54.1; H, 8.18. Found: C, 53.4; H, 8.33.

Actually, the formation of a metal–metal bond, as was proposed[4] to be present in "$[Mo(CNCMe_3)_4Cl]_2$", from the reaction of a molybdenum monomer with excess isocyanide ligand runs counter to the overwhelming evidence that Mo–Mo bonds undergo facile cleavage upon reaction with isocyanides.[9,10] Accordingly, we would not expect "$[Mo(CNCMe_3)_4Cl]_2$" to be stable in the presence of an excess of *tert*-butyl isocyanide.

This result turns out to be of additional significance since we find that the cyclic voltammogram[11] of a solution of $[Mo(CNCMe_3)_6Cl]Cl$ in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane is characterized by a single oxidation, $[Mo(CNCMe_3)_6Cl]^+ \rightarrow [Mo(CNCMe_3)_6Cl]^{2+} + e^-$, with an $E_{1/2}$ value for the couple (+0.60 V vs. SCE) that is the same as that we had attributed[1] to the species $[Mo(CNCMe_3)_6]^{2+,3+}$. In other words, this couple is identical with that which appears in the cyclic voltammogram of $[Mo(CNCMe_3)_7](PF_6)_2$ following exhaustive electrolysis at +1.2 V, i.e., at a potential anodic of the oxidation $[Mo(CNCMe_3)_7]^{2+} \rightarrow [Mo(CNCMe_3)_7]^{3+} + e^-$ ($E_{1/2} = +1.12$ V vs. SCE).[1] In accord with this result we find that the X-band ESR spectrum[11] of a dichloromethane glass (−160 °C) containing the paramagnetic cation $[Mo(CNCMe_3)_6Cl]^{2+}$ is identical with that of the species with $E_{1/2} = +0.60$ V, which is formed[1] upon electrolyzing $[Mo(CNCMe_3)_7](PF_6)_2$. This ESR spectrum is in turn very similar to that which is shown in Figure 2 of ref 1 and which characterizes the related methyl isocyanide complex. Accordingly, it is now clear that in the case of the complexes $[Mo(CNR)_7](PF_6)_2$ ($R = CH_3$, C_6H_{11}, or CMe_3) and $[Mo(CNR)_6PR'_3](PF_6)_2$ ($R = CH_3$, C_6H_{11}, or CMe_3 and $R' = Et$ or *n*-Pr), the species that are formed upon ligand loss (either RNC or PR'_3) following the one-electron oxidation of the parent complex are not the species $[Mo(CNR)_6]^{3+}$ but rather $[Mo(CNR)_6Cl]^{2+}$. A similar explanation presumably holds in the case of the properties of the analogous tungsten complexes $[W(CNR)_7](PF_6)_2$ ($R = C_6H_{11}$ or CMe_3) and $[W(CNCMe_3)_6(PR'_3)](PF_6)_2$ ($R' =$ *n*-Pr or *n*-Bu).[1]

The generality of this phenomenon in the isocyanide chemistry of molybdenum is established by measurements on the related phenyl isocyanide complexes $[Mo(CNPh)_7](PF_6)_2$[12] and $[Mo(CNPh)_6Cl]Cl$.[13,14] The electrolysis of dichloromethane solutions of $[Mo(CNPh)_7](PF_6)_2$ at potentials anodic of that necessary for the one-electron oxidation $[Mo(CNPh)_7]^{2+} \rightarrow [Mo(CNPh)_7]^{3+} + e^-$ ($E_{1/2} = +1.42$ V vs. SCE),[12] leads to the slow formation of $[Mo(CNPh)_6Cl]^{2+}$ (identified by $E_{1/2} = +0.93$ V vs. SCE).[15]

The final question of import concerns the source of chloride, which is necessary to convert $[Mo(CNR)_7]^{n+}$ to $[Mo(CNR)_6Cl]^{(n-1)+}$. Dichloromethane solutions of $[Mo(CNCMe_3)_7](PF_6)_2$ have considerable stability (as monitored by cyclic voltammetry) so that we can exclude the possibility of reaction between the solvent and this complex. The other possibilities are (a) the reaction between the CH_2Cl_2 solvent and the molybdenum(III) species $[Mo(CNCMe_3)_7]^{3+}$, following its generation at the electrode surface, or (b) diffusion of chloride ion from the SCE reference electrode or auxiliary electrode. With the configuration we use in our electrochemical cell,[16] we can show that diffusion from the SCE electrode is not the source of chloride. While we cannot rule out the possibility of a relatively slow reaction occurring between $[Mo(CNCMe_3)_7]^{3+}$ and dichloromethane, the main chloride source is that which is generated in the auxiliary electrode compartment and diffuses into the working compartment of the cell during the period of the exhaustive electrolysis experiments.[17] Furthermore, we find that through the deliberate addition of chloride ion (in the form of benzyltriethylammonium chloride) to solutions of $[Mo(CNCMe_3)_7](PF_6)_2$ in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane, the rate of formation of $[Mo(CNCMe_3)_6Cl]^{n+}$ ($n = 1$ or 2) is significantly enhanced. Accordingly, our results are readily interpretable in terms of the equilibria $[Mo(CNR)_7]^{n+} + Cl^- \rightleftarrows [Mo(CNR)_6Cl]^{(n-1)+} + RNC$[18] and $[Mo(CNR)_6(PR'_3)]^{n+} + Cl^- \rightleftarrows [Mo(CNR)_6Cl]^{(n-1)+} + PR'_3$, and pertain to both the molybdenum(II) and the molybdenum(III) oxidation states.[19]

