, 20902-45-8; TgSSTg, 54495-24-8; $KAuBr_4$, 14323-32-1; Au, 7440-57-5; $CySO_3H\cdot HBr$, 74562-84-8; $(hCy)SO_3H$, 504-33-6; $PaSO_3H$, 23400-34-2; TgOH, 492-61-5; NaSTg, 10593-29-0; TgSH, 7534-35-2.

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(14) Puddephatt, R. J. "The Chemistry of Gold"; Elsevier: Amsterdam, 1978; pp 203–208.

Contribution No. 3470 from the Department of Chemistry,
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Mobility of the μ_3:η^2-CO Ligand in $Cp_3Nb_3(CO)_7$

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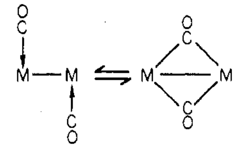
Received February 14, 1980

Migration of carbonyl ligands about the periphery of a metal cluster is a common phenomenon and one which may be relevant to the migration of chemisorbed CO to sites of active chain growth in certain heterogeneous Fischer–Tropsch reactions. To date, migration within molecules has been observed for carbonyls which are bound in terminal μ_2:η^1 or μ_3:η^1 modes,[1] and the low activation energies observed may be due to the compensatory nature of the physical mechanism: concerted processes (eq 1) maintain an invariant valence-electron count at each metal. Some of the more reactive sites on clean metal surfaces are the nonplanar irregularities termed "steps" and "kinks".[2] Here, η^2 binding of CO (via both carbon and oxygen) to an angular array of metal atoms is likely; this represents a potential precursor state both to CO dissociation and to hydrogenation of the CO bond. Since the spectroscopic and structural tools available to the molecular chemist are more definitive of structure and dynamics than those currently employed by surface chemists,[2] compounds containing η^2 carbonyls are a potentially rich source of information concerning chemisorbed CO. Our earlier attempt[3] to observe migration of the μ_2:η^2-CO ligand in $Mn_2(CO)_5(Ph_2PCH_2PPh_2)_2$ yielded a lower limit (15.6 kcal/mol) on $\Delta G^\ddagger$ for such a process; this relatively high barrier to migration can be attributed to the 18 e → 16 e transformation associated with attaining the transition state. We report here the first observation of mobility of a six-electron-donor carbonyl ligand.



(1)

Experimental Section

All operations were carried out under a nitrogen atmosphere in solvents dried with NaK alloy. NMR spectra (^1H and ^{13}C) were recorded on Varian XL-100 (FT) and HR-220 spectrometers. Rate constants were determined by line-shape analysis using the program DNMR;[4] activation parameters were derived from a least-squares fit of the resulting rate constants.

$(C_5H_4R)Nb(CO)_4$ (R = H, Me). This procedure is a modification of an earlier report.[5] $NbCl_5$ (4 g, 0.015 mol) was dissolved in 30 mL of 1,2-dimethoxyethane (dme) and placed in the 400-mL glass liner of a high-pressure bomb. To this was added Na/K alloy (3.5 mL, 0.09 mol) and a stir bar. The liner was placed in the bomb, and the reaction was stirred under CO (100 atm, 1.2 mol) at 25 °C for 24 h. The resulting solution of $Nb(CO)_6^-$ [ν(CO) at 1853 cm^{-1}] was reacted *slowly* with a THF solution of $Hg(C_5H_4R)Cl$ (R = H, Me) (0.02 mol), made from the reaction of $HgCl_2$ (5.44 g, 0.02 mol) and $Na(C_5H_4R)\cdot dme$ (0.02 mol) in THF; this reaction was marked by gas evolution and precipitation of Hg. The reaction solution was filtered and the filtrate taken to dryness. The solid residues were placed in a sublimer. Red crystals of $(C_5H_4R)Nb(CO)_4$ sublimed at 65 °C (0.001 torr); yield 30% based on $NbCl_5$.

