Likewise, $E_{pa}(10) - E°'(11) = 0.059 \log (K_{18}/K_{19}) = +1.7 \pm 0.2$ V,[44] where K_{19} is the formation constant of the Mo(VI)–quinone complex:

$$[MoO(S_2CNEt_2)_2]^{2+} + Q \rightleftharpoons [MoO(Q)(S_2CNEt_2)_2]^{2+} \quad K_{19} \qquad (19)$$

Thus, each increment of negative charge on the quinone ligand increases its tendency to bind to the Mo(VI) center by a factor of $\sim 10^{29}$. Combination of these results gives $E°'(9) + E_{pa}(10) - E°'(11) - E°'(12) = 0.059 \log (K_{17}/K_{19}) = 3.4$ V. If the Mo(VI)–quinone formation constant, K_{19}, is ≥ 1, then $K_{17} \geq 10^{58}$. Clearly, an equilibrium constant of at least this order of magnitude is needed to drive the oxidative-addition reaction to completion in the face of its highly unfavorable electron-transfer energetics (i.e., $K_{16} \approx 10^{-60}$).

For Cl_4Q and Br_4Q reaction 16 is not quite as unfavorable ($\Delta E = -2.2$ V, $K_{16} = 10^{-37}$) as for the other three quinones. However, the potentials of these $Q/SQ^{\bullet -}$ and $SQ^{\bullet -}/cat^{2-}$ redox couples are still shifted in the positive direction by 1.5–1.7 V by complexation (Table III). Thus, either oxidative addition (eq 1) is inherently more favorable for Cl_4Q and Br_4Q or the magnitude of Mo(VI)–quinone interaction (K_{19}) is smaller for these compounds.

Other metal–catecholate and –semiquinone complexes that have been formed by oxidative addition also exhibit large positive shifts in $Q/SQ^{\bullet -}$ and $SQ^{\bullet -}/cat^{2-}$ redox potentials.[7b,c,11,18c,20a] These reports apparently represent further instances in which strong metal–ligand interactions facilitate oxidative addition by overcoming unfavorable electron-transfer thermodynamics. The balance between complexation and electron-transfer reactivity may be a finely established one, because Balch[7a] has noted that certain potential oxidative-addition reactions (e.g., $Ir(CO)(Cl)(PPh_3)_2$ reacted with PhenQ or 1,2-NaphQ and $Pt(PPh_3)_2(Cl)_2$ reacted with Cl_4Q) yield no product. Likewise, we observe that acenaphthenequinone fails to react with $MoO(S_2CNEt_2)_2$. Further understanding in this area will require more thorough examination of the relative contributions of complexation and electron-transfer energetics to oxidative-addition reactions.

Acknowledgment. Support of this research by the National Science Foundation under Grant No. CHE-84-09594 is gratefully acknowledged.

---

[44] Because reaction 10 is irreversible, we have used the anodic peak potential, $E_{pa}(10)$, rather than the thermodynamic $E°'$ value in this calculation. This irreversibility appears to derive from a rapid chemical reaction following reversible electron transfer rather than slow charge-transfer kinetics. We estimate that $E_{pa}(10)$ differs from $E°'(10)$ by no more than 0.1–0.2 V on the basis of the observation that a nearly equal spacing (0.66 ± 0.1 V) exists between the $Q/SQ^{\bullet -}$ and $SQ^{\bullet -}/cat^{2-}$ potentials in the complexes (eq 10 minus eq 9) and in the free ligands (eq 11 minus eq 12) (cf. Table III).

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Reversible Intramolecular Isomerization Associated with the Electron-Transfer Reactions of Mixed-Carbonyl-Isocyanide-Phosphine Complexes of Molybdenum of the Type $[Mo(CO)_2(CNR)_2(PR'_3)_2]^{+/0}$

Kay A. Conner and Richard A. Walton*

Received May 23, 1986

Neutral species of the type $Mo(CO)_2(CNR)_2(PR'_3)_2$ (R = methyl, isopropyl, *tert*-butyl, cyclohexyl, *p*-tolyl, xylyl, mesityl, 2,4,6-tri-*tert*-butylphenyl; $PR'_3 = PEt_3$, P-*n*-Pr_3, PEt_2Ph, $PMePh_2$, PPh_3) have been synthesized and found to exist as a single isomer with a trans disposition of phosphine ligands and cis arrangements of the pairs of CO and RNC groups in the case of R = alkyl and PR'_3 = any phosphine except (in some instances) PPh_3. For the analogous aryl isocyanide complexes, spectroscopic evidence (IR and ^1H and $^{31}P\{^1H\}$ NMR) suggests that a mixture of isomers is present. In all instances (i.e., R = alkyl and aryl) electrochemical and chemical oxidations afford the paramagnetic 17-electron all-trans cations $[Mo(CO)_2(CNR)_2(PR'_3)_2]^+$, which have been isolated as their PF_6^- salts in a few cases. The monocations have been characterized by IR and X-band ESR spectroscopies. Rereduction of these cations results in a very rapid reisomerization to the isomer or equilibrium mixture of isomers that are present in the parent neutral complexes, except in the cases of $Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2$, $Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(PMePh_2)_2$, and $Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(P\text{-}n\text{-}Pr_3)_2$. For these three complexes rereduction affords solutions of the neutral all-trans isomers, which can be characterized spectroscopically before they slowly reisomerize to the mixtures of isomers that contain cis CO groups. From cyclic voltammetric measurements on solutions of these complexes in 0.1 M $n\text{-}Bu_4NPF_6/CH_2Cl_2$, the equilibrium constants for the redox cross-reactions $trans^0 + cis^+ \rightleftharpoons trans^+ + cis^0$ show that these equilibria lie far to the right; this is attributable to the high thermodynamic stability of the $trans^+$ and cis^0 species. The homogeneous chemical rate constants for the cis–trans isomerizations of $Mo(CO)_2(CNR)_2(PR'_3)_2$ have been evaluated. For the processes

$$cis^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans^+ \qquad trans^0 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} cis^0$$

it is clear that $k_1 > k_2$. The intramolecular isomerizations can be interpreted in terms of sequential trigonal twists.

Introduction

One of the premises of the theoretical treatment for heterogeneous electron-transfer rates is that smaller rate constants can be expected for redox couples that have greater structural differences between the oxidized and reduced forms than for those in which there is little or no structural change accompanying electron transfer.[1,2] However, the assumption that structural inferences can be made on the basis of reversibility, or lack of it, in electrochemical processes has been shown to be misleading when electrochemically induced isomerization is involved. When the mechanism shown in eq 1 holds, where O1 represents the reactant

$$O1 + e^- \rightleftharpoons R2 \qquad (1)$$

in one structural form and R2 the reduced product having a

---

[1] Weaver, M. J. *Inorganic Reactions and Methods*; Zuckerman, J., Ed.; Verlag Chemie: Weinheim, FRG, in press.

[2] Tulyathan, B.; Geiger, W. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *109*, 325.

0020-1669/86/1325-4422$01.50/0

changed structure, then the prediction of slow electron transfer may be valid. However, if one of two alternative pathways is possible

$$O1 \rightleftharpoons O2 + e^- \rightleftharpoons R2 \qquad (2)$$

or

$$O1 + e^- \rightleftharpoons R1 \rightleftharpoons R2 \qquad (3)$$

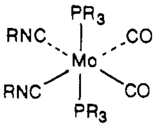
then the rate of electron transfer is often found to be very fast.[3] Equation 2 represents a chemical reaction followed by an electron transfer (CE mechanism), and eq 3 represents an electron-transfer step preceding a chemical reaction (EC mechanism). Bond and co-workers[3,4] have incorporated eq 2 and 3 into the so-called "square scheme"

$$\begin{tikzcd} e^- + O1 \arrow[r, shift left] \arrow[d, shift left] & R1 \arrow[l, shift left] \arrow[d, shift left] \\ e^- + O2 \arrow[r, shift left] \arrow[u, shift left] & R2 \arrow[l, shift left] \arrow[u, shift left] \end{tikzcd} \qquad (4)$$

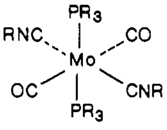
in which there is also the possibility of a second-order cross-reaction:

$$O2 + R1 \rightleftharpoons O1 + R2 \qquad (5)$$

There has been considerable interest in electrochemically induced isomerization,[3-13] which can be explained in terms of the square scheme (eq 4), with particular emphasis on the oxidation of 18-electron carbonyl compounds to the 17-electron species. Recently, a series of mixed-carbonyl-alkyl isocyanide-phosphine complexes, $Mo(CO)_2(CNR)_2(PR'_3)_2$ (R = CH_3, CMe_3, C_6H_{11}; PR'_3 = PEt_3, P-*n*-Pr_3, $PMePh_2$, $PEtPh_2$), was prepared in our laboratory[14] and shown to have structure I. In subsequent studies directed at exploring their redox chemistry,[15] these complexes were discovered to undergo rapid intramolecular isomerizations to the all-trans species, structure II, following electrochemical oxidation to the monocation. Similar behavior was found upon oxidation of *cis*-$Mo(CO)_2(CNC_6H_{11})_4$ to the trans isomer.