Registry No. $[Mo(CNCMe_3)_4Cl]_2$, 52022-18-1; $[Mo(CNCMe_3)_6Cl]Cl$, 66652-50-4.

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(11) Electrochemical and ESR spectral measurements were carried out as described in ref 1.

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(15) The paramagnetic $[Mo(CNPh)_6Cl]^{2+}$ cation is further identifiable through its ESR spectrum (CH_2Cl_2 glass at −160 °C), which displays an asymmetric signal with a *g* value of ~1.92. Full details are available upon request to R.A.W.

(16) We use an H-type cell with a fine-porosity frit between the reference (SCE electrode) and working compartments and a medium-porosity fit between the auxiliary (Pt wire electrode) and working compartments.

(17) Cyclic voltammetry was used to monitor the generation of chloride ion ($E_{p,a} \approx +1.1$ V) in the auxiliary electrode compartment.

(18) Equilibria of this type were first studied by Lippard and co-workers. See: Lippard, S. J. *Prog. Inorg. Chem.* **1976**, *21*, 99. Giandomenico, C. M.; Dewan, J. C.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 1407.

(19) Support from the National Science Foundation (Grant CHE79-09233) is gratefully acknowledged.

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Effect of Ligand Strain on the Redox Properties of Metal Complexes

Sir:

The "cage" macrocyclic ligands such as the sepulchrate ligand developed by Sargeson and co-workers[1,2] effect great changes in the redox properties of the metals they encapsulate. For example, the cobalt sepulchrate 3+/2+ couple shows a 10^5-fold increase in redox rate over the similar cobalt tris(ethanediamine) 3+/2+ couple. Much of this may be due simply to the effect of the rigidity of the ligand on the size and energy of the metal complex.

In this paper we seek to predict the general effects of a rigid cage ligand on the redox rate and potential of its complexes. For simplicity, we assume the ligand and the metal are sufficiently symmetric that all of the metal–ligand bonds will have the same force constant. In effect, the ligand is assumed to act as a large spring—which has its own preferred size and force constant—surrounding the metal.

Let us suppose that the ligand prefers an equilibrium position x_1 with a force constant f_1 around this position. Let us

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also suppose that the metal prefers the ligand in equilibrium position x_m with force constant f_m. The energy with the ligand at position x would then be

$$E = \tfrac{1}{2}[f_m(x - x_m)^2 + f_l(x - x_l)^2] \tag{1}$$

The equilibrium position will be the value of x such that $F = dE/dx = 0$:

$$dE/dx = (f_m + f_l)x - (f_m x_m + f_l x_l) \tag{2}$$

Solving for $F = 0$

$$x_{eq} = \frac{f_m x_m + f_l x_l}{f_m + f_l} \tag{3}$$

Note that the force

$$\begin{aligned} F &= (f_m + f_l)x - (f_m + f_l)x_{eq} \\ &= (f_m + f_l)(x - x_{eq}) \end{aligned} \tag{4}$$

Thus the system acts as an harmonic oscillator with force constant $f_m + f_l$ and equilibrium position x_{eq}.

The inner-sphere reorganizational energy for self electron transfer can be estimated to be

$$\Delta E_{is} = \frac{n}{2}\left(\frac{f_2 f_3}{f_2 + f_3}\right)(\Delta r)^2 \tag{5}$$

where f_2 and f_3 are the effective force constants for the metal–ligand bonds in the M(II) and M(III) species, Δr is the difference in equilibrium bond distances between the two species, and n is the number of ligators.[3]

From eq 4, we see that the effective force constants for the species in terms of those for the metal complex without ligand strain are

$$f_2 = f_{m2} + f_l \quad \text{and} \quad f_3 = f_{m3} + f_l \tag{6}$$

where f_{m2} and f_{m3} are the force constants for the metal–ligand bonds in the absence of ligand strain. Likewise

$$x_2 = \frac{f_{m2}x_{m2} + f_l x_l}{f_{m2} + f_l} \quad \text{and} \quad x_3 = \frac{f_{m3}x_{m3} + f_l x_l}{f_{m2} + f_l} \tag{7}$$

where x_2 and x_3 are the equilibrium distances with ligand strain, and x_{m2} and x_{m3} the distances when there is no ligand strain.

