a magnetic stirring bar and an inlet for nitrogen atmosphere was equipped with a reflux condenser leading to an outlet for nitrogen gas. To the predried flask was added 9.12 g (105 mmol) of lithium bromide. The flask was again flushed with nitrogen, and 100 mL of diethyl ether was introduced with a double-ended needle. After 2 min of stirring, 3.93 g (104 mmol) of sodium borohydride was introduced to the solution under nitrogen atmosphere. The reaction mixture was maintained under 25 °C with stirring for 48 h. White solid sodium bromide formed. The reaction mixture was then kept at 34 °C with stirring for 30 min. The completed reaction showed a separation between the clear solution of lithium borohydride and the sodium bromide as a white precipitate. The clear solution of lithium borohydride in diethyl ether was transferred by a double-ended needle into a weighed 250-mL flask. The flask was connected to a distillation setup and heated to distill off diethyl ether, collecting it in a graduated cylinder, until the temperature of the oil bath reached 100 °C and no more diethyl ether distilled. There was obtained 75 mL of diethyl ether and 2.52 g of unsolvated lithium borohydride. Thus, a quantitative yield of 97% pure lithium borohydride was obtained. The lithium borohydride exhibited a melting point of 276–279 °C dec (lit.[11] 275–278 °C dec). This was also confirmed by a ^{11}B NMR spectrum. The spectrum showed a quintet centered at −40.69 ppm in diethyl ether to the reference $BF_3 \cdot OEt_2$, identical with the behavior of commercial $LiBH_4$.

Stoichiometry of Reaction of Sodium Borohydride with Lithium Halide in Diethyl Ether Using Mechanical Stirring with Glass Beads. In a typical experiment, a three-necked, 2-L, round-bottom flask with sidearm containing glass beads (6-mm diameter, 180 g ≈ ¹/₄ volume of the solvent), a mechanically operated Teflon paddle (9-cm length), and an inlet for nitrogen was equipped with a reflux condenser leading to a bubbler outlet for the nitrogen gas. In the predried flask was placed 19.65 g (500 mmol) of $NaBH_4$ (98% pure, J. T. Baker Chemical Co.) and 45.6 g (525 mmol) of LiBr (99% pure, M. C. & B.) under a nitrogen atmosphere. The flask was again flushed with nitrogen, and 500 mL of diethyl ether was introduced with a double-ended needle. The reaction was carried out at 25 °C with overhead stirring for 18 h and at 35 °C for 0.5 h. Insoluble sodium bromide is formed as a white solid and precipitated out completely. The clear solution of $LiBH_4$ in diethyl ether was transferred by a double-ended needle into a 500-mL volumetric standard flask. Approximately 350 mL were collected. An additional 50 mL of ether was added to the flask by a double-ended needle, and the flask was then maintained at reflux conditions with stirring for 15 min. On cooling, a clear solution was observed above the NaBr precipitate. This solution was also transferred to the volumetric flask. The ether extraction of $LiBH_4$ from the precipitate was repeated twice, and the solutions were collected in the standard flask. The solution was made up to the mark, and the concentration of borohydride was determined to be 0.849 M by hydrolysis of a clear aliquot using a glycerine/H_2O/THF mixture for the hydrolysis.[12] The remaining slurry was filtered and the volume of the filtrate made up to 50 mL. The concentration of borohydride in this filtrate was found to be 0.53 M. Hence, the total recovery of $LiBH_4$ corresponds to 451 mmol (0.849 × 500 + 50 × 0.53) out of 500 mmol, a yield of 90%. Unsolvated $LiBH_4$ can be obtained as described above.

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Reformulation of the Molybdenum(I) Complex [Mo(CNCMe₃)₄Cl]₂ and Its Relevance to Previous Studies on Alkyl Isocyanide Complexes of Molybdenum and Tungsten

Sir:

Following the electrochemical oxidation of the homoleptic alkyl isocyanide complexes $[M(CNR)_7](PF_6)_2$ (M = Mo or W; R = CH_3, CMe_3, or C_6H_{11})[1,2] and the mixed alkyl isocyanide-phosphine complexes $[M(CNR)_6(PR'_3)](PF_6)_2$ (M = Mo or W; R = CH_3 or CMe_3; R′ = Et, *n*-Pr, or *n*-Bu)[1,2] there is slow ligand loss (CNR in the case of $[M(CNR)_7]^{2+}$ and PR′₃ from $[M(CNR)_6(PR'_3)]^{2+}$) to produce ESR-active species, which we have suggested[1] might be the molybdenum(III) and tungsten(III) cations $[M(CNR)_6]^{3+}$. This possibility was given further credence when we became aware quite recently of the claim that $[Mo(CNCMe_3)_6](BF_4)_2$ can be prepared by the oxidation of $Mo(CNCMe_3)_6$ using silver tetrafluoroborate.[3] The synthetic route to $Mo(CNCMe_3)_6$ utilizes the potassium amalgam reduction of $[Mo(CNCMe_3)_4Cl]_2$,[5] a complex first described by King and Saran[4] back in 1974. Desirous of investigating the electrochemical properties of $[Mo(CNCMe_3)_6]^{2+}$, we set out to prepare this complex as its tetrafluoroborate salt. During the course of checking the recipe,[3] we found that our attempts to synthesize the complex purported to be $[Mo(CNCMe_3)_4Cl]_2$ led instead to the well-characterized molybdenum(II) complex $[Mo(CNCMe_3)_6Cl]Cl$.[6] The implications of this result are discussed in the present communication.