$(C_5H_4R)_3Nb_3(CO)_7$ (R = H, Me). $C_5H_5Nb(CO)_4$ (0.12 g, 0.4 mmol) was dissolved in 40 mL of hexane (saturated solution) and placed in a toroidal reactor.[6] The solution was photolyzed (550-W medium-pressure Hg lamp) for 20 min with a N_2 flow passing through the solution. After photolysis the solution was taken to dryness and the solid residue placed in a sublimer. Unreacted $(C_5H_5)Nb(CO)_4$ was sublimed away at room temperature (1 mm). $(C_5H_5)_3Nb_3(CO)_7$ was left unsublimed in 95% yield at 70% conversion. A similar procedure was employed for synthesis of $(C_5H_4Me)_3Nb_3(CO)_7$.

Results and Discussion

We have examined the photochemistry of $(C_5H_4R)Nb(CO)_4$ (R = H, CH_3) as an extension of our earlier work with $CpV(CO)_4$.[6] In hexane, irradiation of $CpNb(CO)_4$ yields $Cp_3Nb_3(CO)_7$, an asymmetric trimer whose structure (I) has been established independently by Herrmann, Ziegler, Weidenhammer, and Biersack;[7] the molecule contains no elements of symmetry. The ^1H NMR spectrum of $(C_5H_5)_3$-

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(1) Band, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639.

(2) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

(3) Caulton, K. G.; Adair, P. *J. Organomet. Chem.* **1976**, *114*, C11. A η^2-carbonyl has also been identified in $Cp_2Nb(CO)_3MoCp$: Pasynskii, A.; Skripkin, Y.; Eremenkov, I. L.; Kalinnikov, V.; Aleksandrov, G.; Andrianov, V. G.; Struchkov, Y. *J. Organomet. Chem.* **1979**, *165*, 49.

(4) Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN.

(5) Werner, R. P. M.; Filbey, A. H.; Manastyrskyj, S. A. *Inorg. Chem.* **1964**, *3*, 298.

(6) Lewis, L.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 1840.

(7) Herrmann, W. A.; Ziegler, M. L.; Weidenhammer, K.; Biersack, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 960.

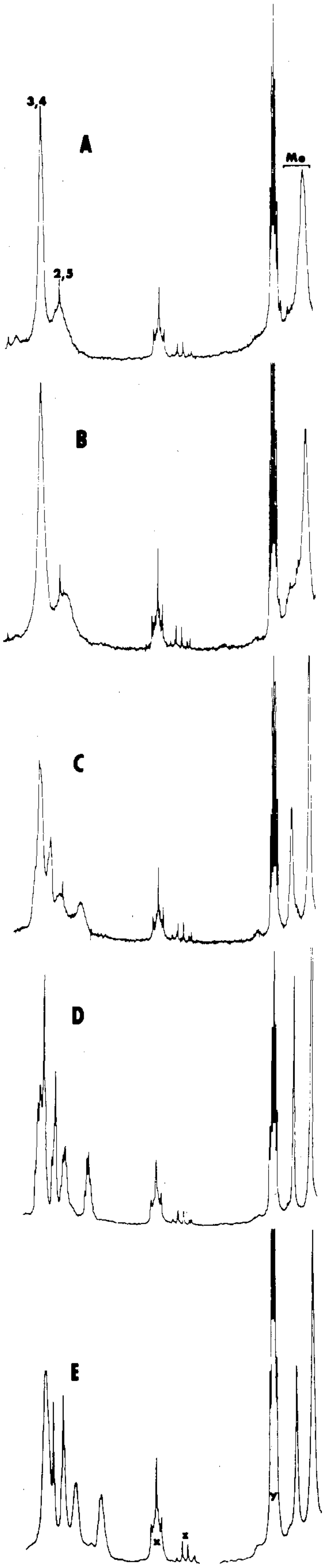
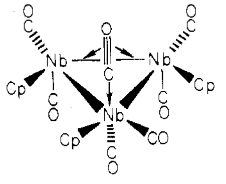
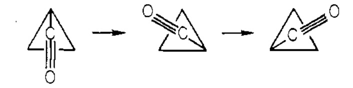


Figure 1. 100-MHz ^{1}H NMR spectra of $(C_5H_4CH_3)_3Nb_3(CO)_7$ in $C_6D_5CD_3$ at various temperatures. Ring protons appear at left and methyl protons at right. Impurity peaks marked "X", "Y", and "Z" are THF, $C_6D_5CD_2H$, and Et_2O, respectively. Spectral changes are reversible with temperature: (A) +60 °C, (B) +49 °C, (C) +26 °C, (D) −16 °C, (E) −56 °C.