I



II

This work introduced the first examples of the electrochemically induced isomerizations of complexes of the type $MX_2Y_2Z_2$ that contain the $M(CO)_2$ unit (M = a group 6 metal). Since these results have an important bearing upon problems relating to the electrochemical activation of organometallic molecules, the preliminary study has been expanded to include a wider range of isocyanide and phosphine ligands as well as to characterize this series of complexes more thoroughly spectroscopically. Details of this more complete study are described herein.

Experimental Section

Starting Materials. $Mo(CO)_6$ and $W(CO)_6$ were purchased from Pressure Chemical Co., allyl chloride from Aldrich, phosphine ligands and cyclohexyl isocyanide from Strem, and xylyl isocyanide from Fluka Chemical Co. The isocyanide ligands, RNC, where R = methyl, isopropyl, *tert*-butyl, cyclohexyl, *p*-tolyl, mesityl, and 2,4,6-tri-*tert*-butylphenyl were prepared by literature procedures.[16,17] The acetonitrile complex $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(NCCH_3)_2$ was prepared from the reaction between $Mo(CO)_6$, allyl chloride, and acetonitrile,[18] and its tungsten analogue was obtained by a similar procedure.[19] The oxidizing agent ferrocenium hexafluorophosphate, $(Cp_2Fe)PF_6$, was obtained by using the procedure described in the literature.[20]

Reaction Procedures. All reactions were carried out under an atmosphere of dry nitrogen by using standard vacuum-line techniques. Commercial grade solvents were distilled and deoxygenated by purging with N_2 gas prior to use.

When compounds were prepared by analogous procedures, synthetic details of representative compounds only are given. Where microanalytical data are not given, compounds were identified on the basis of their spectroscopic and electrochemical properties, which were very similar to other derivatives of their type.

A. Preparation of $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CNR)_2$. The general procedure for preparing these isocyanide-substituted complexes, which is based upon that first described by King and Saran[21] in the case of the alkyl isocyanide derivatives, is as follows. Approximately 0.5 g of the acetonitrile complex $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CH_3CN)_2$ was dissolved in 20 mL of CH_2Cl_2 at room temperature. Two equivalents of isocyanide were added, causing an immediate color change from orange to red as the isocyanide replaced the labile acetonitrile ligands. This solution was then stirred for about 30 min. For the alkyl isocyanide derivatives (R = Me, *i*-Pr, *t*-Bu, or Cy), a solid could be isolated by reduction of the volume of solution and addition of hexanes. Yields of 85–90% were obtained. This treatment did not result in solids for the aryl isocyanide derivatives (R = *p*-tol, xylyl, or mesityl); only dark red oils could be recovered. Further efforts to produce these complexes as solids led to decomposition. These three aryl isocyanide derivatives were characterized by IR spectroscopy and cyclic voltammetry[22] and were subsequently generated as needed for the next step in the reaction procedure without any effort being made to isolate them from the reaction mixtures.

The only aryl isocyanide complex that was isolated as a solid was that of 2,4,6-tri-*tert*-butylphenyl isocyanide. Two equivalents of this solid isocyanide ligand and 1 equiv of the acetonitrile starting material were placed in a flask, CH_2Cl_2 was added, and the solution was stirred for 30 min. Reduction of the volume of this solution resulted in a red oil, but it is possible, by trituration of this oil in methanol, to obtain the complex as a powder. Although the complex is fairly soluble in methanol, this process can be repeated; i.e., the remaining solution can again be reduced to an oil, more methanol added with trituration, and more powder formed. This complex could be prepared in 75% yield.[22]

B. Preparation of $Mo(CO)_2(CNR)_2(PR'_3)_2$. Two ways were used to prepare these complexes. The first procedure is a very general one, which has been found to succeed with any combination of isocyanide and phosphine ligands tried thus far. It is however a fairly tedious method; it invariably results in oily products that are difficult to work up, and the yields are usually in the 40–50% range. The second procedure (which utilizes $Mo(CO)_2(NCCH_3)_2(PR'_3)_2$) is a cleaner reaction giving high yields, but is limited to PPh_3 (and perhaps P-*n*-Bu_3).[24,25] Both procedures rely on the phosphine-assisted elimination of allyl chloride.

Method 1. A quantity of $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CNR)_2$ was dissolved in about 20 mL of CH_2Cl_2. A slight excess over 2 equiv of PR'_3 was

---

[3] Bond, A. M.; Oldham, K. B. *J. Phys. Chem.* **1983**, *87*, 2492 and references therein.

[4] Bond, A. M.; Carr, S. W.; Colton, R. *Organometallics* **1984**, *3*, 541.

[5] Wimmer, F. L.; Snow, M. R.; Bond, A. M. *Inorg. Chem.* **1974**, *13*, 1617.

[6] Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1975**, *14*, 2526.

[7] Bond, A. M.; Grabaric, B. S.; Jackowski, J. J. *Inorg. Chem.* **1978**, *17*, 2153.

[8] Elson, C. M. *Inorg. Chem.* **1976**, *15*, 469.

[9] Rieke, R. D.; Kojima, H.; Öfele, K. *J. Am. Chem. Soc.* **1976**, *98*, 6735.

[10] Rieke, R. D.; Kojima, H.; Öfele, K. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 538.

[11] Darensbourg, D. *Inorg. Chem.* **1979**, *18*, 14.

[12] Bond, A. M.; Darensbourg, D.; Mocellin, E.; Stewart, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 6827.

[13] Bond, A. M.; Grabaric, B. S.; Grabaric, Z. *Inorg. Chem.* **1978**, *17*, 1013.

[14] Deaton, J. C.; Walton, R. A. *J. Organomet. Chem.* **1981**, *219*, 187.

[15] Conner, K. A.; Walton, R. A. *Organometallics* **1983**, *2*, 169.

[16] Weber, W. D.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530.

[17] Yamamoto, Y.; Aoki, K.; Yamakazi, H. *Inorg. Chem.* **1979**, *18*, 1681.

[18] Hayter, R. G. *J. Organomet. Chem.* **1968**, *13*, C1.

[19] Brisdon, B. J.; Cartwright, M.; Edwards, D. A.; Paddick, K. E. *Inorg. Chim. Acta* **1980**, *40*, 191.

[20] Hendrickson, D. N.; Sohn, Y. S.; Gray, H. B. *Inorg. Chem.* **1971**, *10*, 1559.

[21] King, R. B.; Saran, M. S. *Inorg. Chem.* **1974**, *13*, 74.

[22] Their properties, which are described in full detail elsewhere (see: Conner, K. A. Ph.D. Thesis, Purdue University, 1985), are very similar to those that characterize the related alkyl isocyanide derivatives.[21,23]

[23] Brisdon, B. J.; Conner, K. A.; Walton, R. A. *Organometallics* **1983**, *2*, 1159.

[24] Friedel, H.; Renk, I. W.; tom Dieck, H. *J. Organomet. Chem.* **1971**, *26*, 247.

[25] Although $Mo(CO)_2(NCCH_3)_2(PR'_3)_2$ can be isolated in the case of either PPh_3 or P-*n*-Bu_3 (see ref 24), only the PPh_3 derivative was prepared in this work.

added and the solution stirred at room temperature overnight. The CH_2Cl_2 solution was then reduced in volume to 5–10 mL and placed on a 2 × 15 cm alumina column and eluted with 6:1 dichloromethane:hexanes. A yellow or orange band was collected, and the solvent was stripped off, leaving a yellow or orange oil. The oils could be purified in various ways as detailed under the individual complexes. This is in essence the method we used previously[14] to prepare samples of the *tert*-butyl isocyanide complexes $Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PR'_3)_2$ (PR'_3 = PEt_3, P-*n*-Pr_3, $PMePh_2$) that were the subject of our preliminary report.[15] Accordingly, preparative details for the aryl isocyanide complexes only will be presented here.

(i) $Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2$. $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(NCCH_3)_2$ (0.5 g, 1.61 mmol) and xylyl isocyanide (0.42 g, 3.20 mmol) were stirred together in 20 mL of CH_2Cl_2 for 30 min. A quantity of PEt_2Ph (0.7 mL) was syringed into the flask, and the solution was stirred for 12 h at room temperature. The reaction mixture, after first being reduced in volume, was chromatographed as described above. The product, a yellow-brown oil, was triturated with 50 mL of petroleum ether to yield a yellow powder, which was recrystallized from a minimum volume of CH_2Cl_2 and EtOH; yield 50%. Anal. Calcd for $C_{40}H_{48}MoN_2O_2P_2$: C, 64.34; H, 6.48. Found: C, 63.64; H, 6.55.