The yellow complex "$[Mo(CNCMe_3)_4Cl]_2$" is prepared[4] through the reaction of the (η³-allyl)molybdenum(II) derivative $(\eta^3\text{-}C_3H_5)Mo(CO)_2(NCCH_3)_2Cl$ with Me_3CNC in methylcyclohexane under reflux. We obtained a yellow product by the published procedure,[4] which, as far as we can tell, has properties that are fully in accord with those described in the literature.[7] Furthermore we find that the properties of this product are identical[8] with those of $[Mo(CNCMe_3)_6Cl]Cl$ as reported by Lippard and co-workers.[6] The conclusion that the latter formulation is indeed correct is further supported by microanalytical data. Anal. Calcd for $C_{30}H_{54}N_6MoCl_2$: C,

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(2) Wood, T. E.; Deaton, J. C.; Corning, J.; Wild, R. E.; Walton, R. A. *Inorg. Chem.*, **1980**, *19*, 2614.
(3) Berry, D. E. Ph.D. Thesis, University of Bristol, 1977. We are grateful to Dr. Michael Green, University of Bristol, for drawing our attention to this work.
(4) King, R. B.; Saran, J. S. *Inorg. Chem.* **1974**, *13*, 2453.
(5) We have been informed by Professor G. Wilkinson, Imperial College, London, that an alternative route to $Mo(CNCMe_3)_6$ has been devised and that this will be the subject of a forthcoming paper.
(6) Lam, C. T.; Novotny, M.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1978**, *17*, 2127.
(7) We find the following properties for this product (literature data from ref 4 in parentheses): mp 162–164 °C dec (161 °C); $\nu(C≡N)$ (CH_2Cl_2 solution) 2137 s, 2117 sh cm⁻¹ (2146 s, 2123 sh cm⁻¹); ¹H NMR δ 1.55, singlet (δ 1.57).
(8) In addition to the properties quoted in ref 7, we find that the electronic absorption spectrum of a methanol solution of this material has λ_{max} values of 400, 278, and 237 nm, in excellent agreement with literature data, viz., 404, 278, and 235 nm for an authentic sample of [Mo(CNCMe₃)₆Cl]Cl.[6]

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$_3$)$_4$Cl]$_2$", 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$_3$)$_4$Cl]$_2$" 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$_3$)$_6$Cl]Cl in 0.2 M tetra-*n*-butylammonium hexafluorophosphate–dichloromethane is characterized by a single oxidation, [Mo(CNCMe$_3$)$_6$Cl]$^+$ → [Mo-(CNCMe$_3$)$_6$Cl]$^{2+}$ + 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$_3$)$_7$]$^{2+}$ → [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$_3$)$_6$Cl]$^{2+}$ 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$_6$H$_{11}$, or CMe$_3$) and [Mo-(CNR)$_6$PR′$_3$](PF$_6$)$_2$ (R = CH$_3$, C$_6$H$_{11}$, 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)$_6$Cl]$^{2+}$. A similar explanation presumably holds in the case of the properties of the analogous tungsten complexes [W(CNR)$_7$](PF$_6$)$_2$ (R = C$_6$H$_{11}$ 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)$_6$Cl]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)$_7$]$^{2+}$ → [Mo(CNPh)$_7$]$^{3+}$ + e$^-$ ($E_{1/2}$ = +1.42 V vs. SCE),[12] leads to the slow formation of [Mo(CNPh)$_6$Cl]$^{2+}$ (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)$_6$Cl]$^{(n-1)+}$. 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$_2$Cl$_2$ solvent and the molybdenum(III) species [Mo(CNCMe$_3$)$_7$]$^{3+}$, fol-

lowing 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$_3$)$_6$Cl]$^{n+}$ (n = 1 or 2) is significantly enhanced. Accordingly, our results are readily interpretable in terms of the equilibria [Mo(CNR)$_7$]$^{n+}$ + Cl$^-$ ⇌ [Mo(CNR)$_6$Cl]$^{(n-1)+}$ + RNC[18] and [Mo(CNR)$_6$(PR′$_3$)]$^{n+}$ + Cl$^-$ ⇌ [Mo-(CNR)$_6$Cl]$^{(n-1)+}$ + PR′$_3$, and pertain to both the molybdenum(II) and the molybdenum(III) oxidation states.[19]

Registry No.   [Mo(CNCMe$_3$)$_4$Cl]$_2$, 52022-18-1; [Mo-(CNCMe$_3$)$_6$Cl]Cl, 66652-50-4.

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(15) The paramagnetic [Mo(CNPh)$_6$Cl]$^{2+}$ cation is further identifiable through its ESR spectrum (CH$_2$Cl$_2$ 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 ($E_{p,a}$ ≈ +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.
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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_l with a force constant f_l around this position. Let us

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