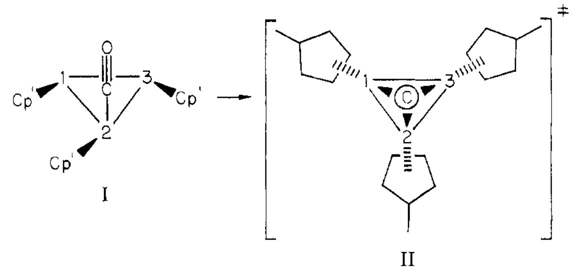
I

$Nb_3(CO)_7$[8] at 16 °C (220 MHz in C_6D_6) consists of two resonances at δ 4.96 and 4.83 of relative intensity 1:2. The cyclopentadienyl singlet evident above 48 °C unequivocally establishes the occurrence of *some* migratory process (eq 2)



(2)

of the μ_3:η^2-CO ligand in I to all metal centers; this process is a necessary but not sufficient condition for averaging all three C_5H_5 rings of I. The mechanistic details of this rearrangement are better sensed by the diastereotopic protons of the methylcyclopentadienyl ligand.[9] Note that substitution of one methyl on each ring of I yields a ground-state geometry which has 12 nonequivalent ring protons. The coalescence of the methyl resonances of $(C_5H_4CH_3)_3Nb_3(CO)_7$[10] in the variable-temperature ^{1}H NMR spectra of $(C_5H_4CH_3)_3Nb_3(CO)_7$ (Figure 1) is due in part to the degenerate rearrangement of the μ_3:η^2-CO ligand shown in eq 2. By 60 °C, the 3,4 ring protons[11] have almost completed their coalescence while the 2,5 protons have begun to sharpen to a single signal.[12] This permits the conclusion that the μ_3:η^2-CO ligand motion which contributes to the time averaging of the three ring centers, the ring methyls, and the niobium atoms simultaneously produces a time-averaged mirror plane perpendicular to each C_5 ring plane; in view of the asymmetric character of the $[CpNb(CO)_2]_3$ framework to which the μ_3:η^2-CO ligand is attached, a second dynamic process is thus implied (see below). A line-shape analysis of the methyl resonances in Figure 1 yields an Arrhenius E_a of 17 kcal/mol (log A = 13.6); the coalescence observed for $(C_5H_5)_3Nb_3(CO)_7$ displays similar energetics. Rearrangement of I to species II, of C_{3v} symmetry, accomplishes the observed averaging of ring protons.[13] Since



I

II

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(8) The three major terminal-CO infrared absorptions observed in solution closely resemble those of the solid (with an increase of 6–13 cm^{-1} on going into solution). This suggests a solution structure identical with that in the solid.

(9) Nuclei attached directly to niobium (^{93}Nb, 100% $I = {}^9/_2$) experience quadrupolar broadening to the extent that fluxional processes are better detected by using more remote nuclei. The ring carbons are broad (60 Hz) in $(C_5H_4Me)_3Nb_3(CO)_7$ at −15 °C; the carbonyl carbons are nearly 3 times broader at ~247 ppm. See also: Wong, K. S.; Scheidt, W. R.; Labinger, J. A. *Inorg. Chem.* **1979**, *18*, 136.