(ii) $Mo(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2$. Procedure i was followed up to the point when the compound was obtained as an oil. The bright orange oily product was triturated with a large volume (50–75 mL) of methanol until an orange powder formed. The powder was recrystallized from CH_2Cl_2/MeOH; yield 58%. Anal. Calcd for $C_{38}H_{60}MoN_2O_2P_2$: C, 62.12; H, 8.23. Found: C, 61.86; H, 8.41.

(iii) $Mo(CO)_2(CNxylyl)_2(PMePh_2)_2$. Derivatives made with this phosphine were the most difficult to isolate as solids. After procedure i was followed to the stage when the compound was obtained as an oil, a small amount of yellow solid was eventually recovered by trituration of the oily yellow product with a 1:1 mixture of petroleum ether and Et_2O; yield 11%.

(iv) $Mo(CO)_2(CNmesityl)_2(P\text{-}n\text{-}Pr_3)_2$. This was prepared by a procedure analogous to ii; yield 42%. Anal. Calcd for $C_{40}H_{64}MoN_2O_2P_2$: C, 62.98; H, 8.46. Found: C, 62.41; H, 8.96.

(v) $Mo(CO)_2(CN\text{-}p\text{-}tol)_2(PEt_2Ph)_2$. This compound was prepared as in procedure i up to the stage when it was obtained as an oil. The dark yellow-brown oil was treated with diethyl ether, which dissolved most of the brown material and left a mustard yellow powder. The powder was recrystallized from a minimum volume of CH_2Cl_2 upon the addition of Et_2O after being stored at 0 °C overnight; yield 33%.

(vi) $Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(P\text{-}n\text{-}Pr_3)_2$. This complex was prepared as in procedure ii; yield 53%. Anal. Calcd for $C_{58}H_{100}MoN_2O_2P_2$: C, 68.61; H, 9.93. Found: C, 68.55; H, 10.18.

(vii) $Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(PMePh_2)_2$. After procedure i was followed, a small amount of yellow powder precipitated out of a CH_2Cl_2/EtOH solution at 0 °C; yield <10%.

Method 2. The second method of preparing $Mo(CO)_2(CNR)_2(PR'_3)_2$ starts with $Mo(CO)_2(NCCH_3)_2(PPh_3)_2$, a complex first prepared by Friedel et al.,[24,25] which can be made by reacting $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(NCCH_3)_2$ with PPh_3 in CH_3CN at 60 °C for 10 min.

In a typical reaction, 0.3 g of $Mo(CO)_2(NCCH_3)_2(PPh_3)_2$ was suspended in 10 mL of CH_2Cl_2 at room temperature. An amount of isocyanide in slight excess of 2 equiv was added to the suspension whereupon any solid immediately dissolved. The solution was stirred for 30 min and reduced in volume, and Et_2O was added until a yellow precipitate formed. The solid was filtered off and recrystallized from CH_2Cl_2 and EtOH.

(i) $Mo(CO)_2(CNxylyl)_2(PPh_3)_2$. Since xylylNC is a solid, it was added to the flask along with the $Mo(CO)_2(CH_3CN)_2(PPh_3)_2$ before the solvent was added; yield 65%. Anal. Calcd for $C_{56}H_{48}MoN_2O_2P_2$: C, 71.64; H, 5.15. Found: C, 70.51; H, 5.71.

(ii) $Mo(CO)_2(CNMe)_2(PPh_3)_2$. Yield: 76%. Anal. Calcd for $C_{42}H_{36}MoN_2O_2P_2$: C, 66.49; H, 4.78. Found: C, 66.12; H, 5.10.

(iii) $Mo(CO)_2(CN\text{-}i\text{-}Pr)_2(PPh_3)_2$. Yield: 93%. Anal. Calcd for $C_{46}H_{44}MoN_2O_2P_2$: C, 67.81; H, 5.44. Found: C, 67.44; H, 5.21.

(iv) $Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PPh_3)_2$. Yield: 83%. Anal. Calcd for $C_{48}H_{48}MoN_2O_2P_2$: C, 68.41; H, 5.74. Found: C, 68.13; H, 5.37.

(v) $Mo(CO)_2(CNCy)_2(PPh_3)_2$. Yield: 85%. Anal. Calcd for $C_{52}H_{52}MoN_2O_2P_2$: C, 69.74; H, 5.86. Found: C, 68.99; H, 5.86.

C. Preparation of $[Mo(CO)_2(CNR)_2(PR'_3)_2]PF_6$. Chemical oxidation of some of the alkyl isocyanide derivatives was attempted with tropylium hexafluorophosphate used as the oxidant. For example, upon the addition of 1 equiv of $C_7H_7PF_6$ to a yellow solution of $Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PMePh_2)_2$, an orange color was immediately generated. This solution had spectroscopic and electrochemical properties identical with those of the electrochemically generated cation. However, the product could only be obtained as an oil that quickly decomposed. Similar results occurred when ferrocenium hexafluorophosphate was used as the oxidant. However, hexafluorophosphate salts of some aryl isocyanide derivatives were obtained in solid form by reacting 1 equiv of the neutral complex with 1 equiv of $(Cp_2Fe)PF_6$ in dichloromethane.

(i) $[Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2]PF_6$. In a typical reaction, 5 mL of CH_2Cl_2 were added to a flask containing 0.1 g (0.134 mmol) of $Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2$ and 0.045 g (0.136 mmol) of $(Cp_2Fe)PF_6$. The solution turned red instantly, and the addition of 30 mL of Et_2O caused the precipitation of a red solid. The solid could be filtered off in air, washed with copious amounts of Et_2O to remove the Cp_2Fe and any unreacted $Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2$, and dried in vacuo. Since both Cp_2Fe and the neutral starting complex dissolve in diethyl ether, it was preferable to start with slightly less than 1 equiv of $(Cp_2Fe)PF_6$, as excess $(Cp_2Fe)PF_6$ was very difficult to separate from $[Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2]PF_6$. Yield: 85%. Anal. Calcd for $C_{40}H_{48}F_6MoN_2O_2P_3$: C, 53.88; H, 5.43. Found: C, 53.10; H, 5.84.

(ii) $[Mo(CO)_2(CNmesityl)_2(P\text{-}n\text{-}Pr_3)_2]PF_6$. Yield: 80%.

(iii) $[Mo(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2]PF_6$. Yield: 87%.

(iv) $[Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(P\text{-}n\text{-}Pr_3)_2]PF_6$. Yield: 82%.

Physical Measurements. Details of the electrochemical techniques used to study these complexes are described elsewhere;[23] potentials were referenced to the Ag/AgCl electrode and measurements were conducted on 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) in CH_2Cl_2 solutions of the complexes. Under our experimental conditions the ferrocenium–ferrocene couple has $E_{1/2}$ = +0.47 V vs. Ag/AgCl. Infrared spectra of Nujol mulls and solutions were recorded on an IBM Instruments IR/32 FTIR spectrometer. Electronic absorption spectra of CH_2Cl_2 solutions were measured with an IBM Instruments 9420 (900–300 nm) UV-visible spectrophotometer, ^1H NMR spectra, which were recorded at 90 MHz on a Perkin-Elmer R32 spectrometer or at 200 MHz with a Varian XL-200 spectrometer, are referenced to the residual protons of the incompletely deuterated solvent. Measurements of the $^{31}P\{^1H\}$ NMR spectra were carried out by using a Varian XL-200 spectrometer operated at 80.98 MHz using an internal deuterium lock and 85% H_3PO_4 as an external standard; positive chemical shifts are measured downfield of the H_3PO_4 reference. X-Band ESR spectra of frozen dichloromethane solutions were recorded at ca. −160 °C with the use of a Varian E-109 spectrometer. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results and Discussion

(a) Synthesis and Electrochemical Characterizations. The synthesis of $Mo(CO)_2(CNR)_2(PR'_3)_2$ involves either the reaction of the preformed bis(isocyanide) complex $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CNR)_2$ with a slight excess of the phosphine PR'_3 or, in the case of the PPh_3 derivatives, the reaction of the bis(nitrile) complex $Mo(CO)_2(NCCH_3)_2(PPh_3)_2$[24] with the appropriate RNC ligand. The former method is based upon that used previously to prepare the alkyl isocyanide complexes,[14] and is extended here to include their aryl isocyanide analogues. The η^3-allyl compounds $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CNR)_2$ (R = *t*-Bu, *p*-tol, xylyl, mesityl, *t*-Bu_3Ph) exhibit IR spectra (measured in CH_2Cl_2) that are characterized by two ν(CO) modes (1960 (±5) s and 1880 (±7) s cm^{-1}) and two ν(CN) modes (2192–2151 m–s and 2182–2139 m–s cm^{-1}).[22] The electrochemical properties of the aryl isocyanide derivatives of the type $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CNR)_2$, as measured by the cyclic voltammetry (CV) technique using a Pt-bead electrode, are very similar to the properties reported previously for $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CN\text{-}t\text{-}Bu)_2$.[23] Single-scan cyclic voltammograms of solutions of these complexes in 0.1 M TBAH/CH_2Cl_2 show an oxidation at $E_{pa} \sim +0.90$ V vs. Ag/AgCl and a coupled reduction wave at $E_{pc} \sim +0.50$ V vs. Ag/AgCl. This coupled process is neither electrochemically nor chemically reversible. Additional redox processes are seen at $E_{pa} \sim +2.0$ V and $E_{pc} \sim -2.0$ V vs. Ag/AgCl, both near the limits of the potential range scanned.[23,26]