In the case with ligand strain, then

$$\Delta r = \left(\frac{f_{m2}x_{m2} + f_l x_l}{f_{m2} + f_l}\right) - \left(\frac{f_{m3}x_{m3} + f_l x_l}{f_{m3} + f_l}\right) = \frac{f_{m2}f_{m3}(x_{m2} - x_{m3}) + f_l[f_{m2}(x_{m2} - x_l) + f_{m3}(x_l - x_{m3})]}{(f_{m2} + f_l)(f_{m3} + f_l)} \tag{8}$$

With the definition $(x_{m2} - x_{m3}) = \Delta r_0$, the difference in metal–ligand distance with no strain, the inner-sphere reorganizational energy becomes

$$\Delta E_{is} = \frac{n}{2}\,\frac{(f_{m2}f_{m3}(\Delta r_0) + f_l[f_{m2}(x_{m2} - x_l) + f_{m3}(x_l - x_{m3})])^2}{(f_{m2} + f_{m3} + 2f_l)(f_{m2} + f_l)(f_{m3} + f_l)} \tag{9}$$

By changing the energy of the M(II) complex relative to the M(III), the ligand strain will affect the reduction potential of the couple. Assume the unstrained complex has reduction potential $\mathscr{E}°$. The change in reduction potential when there is ligand strain will be proportional to the change in energy in the M(III) state minus the change in the M(II) state. For example, stabilization of the M(II) relative to the M(III) would result in a more positive reduction potential. Thus, for one electron

$$F(\Delta\mathscr{E}°) = \Delta E_3 - \Delta E_2 \tag{10}$$

where $\Delta\mathscr{E}°$ is the change in $\mathscr{E}°$ with ligand strain, ΔE_2 is the difference in energy between the M(II) species with and without ligand strain, and ΔE_3 is the energy difference for the M(III) species.

The energy differences ΔE_3 and ΔE_2 are functions of the displacement from the unstrained case and the force constants:

$$\Delta E_2 = \tfrac{1}{2}nf_2(x_2 - x_{m2})^2 \quad \text{and} \quad \Delta E_3 = \tfrac{1}{2}nf_3(x_3 - x_{m3})^2 \tag{11}$$

Thus

$$\Delta E_3 - \Delta E_2 = \tfrac{1}{2}n[f_3(x_3 - x_{m3})^2 - f_2(x_2 - x_{m2})^2] \tag{12}$$

Substitution for x_3 from eq 3 gives

$$\begin{aligned} x_3 - x_{m3} &= \left(\frac{f_{m3}x_{m3} + f_l x_l}{f_{m3} + f_l}\right) - \left(\frac{x_{m3}(f_{m3} + f_l)}{f_{m3} + f_l}\right) \\ &= \frac{f_l(x_l - x_{m3})}{f_{m3} + f_l} \end{aligned} \tag{13}$$

Thus

$$\begin{aligned} F(\Delta\mathscr{E}°) &= \frac{n}{2}f_l^2\left[f_3\left(\frac{x_l - x_{m3}}{f_{m3} + f_l}\right)^2 - f_2\left(\frac{x_l - x_{m2}}{f_{m2} + f_l}\right)^2\right] \\ &= \frac{n}{2}f_l^2\left[\left(\frac{(x_l - x_{m3})^2}{f_3}\right) - \left(\frac{(x_l - x_{m2})^2}{f_2}\right)\right] \end{aligned} \tag{14}$$

For f_l small relative to f_{m2} and f_{m3}, the quantity inside the brackets will not change much with change in f_l, and thus an approximately parabolic relation between $\Delta\mathscr{E}°$ and the force constant f_l should be observed in this range.

For a view of the effect of the ligand strain on a metal ion's redox properties, calculations using the derived equations have been performed.

For a proper use of these equations to estimate the result of modifying the rigidity of the ligand on the redox properties of a complex, values of the ligand size and force constant are needed. We have treated the cobalt sepulchrate case by assuming that all of the ligand's rigidity is derived from bending the capping N. For simplicity, we ignore contributions from more complicated modes. Using a value of 1.0×10^{-11} erg/rad^2 for the N bending force constant,[4] we estimate the ligand force constant to be 0.23 mdyn/Å. We used the cobalt tris(ethanediamine) distances of x_2 = 2.176 Å[5] and x_3 = 1.964 Å[6] and the cobalt hexaammine force constants of f_{m3} = 1.8 mdyn/Å and f_{m2} = 0.8 mdyn/Å[7] as the parameters for the sepulchrate unstrained case. The ligand radius was estimated to be 2.0 Å from models.