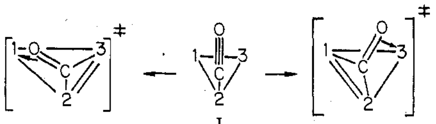
(10) The infrared spectrum of this compound is identical with that of $(C_5H_5)_3Nb_3(CO)_7$ in the region 1600–2100 cm^{-1}.

(11) The chemical shift assignment of the 2,5 and 3,4 protons could be reversed with no consequence to the arguments we present concerning rearrangement of I.

(12) Since the dynamic NMR effects occur in a temperature range which brackets 25 °C, the spectrometer frequency has a dramatic effect on the appearance of the spectrum of $(C_5H_4CH_3)_3Nb_3(CO)_7$. At 60 MHz, the spectrum resembles that in Figure 1B, while at 220 MHz (and at the usual probe temperature of 16 °C), the spectrum resembles Figure 1D.

(13) We assume rotation of the $C_5H_4CH_3$ ring about an axis from its center to the attached niobium which is rapid on the NMR time scale; slow rotation has, to our knowledge, never been observed.

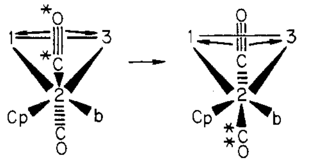
the process I → II involves conversion of the μ_3:η^2-CO to a two-electron-donor μ_3 bridge, it may be accompanied by the formation of two Nb=Nb double bonds (delocalized over the metal triangle). Structures IIIa and IIIb represent alternative



IIIa I IIIb

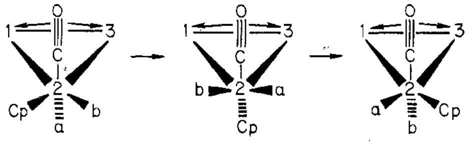
structures which accomplish the observed kinetic symmetrization while requiring the formation of only one Nb=Nb bond. It is notable that the four-electron-donor binding geometry in III has not been observed for CO, although it is known for isoelectronic C=CH$_2$.[14]

At a temperature of 26 °C, the μ_3:η^2-carbonyl rearrangement shown in eq 2 has been slowed, yet some dynamic process still occurs to yield three rather than the six resonances for the 2 and 5 ring protons expected for structure I. A process such as eq 3, which effects transfer of the μ_3:η^2-CO functionality to the opposite face of the triangle, yields a time-average mirror plane *coincident* with the Nb$_3$ plane. In spite of the successful prediction of three 2,5 proton chemical shifts, this process is inconsistent with the observed spectra since it requires *three* distinct methyl resonances.



(3)

On the other hand, the local deformation process in eq 4 generates a time-averaged mirror plane *perpendicular* to the Nb$_3$ triangle. While this generates the observed three chemical shifts for the 2 and 5 protons, it does so in a curious fashion. The ring protons on Nb(2) yield an AA′BB′ spin system as a result of the mirror symmetry of IV. The rings on Nb(1) and Nb(3) are equivalent, but each is a CDEF spin system, containing more lines than the AA′BB′ set. It follows that the 2,5 proton resonance associated with Nb(2) should be notably better resolved (i.e., "taller" or "sharper") than that (those) on the remaining rings. This conforms to the spectra observed at −56 °C (see also the expanded spectrum in Figure 2). We assign multiplets a and b to the 3,4 and 2,5 protons, respectively, on Nb(2). Multiplets c–f comprise the CDEF spin systems of the remaining rings.[15] The rapid occurrence of the process in eq 4 also explains the observation of two, not three, methyl resonances at −56 °C; this process begins to slow perceptibly at −78 °C.



(4)

IV

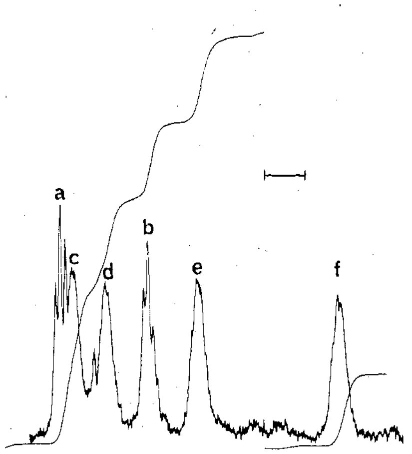


Figure 2. Expanded spectrum of the ring protons of (C$_5$H$_4$CH$_3$)$_3$Nb$_3$(CO)$_7$ in C$_6$D$_6$ at 220 MHz and 16 °C. Horizontal bar indicates 20 Hz.