The electrochemical properties of $Mo(CO)_2(CNR)_2(PR'_3)_2$ were investigated by cyclic voltammetry (CV) and controlled-potential electrolysis (CPE). CV and coulometric measurements were made on degassed dichloromethane solutions containing 0.1 M TBAH as supporting electrolyte. Figure 1 shows a CV of $Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(P\text{-}n\text{-}Pr_3)_2$ that is typical of those exhibited by the complexes of this type; a scan to positive potentials starting

---

(26) For the *t*-BuNC complex, these processes are seen at $E_{p,a}$ = +1.65 V and $E_{p,c}$ = −2.07 V vs. SCE, respectively. These data were not included in our previous report of the electrochemical behavior of $(\eta^3\text{-}C_3H_5)MoCl(CO)_2(CN\text{-}t\text{-}Bu)_2$.

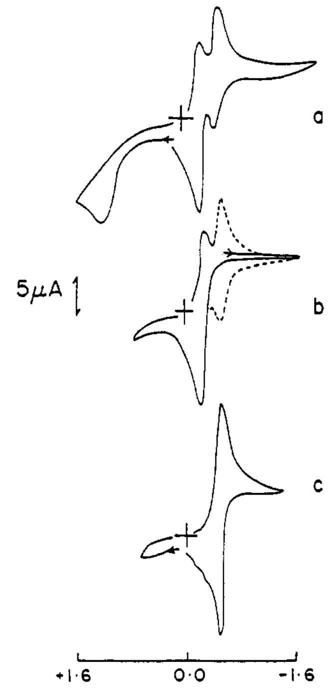


Figure 1. Cyclic voltammograms in 0.1 M TBAH/CH_2Cl_2 of $Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(P\text{-}n\text{-}Pr_3)_2$: (a) positive scan starting at 0.0 V; (b) negative scan starting at -0.4 V (dotted line shows the second scan); (c) scan after controlled-potential electrolysis at +0.1 V.

Table I. $E_{1/2}$ Values for CH_2Cl_2 Solutions of $Mo(CO)_2(CNR)_2(PR'_3)_2$[a]

compound	$E_{1/2}$(cis), V	$E_{1/2}$(trans), V
$Mo(CO)_2(CNCy)_4$	-0.045	-0.28
$Mo(CO)_2(CNMe)_2(PPh_3)_2$	+0.02	-0.20
$Mo(CO)_2(CN\text{-}i\text{-}Pr)_2(PPh_3)_2$	+0.01	-0.22
$Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PEt_3)_2$	-0.23	-0.48
$Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(P\text{-}n\text{-}Pr_3)_2$	-0.24	-0.49
$Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PMePh_2)_2$[b]	-0.045	-0.29
$Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PPh_3)_2$	-0.02	-0.24
$Mo(CO)_2(CNCy)_2(PPh_3)_2$	-0.01	-0.23
$Mo(CO)_2(CN\text{-}p\text{-}tol)_2(PEt_2Ph)_2$	+0.05	-0.15
$Mo(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2$[b]	-0.01	-0.23
$Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2$[b]	+0.06	-0.17
$Mo(CO)_2(CNxylyl)_2(PMePh_2)_2$	+0.13	-0.07
$Mo(CO)_2(CNxylyl)_2(PPh_3)_2$	+0.17	-0.05
$Mo(CO)_2(CNmesityl)_2(P\text{-}n\text{-}Pr_3)_2$[b]	-0.06	-0.28
$Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(P\text{-}n\text{-}Pr_3)_2$[b]	+0.11	-0.25
$Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(PMePh_2)_2$	+0.15	-0.09
$W(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2$	0.00	-0.20

[a] Measured in 0.1 M TBAH/CH_2Cl_2 at a Pt-bead working electrodes, in V vs. Ag/AgCl. [b] A chemically oxidized sample of this complex as its PF_6^- salt had a CV that exhibited a single couple at the same potential as that of $E_{1/2}$(trans).

from 0 V shows an irreversible oxidation at $E_{pa} \sim 1.3$ V and two couples at negative potentials ($E_{1/2}$ values of -0.24 and -0.49 V in this case) corresponding to an oxidation and a reduction, respectively. If the scan is started at a potential between these two couples and carried out in a negative direction (Figure 1b) it is found that the species responsible for the more negative couple is not present, and in fact is produced only after the first oxidation has occurred. That this is a product wave of the oxidative half of the more positive couple is apparent from an examination of peak heights: a rapid chemical reaction (isomerization in this case) follows the oxidation of the complex, thus diminishing the amount of the cation available for reduction.

Voltammetric half-wave potentials (vs. Ag/AgCl) in 0.1 M TBAH/CH_2Cl_2 at 22 ± 2 °C and uncorrected for junction potentials are presented in Table I. The assignments $E_{1/2}$(cis) and $E_{1/2}$(trans) are based upon previously discussed stereochemical considerations.[15] All the complexes reported had an additional redox process, an irreversible oxidation ≥1.0 V, which has not been included in this table. This oxidation is presumably due to the electrode reaction $[Mo(CO)_2(CNR)_2(PR'_3)_2]^+ \rightarrow [Mo(CO)_2(CNR)_2(PR'_3)_2]^{2+} + e^- \rightarrow$ products. A similar reaction has been studied for $Mo(CO)_2(dppm)_2$.[6] The lack of reversibility may reflect the structure changes that are expected to be associated with the formation of such a 16-electron species[27] or the occurrence of rapid chemical reactions.

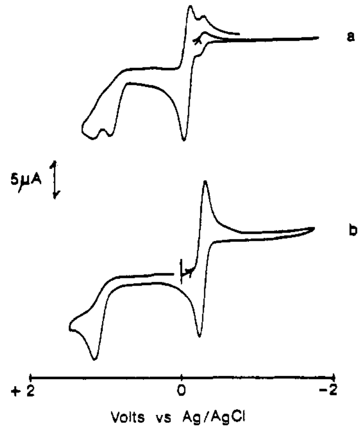


Figure 2. Cyclic voltammograms in 0.1 M TBAH/CH_2Cl_2 of $Mo(CO)_2(CNmesityl)_2(P\text{-}n\text{-}Pr_3)_2$: (a) negative scan starting at -0.2 V showing the presence of some trans isomer initially; (b) scan after controlled-potential electrolysis at +0.2 V.

Bulk electrolysis of the alkyl isocyanide derivatives carried out at potentials more positive than those corresponding to the first couple (i.e., $E_{1/2}$(cis) in Table I) converted the pale yellow solutions to bright orange and produced voltammograms (Figure 1c) with just one couple ($E_{1/2}$(trans) in Table I). The oxidations were shown by coulometry to be one-electron processes ($n = 1.0 \pm 0.1$), and the couples ($E_{1/2}$(trans)) were characterized by values for $E_{pa} - E_{pc}$ of 70-90 mV (at scan rates of 200 mV/s) and i_{pa}/i_{pc} ratios that were close to unity for sweep rates ranging from 50 to 1000 mV/s. These orange solutions could be electrochemically reduced back to the parent species (exhibiting CV's identical with Figure 1a) at potentials more negative than those listed as $E_{1/2}$(trans) in Table I with little apparent decomposition as measured by peak currents.

The redox behavior was found to be similar in the three solvents used, viz. dichloromethane, acetonitrile, and acetone. However, the $E_{1/2}$ values of the couples shifted to more positive potentials in the order $CH_2Cl_2 < CH_3CN < (CH_3)CO$. Thus, for $Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PMePh_2)_2$, in CH_2Cl_2, $E_{1/2}$(cis) = -0.07 V and $E_{1/2}$(trans) = -0.31 V; in CH_3CN, $E_{1/2}$(cis) = +0.02 V and $E_{1/2}$(trans) = -0.22 V; and in acetone, $E_{1/2}$(cis) = +0.07 V and $E_{1/2}$(trans) = -0.16 V.