The calculated metal–ligand bond distances for cobalt sepulchrate, from eq 3, are x_2 = 2.14 Å and x_3 = 1.97 Å. These compare with the actual values of 2.16 and 1.99 Å.

The calculated ΔE_{is} with no ligand strain is 45.0 kJ/mol. With use of eq 9, with ligand strain it is 35.1 kJ/mol. This represents a reduction of some 10 kJ/mol, to be compared to a difference of 17 kJ/mol in activation energy between the

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$Co(en)_3$ and Co(sep) couples.

Likewise, from eq 14, the predicted change in reduction potential from the unstrained case is -0.029 V. The reduction potential of Co(sep) is 0.04 V less than that of $Co(en)_3$.

This crude calculation gives a fair rationalization of the cobalt sepulchrate redox properties. Presumably, better estimates of force constants using force field calculations could yield even better results.

This model may also be applicable to the study of metallo redox proteins. A protein, which can be viewed as a large ligand, could thus enormously affect the redox properties of its enclosed metal. Of course, the complications of deviation from simple geometry will be more pronounced with a protein than with a more symmetric cage ligand, and would require a more general force field analysis. The calculations in this paper hint at the significance of pocket size and ligand rigidity in determining redox properties.

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Autocatalytic Isomerizations of Square-Planar Complexes

Sir:

We read with interest the note by Louw and van Eldik[1] describing the autocatalyzed isomerizations (1) (L = PEt_3 or PMe_2Ph)

$$cis\text{-}[PtI_2L_2] \rightleftarrows trans\text{-}[PtI_2L_2] \qquad (1)$$

We would like to emphasize that this mechanism is probably quite common, and we have recently cited several likely examples.[2] To the best of our knowledge, the term "autocatalysis" was first applied to isomerizations of these types by ourselves in 1979.[3]

Perhaps the earliest reported reactions that may be classified in this category are those of Chatt and Wilkins in 1952.[4] The complexes $[PtCl_2L_2]$ (L = $AsEt_3$ or $SbEt_3$) isomerize spontaneously, even in nonpolar solvents. When halide-bridged $[Pt_2(\mu\text{-}Cl)_2Cl_2(AsEt_3)_2]$ is added to the solutions to scavenge any free ligand, the isomerization reaction is either quenched (L = $AsEt_3$) or markedly slowed (L = $SbEt_3$). This is clearly analogous to the use, by Louw and van Eldik,[1] of $[Ir(cod)(phen)]ClO_4$ to scavenge catalyzing ligands. Other examples of autocatalysis have been cited elsewhere.[2]

Louw and van Eldik suggest[1] that loss of the catalyzing ligand L may be accompanied by halide-bridged dimer formation (eq 2), though its concentration in solution was never great enough for NMR detection.

$$2[PtI_2L_2] \rightleftarrows [Pt_2(\mu\text{-}I)_2I_2L_2] + 2L \qquad (2)$$

The spontaneous isomerization of *trans*-$[PtCl_2(CO)L]$ to its cis isomer, which probably also proceeds via autocatalysis involving CO loss,[3,5] was accompanied by formation of 5–20% of $[Pt_2(\mu\text{-}Cl)_2Cl_2L_2]$. In these examples, the catalyzing ligand, namely, CO, is gaseous and thus may be readily lost from solution, allowing a significant buildup of the dimeric species during the isomerization.

Finally, we have noted that the ligand elimination steps (2) or (3) can be either solvent-assisted or spontaneous,[2] though

$$[PtX_2L_2] \rightleftarrows [PtX_2L] + L \qquad (3)$$

it seems likely that even nonpolar solvents will associate with a three-coordinate platinum(II) intermediate. There now seems to be ample evidence that even nonpolar solvents such as benzene can cause elimination of ligands from platinum and palladium complexes in which the ligands are normally regarded as being strongly bonding, and the mechanistic consequences of such eliminations can be profound.[2] This latest example by Louw and van Eldik provides yet more evidence for the importance of solvents in reactions of square-planar complexes.

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Additions and Corrections

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A. Dedieu: Theoretical Study of the Olefin Insertion Step in the Chlorotris(triphenylphosphine)rhodium(I)-Catalyzed Hydrogenation of Olefins.

Page 2808. In Figure 6 one should read **11** instead of **13** and **12** instead of **16**.—A. Dedieu

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