Our ability to rule out facile face-to-face transfer of the μ_3:η^2-CO functionality (eq 3) below 26 °C speaks for the stability of this unit and more particularly for the enhanced activation energy of the required 6 e → 2 e donor interconversion (transition state in eq 3). This result from the low-temperature process suggests that structure III may be preferable to II for the μ_3:η^2-CO rearrangement in eq 2.

Several recent efforts to achieve homogeneous variants of Fischer–Tropsch hydrogenations have pointed to the importance of metal–oxygen bonding to the activation of CO.[16] Heterogeneous Fischer–Tropsch reactions, including methanation, have been proposed to proceed through surface carbide intermediates resulting from dissociative CO chemisorption. Since these features are either present or nascent in I (ν(CO) = 1330 cm^{-1}),[7] the reactivity of this cluster toward H$_2$ is of interest. Preliminary observations show the production of methane, ethane, and ethylene from (C$_5$H$_4$R)$_3$Nb$_3$(CO)$_7$ (R = H or Me) under mild conditions (80 °C, 0.9 atm of H$_2$ in benzene or toluene). We will describe these results in detail when mechanistic studies are complete.

Acknowledgment. We thank Professor Herrmann for a preprint describing the crystal structure of (C$_5$H$_5$)$_3$Nb$_3$(CO)$_7$ and the National Science Foundation (Grant CHE 77-10059) for financial support. Douglas Plautz is acknowledged for his contributions to the synthetic work.

Registry No. (C$_5$H$_5$)Nb(CO)$_4$, 12108-03-1; (C$_5$H$_4$Me)Nb(CO)$_4$, 32984-99-9; (C$_5$H$_5$)$_3$Nb$_3$(CO)$_7$, 72228-91-2; (C$_5$H$_4$Me)$_3$Nb$_3$(CO)$_7$, 74381-16-1.

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[14] Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415. A close approximation to this binding mode exists in HFe$_4$(CO)$_{13}^-$: Manassero, M.; Sansoni, M.; Longoni, G. *J. Chem. Soc., Chem. Commun.* **1976**, 919.

[15] These assignments are consistent with the high-temperature chemical shifts: e.g., the broad ring proton resonance in Figure 1A is the average of peaks b, e, and f. Also, the more rapid coalescence of peaks a, c, and d is a consequence of their more similar chemical shifts.

[16] Manriquez, J.; McAlister, D.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716. Demitras, G. C.; Muetterties, E. L. *Ibid.* **1977**, *99*, 2796. Huffman, J. C.; Stone, J. G.; Krusell, W. C.; Caulton, K. G. *Ibid.* **1977**, *99*, 5829.

Correspondence

Volumes of Activation and Mechanistic Assignments in Octahedral Substitution

Sir:

Langford[1] has raised the question of the contribution of nonreacting ligands to volumes of activation (ΔV^*) in octahedral substitution—a topic I had previously remarked upon briefly[2] but which clearly requires further commentary in the broad context of mechanistic assignment.

First, as a matter of historical accuracy, measurement of ΔV^* for the Cr(H$_2$O)$_6^{3+}$ water-exchange reaction[3] was made for the specific purpose of seeking *independent evidence* for the possibility, already apparent to us from consideration of

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[1] Langford, C. H. *Inorg. Chem.* **1979**, *18*, 3288.

[2] Lo, S. T. D.; Sisley, M. J.; Swaddle, T. W. *Can. J. Chem.* **1978**, *56*, 2609.

[3] Stranks, D. R.; Swaddle, T. W. *J. Am. Chem. Soc.* **1971**, *93*, 2783.