CV and coulometry of the aryl isocyanide derivatives, $Mo(CO)_2(CNAr)_2(PR'_3)_2$, produced results similar to those of the alkyl isocyanide derivatives although the $E_{1/2}$ values for both cis and trans isomers occurred in all cases at higher potentials than those of the alkyl isocyanide derivatives (Table I). This result is consistent with the poorer σ-donating ability and/or better π-acceptor ability of aryl isocyanides vs. alkyl isocyanides, which makes the derivatives of the former harder to oxidize. For some of the ArNC complexes, a scan to more negative potentials starting at a potential between the two couples showed the presence of a small amount of the trans isomer that was not the result of electrochemical oxidation (Figure 2a). The wave due to the trans isomer increased significantly once the oxidative wave of the cis isomer had been scanned through; however, the presence of some trans isomer from the start indicated that there was either an equilibrium process taking place in solution between the neutral cis and neutral trans isomers or that both isomers were produced in the original preparation of these complexes. The presence of

---

[27] Kubacek, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4320.

more than one isomer in the neutral solutions and in the solid state was also evident in the IR spectra (vide infra) of the ArNC complexes. Some of the $^{31}P\{^1H\}$ NMR spectra of these compounds confirm that there is more than one isomer as well. Both the IR and NMR spectral results are in contrast to those of the alkyl isocyanide derivatives, which indicated the presence of a single isomer.[14]

Coulometry carried out on the aryl isocyanide derivatives at potentials ~200 mV more positive than $E_{1/2}$(cis) in Table I caused the intensely colored yellow solutions to turn deep red and confirmed that these were one-electron processes. The oxidized solutions exhibited a single reversible couple in their cyclic voltammograms (Figure 2b) with $E_{1/2}$ values corresponding to those of $E_{1/2}$(trans) in Table I. In most cases, subsequent electrochemical reduction of the oxidized solution resulted in the regeneration of the original solution (having the same CV as that in Figure 2a), but for three complexes, $Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(P\text{-}n\text{-}Pr_3)_2$, $Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(PMePh_2)_2$, and $Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2$, the reduced solutions had CV's with only one couple corresponding to an oxidation at the same potential as the solution of the trans cation, indicating that the trans structure had been retained. Figure S1 (see paragraph regarding supplementary material at the end of the paper) shows a series of CV's typical of these three complexes, i.e. the CV of 0.1 M $TBAH/CH_2Cl_2$ solution of $Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(P\text{-}n\text{-}Pr_3)_2$. Solutions of *trans*-$Mo(CO)_2(CNAr)_2(PR'_3)_2$ prepared in this fashion slowly isomerized back to the cis isomer.

The $E_{1/2}$ values in Table I imply that a chemical oxidation is feasible, and this has been investigated by using either tropylium hexafluorophosphate ($C_7H_7PF_6$) or ferrocenium hexafluorophosphate ($[Cp_2Fe]PF_6$) as the oxidant. Although chemically oxidized solutions of alkyl isocyanide derivatives of $Mo(CO)_2(CNR)_2(PR'_3)_2$ had electrochemical and spectroscopic properties identical with those of the electrochemically oxidized solutions, attempts to isolate solid PF_6^- salts of these cationic species were unsuccessful.[15] Aryl isocyanide derivatives however were easily prepared by reaction of the neutral complex with 1 equiv of $(Cp_2Fe)PF_6$. Solutions of these deep red solids had electrochemical and spectroscopic properties identical with those of the electrochemically generated cations.

From the large separation between $E_{1/2}$(cis) and $E_{1/2}$(trans) (on the average, a separation of 220 mV), it is possible to calculate the equilibrium constant for the redox cross-reaction (eq 5 in the Introduction) rewritten as

$$\text{trans}^0 + \text{cis}^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{trans}^+ + \text{cis}^0 \qquad (6)$$

from the relationship[13]

$$K = \frac{k_3}{k_{-3}} = \exp\left\{\frac{F}{nRT}(E°_{\text{trans}} - E°_{\text{cis}})\right\} \qquad (7)$$

Using 0.22 V for the term ($E°_{\text{trans}} - E°_{\text{cis}}$) gives a value for the equilibrium constant K of 5400. Thus the equilibrium of eq 6 lies far to the right for all members of this class of complexes. This is attributable to the high thermodynamic stability of the trans$^+$ and cis^0 species relative to their counterparts in the alternative oxidation states.

Cyclic voltammetry was used to estimate the homogeneous chemical rate constants for the cis–trans isomerizations of the $Mo(CO)_2(CNR)_2(PR'_3)_2$ complexes following the electron transfer. The method of Nicholson and Shain[28] was used, whereby the ratio of the cathodic to anodic peak currents (i_{pc}/i_{pa}) for the cis isomer is related to the amount of time taken during the voltammetric scan. These rate constants, k, listed in Table SI, range from 0.20 to 1.38 s^{-1}, the highest values being associated with complexes having PPh_3 or $t\text{-}Bu_3PhNC$ as ligands. These rates are substantially slower than those measured for the cis–trans isomerization of $Mo(CO)_2[Ph_2P(CH_2)_nPPh_2]_2$ (20–30 s^{-1}),[7] but their similar magnitudes and apparent independence on solvent (little difference in rate constants in CH_2Cl_2, CH_3CN, and acetone for $Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PMePh_2)_2$—Table SI) lend support to the notion that all the complexes in this group isomerize by the same mechanism.[7]

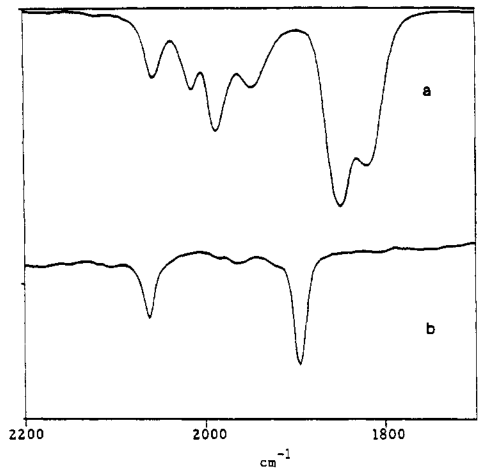


Figure 3. IR spectra of $Mo(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2$ in CH_2Cl_2: (a) neutral complex; (b) complex after electrochemical or chemical oxidation. Solution b can be rereduced to reproduce spectrum a.

(b) Spectroscopic Characterizations and Structural Assignments for the Neutral Complexes. When the alkyl isocyanide derivatives were first reported,[14] they were assigned structure I on the basis of spectroscopic evidence. Their IR spectra in the ν(CO) and ν(CN) regions, both in solution and in the solid state, were in accord with cis arrangements of the CO and RNC groups. One of the complexes reported, $Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PMePh_2)_2$, had three ν(CN) bands, but one of these was assumed (at the time) to be due to an impurity.[14] Singlets in the ^{31}P NMR spectra of these alkyl isocyanide complexes supported the assignment of the trans PR'_3, cis CO, cis CNR geometry. The IR spectra of electrochemically oxidized solutions of these complexes exhibited one band in the ν(CO) region and one in the ν(CN) region, indicating that the 17-electron species adopted an all-trans geometry.[15] IR spectral data for the neutral complexes are listed in Table II and those for the cationic species in Table SII. Subsequently we discovered that the IR spectra of the aryl isocyanide complexes as well as some alkyl isocyanide–PPh_3 complexes which were not studied previously[14] are much more complicated than those of the other alkyl isocyanide derivatives (Table II).

As mentioned in discussing the CV's of the neutral aryl isocyanide complexes, there was some evidence for more than one isomer being present. The IR data support this (Table II). In solution, these complexes exhibit two ν(CO) modes, as expected, but three or four ν(CN) modes (see Figure 3a). A mixture of isomers can explain the large number of bands in the ν(CN) region, but extra bands should then be seen in the ν(CO) region as well. (Note however that the carbonyl bands in Figure 3a are very broad.) Nujol mull IR spectra of most of these complexes were similar to the solution spectra in the ν(CN) region, but had more than two ν(CO) modes.

The possibility that the extra bands were due to impurities was discounted in several ways. As in the case of the alkyl isocyanide derivatives, electrochemical oxidation of the aryl isocyanide complexes produced solutions whose IR spectra had only a single ν(CN) and a single ν(CO) mode in the regions 1908–1885 s and 2159–2049 m cm^{-1}, respectively (Figure 3b). In general, oxidized solutions could be reduced back to neutral species to give IR spectra identical with those of the neutral starting complexes (Figure 3a). Different preparative samples of the same complex had identical IR spectra; the bands had the same locations and intensities, which would not be expected if some of the bands were due to impurities. While it is clear that the monocations exist as a single isomer (all-trans), the question arises as to which isomers are present for the neutral species when there is evidence for more than one.[29]

---

(28) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

Table II. Infrared-Active ν(CO) and ν(CN) Modes of $Mo(CO)_2(CNR)_2(PR'_3)_2$

compound	medium[a]	ν(CO),[b] cm^{-1}	ν(CN), cm^{-1}
$Mo(CO)_2(CNCy)_4$[c]	CH_2Cl_2	1870 s, 1823 s	2152 mw, 2100 sh, 2080 sh, 2045 s
	NM	1868 s, 1820 s	2144 m, 2100 sh, 2070 m, 2036 s
$Mo(CO)_2(CNMe)_2(PEt_3)_2$[c]	NM	1845 s, 1795 s	2120 s, 2095 s
$Mo(CO)_2(CNMe)_2(PPh_3)_2$	CH_2Cl_2	1864 s, 1808 s	2141 m, 2114 m
$Mo(CO)_2(CN\text{-}i\text{-}Pr)_2(PPh_3)_2$	CH_2Cl_2	1862 s, 1808 s	2129 m, 2113 m, 2091 m, 2035 w
$Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PEt_3)_2$	NM	1874 s, 1840 s, ~1800 ms	2105 m, 2048 ms
$Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(P\text{-}n\text{-}Pr_3)_2$[c]	CH_2Cl_2	1842 s, 1792 s	2105 m, 2050 m
	NM	1854 s, 1803 s	2108 m, 2050 m
$Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PMePh_2)_2$[c]	CH_2Cl_2	1860 s, 1808 s	2118 mw, 2100 mw, 2065 mw
	NM	1855 s, 1810 s	2125 m, 2100 m
$Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PPh_3)_2$	CH_2Cl_2	1862 s, 1808 s	2112 m, 2091 m, 2062 m, 2050 sh
$Mo(CO)_2(CNCy)_2(PPh_3)_2$	CH_2Cl_2	1862 s, 1808 s	2116 m, 2087 m, 2050 sh
	NM	1860 s, 1810 s	2130 m, 2107 m, 2072 sh
$Mo(CO)_2(CN\text{-}p\text{-}tol)_2(PEt_2Ph)_2$	CH_2Cl_2	1860 s, 1823 s	2076 m, 2049 w, 2008 sh, 1979 s, 1929 w
	NM	1856 s, 1830 sh, 1817 s	2066 m, 2040 sh, 2008 sh, 1968 s, 1920 m
$Mo(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2$	CH_2Cl_2	1850 s, 1821 s	2058 m, 2014 m, 1987 s, 1950 m
	NM	1869 s, 1848 s, 1825 s	2053 m, 2010 m, 1981 s, 1943 w
$Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2$	CH_2Cl_2	1862 s, 1823 s	2058 m, 2018 w, 1990 sh, 1960 s, 1928 sh
	$CHCl_3$	1862 s, 1821 s	2056 m, 2012 w, 1960 s
	$(CH_3)_2CO$	1866 s[d]	2056 m, 2016 m, 1958 s
	NM	1870 sh, 1848 s, 1825 s, 1818 sh	2060 m, 2016 w, 1960 s
$Mo(CO)_2(CNxylyl)_2(PMePh_2)_2$	CH_2Cl_2	1871 s, 1831 s	2064 m, 2018 m, 1979 s
	NM	1862 sh, 1858 s, 1845 sh, 1823 s	2070 m, 2012 w, 1975 s, 1937 w
$Mo(CO)_2(CNxylyl)_2(PPh_3)_2$	CH_2Cl_2	1873 s, 1837 s	2076 m, 2031 m, 1996 sh, 1977 m
	NM	1865 s, 1835 s	2087 m, 2045 s, 2008 w
$Mo(CO)_2(CNmesityl)_2(P\text{-}n\text{-}Pr_3)_2$	CH_2Cl_2	1850 s, 1815 s	2060 m, 2002 m, 1970 sh, 1942 m
	NM	1865 s, 1846 s, 1829 s	2053 m, 2000 s, 1973 sh, 1939 m
$Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(P\text{-}n\text{-}Pr_3)_2$	CH_2Cl_2	1862 s, 1833 s, 1823 sh	2051 m, 2022 m, 1972 s, 1946 sh
$Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(PMePh_2)_2$	CH_2Cl_2	1871 s, 1846 m, 1831 m	2056 m, 2001 sh, 1979 s
$W(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2$	CH_2Cl_2	1846 s, 1819 s	2053 w, 2016 w, 1977 m, 1937 s
	NM	1858 s, 1844 s, 1831 s	2056 m, 2016 w, 1983 m, 1966 m, 1927 w

[a] NM = Nujol mull recorded on KBr plates. [b] Abbreviations are as follows: m = medium, s = strong, sh = shoulder, w = weak. [c] Data taken from ref 14. [d] Only one band apparent before interference from acetone.

The redox behavior of the three complexes $Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2$, $Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(PMePh_2)_2$, and $Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(P\text{-}n\text{-}Pr_3)_2$ helps to explain the features seen in the IR spectra. For these three complexes, solutions that consisted of predominantly the neutral trans isomer could be generated by first electrochemically oxidizing the neutral "cis" isomer, thereby producing the all-trans cation, and then rereducing that solution. The resulting all-trans neutral species had sufficiently long lifetimes to allow measurement of their IR spectra. The series of spectra for neutral *cis*-, oxidized *trans*-, and neutral *trans*-$Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(PMePh_2)_2$ is shown in Figure 4. The spectra of the all-trans neutral species for all three above-mentioned compounds showed predominantly two bands—one in the ν(CO) region and one in the ν(CN) region. These bands were, as expected, shifted to lower energies compared to the analogous two bands in the spectra of the trans cations, and they also displayed reversed intensities. For the complexes of $t\text{-}Bu_3PhNC$, which are the only ones that had more than two bands originally in the ν(CO) region of their solution IR spectra (Table II), it is clear that the central absorption is the one corresponding to the ν(CO) band of the neutral trans isomer, as is the lowest energy ν(CN) band of the original spectrum. For these two complexes then, it is certain that there is a mixture of at least two isomers in the original neutral solutions. Moreover, it is likely that there are at least two isomers present in solutions of all the samples that exhibit complicated IR spectra. If these isomers are interconverting in solution, as evidenced by some of their ^{31}P NMR spectra (vide infra), then the all-cis species, which is the structure intermediate between the trans PR'_3, cis CO, and cis CNR structure and the all-trans structure (vide infra), must also be present in solution. The all-cis isomer would also have two ν(CO) bands and two ν(CN) bands. If all three aforementioned isomers were present, a total of five ν(CO) and five ν(CN) bands would be expected, some of them very likely coincident with each other.

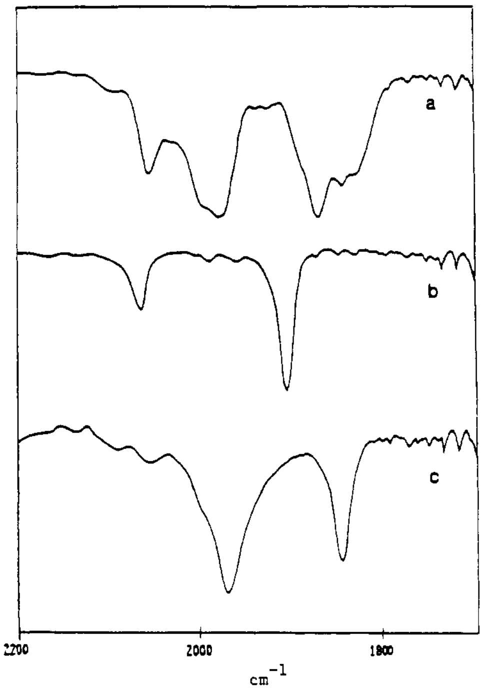


Figure 4. IR spectra of $Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(PMePh_2)_2$ in CH_2Cl_2: (a) neutral complex; (b) complex after oxidation by controlled-potential electrolysis; (c) complex after rereduction of solution b by CPE.

Like the alkyl isocyanide complexes, the aryl isocyanide derivatives with $PR'_3 = P\text{-}n\text{-}Pr_3$ or PPh_3 exhibit only a singlet in their $^{31}P\{^1H\}$ NMR spectra (Table III). Even though there is almost certainly a mixture of isomers present from the start (as evidenced by the IR spectral data), these isomers must interconvert rapidly on the NMR time scale so that only an averaged spectrum

---

(29) The highest energy ν(CN) band of the neutral complexes often occurs very close to the single ν(CN) stretch in the oxidized species (see Figures 3 and 4 and Tables II and SII), which raised the possibility that there may be some oxidized product mixed in with the neutral. However, since the ν(CO) band of the oxidized trans isomers never showed up in the carbonyl region of the neutral samples, it is apparent that this close coincidence in the ν(CN) band positions is fortuitous.

Table III. $^{31}P\{^1H\}$ NMR Spectral Data for $Mo(CO)_2(CNR)_2(PR'_3)_2$[a]

compound	chem shift,[b] δ
$Mo(CO)_2(CNMe)_2(PPh_3)_2$	58.4 s
$Mo(CO)_2(CN\text{-}i\text{-}Pr)_2(PPh_3)_2$	58.8 s
$Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PPh_3)_2$	58.7 s
$Mo(CO)_2(CNCy)_2(PPh_3)_2$	58.9 s
$Mo(CO)_2(CN\text{-}p\text{-}tol)_2(PEt_2Ph)_2$[c]	36.2 s, 25.0 d (24.8), 22.4 d (24.6), 21.8 s
$Mo(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2$	23.8 s
$Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2$[d]	37.9 s, 25.4 d (25.0), 22.0 d (24.6) 21.3 s
$Mo(CO)_2(CNxylyl)_2(PMePh_2)_2$[e]	31.9 s, 21.3 d (24.3), 17.1 d (24.3)
$Mo(CO)_2(CNxylyl)_2(PPh_3)_2$	57.1 s
$Mo(CO)_2(CNmesityl)_2(P\text{-}n\text{-}Pr_3)_2$	24.1 s
$Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(PMePh_2)_2$[f]	19.6 s, 18.0 d (22.9), 13.6 d (23.0)
$W(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2$	−0.42 s

[a] Spectra recorded in 1:1 CD_2Cl_2/CH_2Cl_2; positive chemical shifts measured downfield from 85% H_3PO_4. Abbreviations: s = singlet, d = doublet. [b] Coupling constants in Hz are given in parentheses next to the appropriate chemical shifts. [c] Relative intensities of the resonances were 2:1:1:2. [d] This complex was also measured in $CDCl_3$ and acetone-d_6—the spectra were similar, but the intensities were different. Ratio of peak heights in CD_2Cl_2 was 1:10:10:9. Chemical shifts in $CDCl_3$ were δ 35.8, 23.3 d (24), 20.2 d (24), 19.3 s; relative intensities were 6:1:1:5. Chemical shifts in acetone-d_6 were δ 39.2 s, 26.4 d (25.0), 23.3 (25.0), 22.6 s; relative intensities were 2:5:5:4. [e] Relative intensities of the resonances were 2:5:5. [f] Relative intensities of the resonances were 4:3:3.

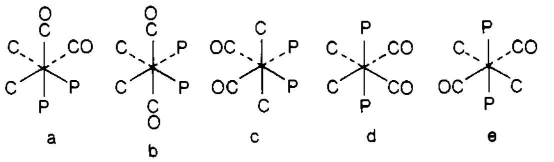
Table IV. ESR Spectra of $[Mo(CO)_2(CNR)_2(PR'_3)_2]^{+}$[a]

compound	$g_\parallel$	$g_\perp$	A,[c] G
$[Mo(CO)_2(CNCy)_4]^{+}$[b]	2.121	1.984	
$[Mo(CO)_2(CN\text{-}i\text{-}Pr)_2(PPh_3)_2]^+$	2.074	1.976	25
$[Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PEt_3)_2]^+$	2.079	1.981	27
$[Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PMePh_2)_2]^+$	2.076[d]	1.976	27
$[Mo(CO)_2(CN\text{-}p\text{-}tol)_2(PEt_2Ph)_2]^+$	2.067	1.979	25
$[Mo(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2]^+$	2.070[d]	1.983	24
$[Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2]^+$	2.062[d]	1.982	25
$[Mo(CO)_2(CNxylyl)_2(PMePh_2)_2]^+$	2.064	1.979	25
$[Mo(CO)_2(CNxylyl)_2(PPh_3)_2]^+$	2.068	1.980	25
$[Mo(CO)_2(CNmesityl)_2(P\text{-}n\text{-}Pr_3)_2]^+$	2.068[d]	1.983	25
$[Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(P\text{-}n\text{-}Pr_3)_2]^+$	2.080[d]	1.979	25
$[Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(PMePh_2)_2]^+$	2.074	1.980	23
$[W(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2]^{+}$[e]	2.212	1.903	

[a] Recorded at −160 °C on electrochemically oxidized 0.1 M $TBAH/CH_2Cl_2$ frozen solutions. [b] This complex had six well-resolved hyperfine lines in the $g_\parallel$ region due to ^{95}Mo and ^{97}Mo (combined abundance 25.15%, $I = {}^5/_2$). [c] Coupling constant of the unpaired electron to two equivalent phosphorus nuclei. [d] This cation prepared chemically as a PF_6^- salt had an ESR spectrum identical with that of its electrochemically generated counterpart. [e] This complex showed no coupling to phosphorus.

is observed. A variable-temperature ^{31}P NMR experiment on $Mo(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2$ over the range +30 to −63 °C revealed no change in the single phosphorus resonance. The spectra of the complexes with $PR'_3 = PEt_2Ph$ or $PMePh_2$ were strikingly different from the others measured. The two PEt_2Ph complexes each have two singlets due to isomers having pairs of equivalent phosphorus ligands and a pattern consisting of a pair of doublets arising from a third isomer. The latter resonances arise from the presence of two inequivalent phosphorus nuclei that are coupled to each other. The $PMePh_2$ complexes have ^{31}P NMR spectra with one singlet and two doublets.

There are five isomeric structures possible for $Mo(CO)_2(CNR)_2(PR'_3)_2$ complexes. They are



where P stands for phosphine and C for an isocyanide ligand. Of these five, only isomer a has inequivalent phosphines and thus must be responsible for the two doublets in the ^{31}P NMR spectra. A simple trigonal twist will convert any of the isomers b–e into the all-cis isomer a. However, since the four isomers with equivalent phosphines would all display singlets in the ^{31}P NMR, it is impossible to assign the singlets in the spectra of the PEt_2Ph and $PMePh_2$ derivatives with any certainty. It seems likely that they are due to either isomer d and/or e, since there is evidence for the existence of these two isomers from the IR spectra.

$^{31}P\{^1H\}$ NMR spectra of $Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2$ were recorded in three solvents—CD_2Cl_2, $CDCl_3$, and acetone-d_6. The resonances—two singlets and two doublets—are present in each solution, but in different ratios (the pair of doublets pattern is the most intense signal in CD_2Cl_2 and acetone-d_6, while the two singlets are predominant in $CDCl_3$—see Table III and Figure S2).

Proton NMR spectra (recorded in CD_2Cl_2) are consistent with the results of the ^{31}P NMR spectra.[30] For example, in the case of $Mo(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2$, whose phosphorus NMR spectrum displayed only a singlet, its proton NMR spectrum is relatively simple. There is a multiplet centered at δ 7.02 due to the phenyl protons of the xylyl groups, a singlet at δ 2.43 due to the methyl protons of xylylNC, a multiplet centered at δ 1.66 due to the methylene protons of the propyl group, and a triplet centered at δ 0.88 due to the methyl protons of the propyl groups. The ^1H NMR spectrum of $Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2$, on the other hand, is more complex. There are three multiplets in the phenyl region centered at δ 7.23, 7.18, and 7.02. The first two arise from the phenyl protons of the phosphine ligands; the third arises from the phenyl protons of xylylNC. There are three singlets at δ 2.40, 2.36, and 2.29 due to the methyl protons of xylylNC, a broad multiplet centered at δ 1.89 due to the $-CH_2-$ protons of PEt_2Ph, and a broad multiplet at δ 0.92 due to the phosphine methyl protons. Again it is the resonances of the methyl groups that are diagnostic. A singlet for the xylylNC methyls and a triplet for the PEt_2Ph methyls would be expected if only one isomer were present (as was seen in the ^1H NMR spectrum of $Mo(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2$, vide supra). Instead we see three singlets for the xylylNC methyls and a broad multiplet for the PEt_2Ph methyls. For this complex then, both the ^1H and $^{31}P\{^1H\}$ NMR spectra confirm the presence of isomers.

Electronic absorption spectral data for neutral $Mo(CO)_2(CNR)_2(PR'_3)_2$ complexes are available in Table SIII. These complexes are all intensely yellow to orange colored. The lower energy transition ($\lambda_{max} \sim 350$ nm for the alkyl isocyanide derivatives and between 395 and 437 nm for the aryl isocyanide complexes) is assigned to a Mo → L charge-transfer transition; it varies slightly with the nature of the alkyl or aryl group. These results are similar to those for the related complexes $Mo(CO)_4(CNR)_2$.[31] The observed decrease in the energy of the Mo → L charge-transfer transition on going from alkyl to aryl isocyanide is consistent with the better π-acceptor properties of the latter ligands. In this context, the electronic absorption spectrum of $Mo(CNPh)_6$ displays three absorption maxima between 300 and 460 nm, all of which have been attributed to Mo ($d\pi$) → CNPh (π^*) transitions.[32]

(c) Characterization of the Monocations. The IR spectral data for these all-trans species (Table SII) have been discussed in the previous section. The X-band ESR spectra of frozen CH_2Cl_2 solutions of both the electrochemical and chemical oxidation products of $Mo(CO)_2(CNR)_2(PR'_3)_2$ reveal species with approximate tetragonal symmetry possessing a single unpaired electron with $g_\perp > g_\parallel$ (Table IV). For purposes of comparison, the ESR spectrum of *trans*-$[Mo(CO)_2(CNCy)_4]^+$ was also re-

---

[30] The proton NMR spectra integrate correctly for the proposed stoichiometry of these complexes.

[31] Connor, J. A.; Jones, E. M.; McEwen, G. K.; Lloyd, M. K.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1246.

[32] Mann, K. R.; Cimolino, M.; Geoffroy, G. L.; Hammond, G. S.; Orio, A. A.; Albertin, G.; Gray, H. B. *Inorg. Chim. Acta* **1976**, *16*, 97.

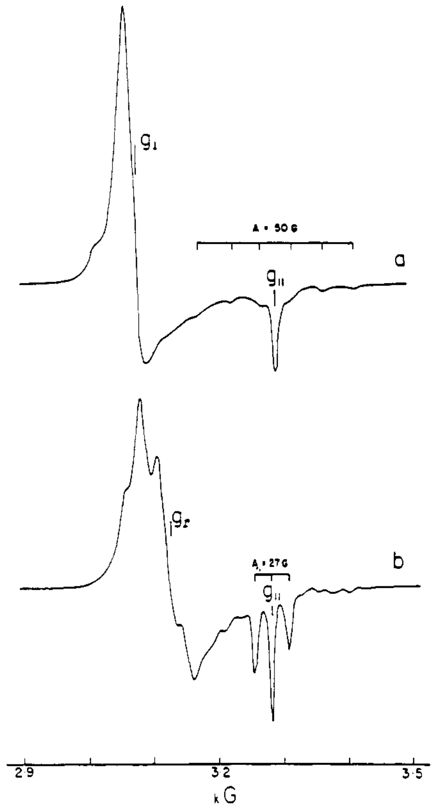
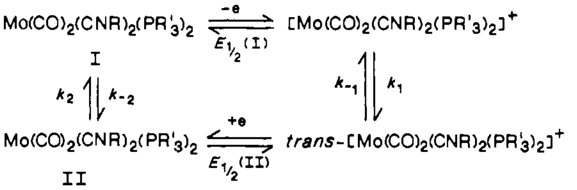


Figure 5. X-Band ESR spectra of frozen CH_2Cl_2 solutions at −160 °C of (a) $[Mo(CO)_2(CNCy)_4]^+$ and (b) $[Mo(CO)_2(CN\text{-}t\text{-}Bu)_2(PMePh_2)_2]^+$.

Scheme I



corded.[33] This species possesses tetragonal symmetry and has $g_x = g_y = 2.121$ and $g_z = 1.984$ (Figure 5a). Hyperfine splitting due to ^{95}Mo and ^{97}Mo (combined abundance = 25.2%, $I = {}^5/_2$) accounts for the apparent asymmetry in the $g_\perp$ signal. The hyperfine lines in the $g_\parallel$ region are well-resolved with $A = 50$ G. Figure 5b shows an ESR spectrum that is typical of the *trans*-$[Mo(CO)_2(CNR)_2(PR'_3)_2]^+$ cations. For the phosphine complexes, the "perpendicular" signal is broader and more structured than that of $[Mo(CO)_2(CNCy)_4]^+$, but only one g value is clearly resolved. The 1:2:1 triplet in $g_\parallel$ results from the interaction of the unpaired electron with two equivalent ^{31}P nuclei ($I = {}^1/_2$). The tri-*t*-butylphenyl isocyanide complexes displayed ESR spectra with a slightly better resolved splitting in the $g_\perp$ region due to interaction with the two equivalent phosphorus nuclei (Figure S3).

The 17-electron species *trans*-$[Mo(CO)_2(CNR)_2(PR'_3)_2]PF_6$ exhibit an electronic absorption band maximum between 516 and 563 nm ($\epsilon \sim (1\text{–}4) \times 10^2$ in CH_2Cl_2 solution), a feature that characterizes the spectra of related 17-electron species such as *trans*-$ReCl_2(CO)_2(PR_3)_2$,[34] $[Re(CNAr)_6]^{2+}$,[35] and $[Re(CNR)_2(NCCH_3)_2(PPh_3)_2]^{2+}$.[36]

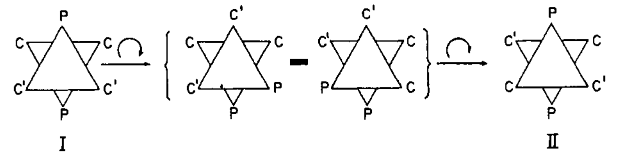


Figure 6. Schematic representation of two sequential twists that could convert isomer I to isomer II without bond breaking. C = CO, C′ = CNR, and P = PR_3.

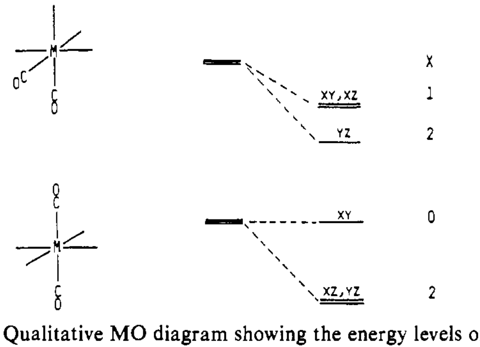


Figure 7. Qualitative MO diagram showing the energy levels of the d_π orbitals for isomers of $M(CO)_2L_4$ (M = a d^6 metal and L = a poorer π-acceptor ligand than CO). X represents the number of CO ligands that can interact with a given d_π orbital. (Adapted from ref 37.)

(d) Concluding Remarks. The electrochemical and spectroscopic data for $[Mo(CO)_2(CNR)_2(PR'_3)_2]^{0/+}$ are in accord with Scheme I. The neutral species $Mo(CO)_2(CNR)_2(PR'_3)_2$ on the basis of the IR and ^{31}P NMR spectral evidence apparently adopt a trans PR'_3, cis CO, and cis CNR structure when R is an alkyl isocyanide and PR'_3 is any of the phosphines studied except PPh_3, while there is substantial evidence for a mixture of isomers in the case of the aryl isocyanide derivatives. This mixture is most likely composed of complexes with cis CO ligands, such as the all-cis isomer and the trans PR'_3, cis CO, cis CNR isomer, since these would be expected to have very similar $E_{1/2}$ values,[37,38] and from the electrochemistry we only see two couples, one attributed to the "cis" isomer in Table I and one to the all-trans isomer.

In any case, oxidation of $Mo(CO)_2(CNR)_2(PR'_3)_2$ (whatever its structure) is followed by rapid isomerization to the all-trans cation that in turn isomerizes back upon electrochemical reduction to the neutral 18-electron species. From this study, it is clear that the order of rates is $k_1 > k_2$ (in the case of the $t\text{-}Bu_3PhNC$ derivatives, k_2 is extremely slow, and it is several hours before any appreciable amount of the neutral trans isomer converts back to a mixture of isomers). Note that for the redox cross-reaction

$$I^+ + II \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} I + II^+ \qquad (8)$$

the order $k_3 > k_{-3}$ holds, as shown by the evaluation of the equilibrium constant for this reaction demonstrated earlier (see eq 6 and 7 in section a).

The similarity of the electrochemical behavior in various solvents as well as the reversibility established by the coulometric experiments support the notion that the structural rearrangement is nondissociative. Figure 6 illustrates a possible mechanism for the intramolecular conversion of I to II. In this figure, isomer I is shown as being the trans PR'_3, cis CO, and cis CNR derivative, but any of the other possible isomers could as easily take its place—as mentioned before, all the other four isomers can convert to the all-cis isomer with a single twist, and from the all-cis to the all-trans isomer with one more twist.

A rationale for the greater stability of the cis geometry for 18-electron d^6-metal dicarbonyl species and the preference of the 17-electron congeners for the trans geometry is given in a qual-

---

(33) The neutral *cis*-$Mo(CO)_2(CNCy)_4$ complex exhibits similar behavior on electrochemical oxidation to the $Mo(CO)_2(CNR)_2(PR_3)_2$ complexes. That is, the cis isomer converts to the all-trans species upon oxidation to the cation (electrochemical and IR spectral data on this complex are included in Tables I, II, IV, and SI).

(34) Hertzer, C. A.; Myers, R. E.; Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2383.

(35) Cameron, C. J.; Tetrick, S. M.; Walton, R. A. *Organometallics* **1984**, *3*, 240.

(36) Allison, J. D.; Fanwick, P. E.; Walton, R. A. *Organometallics* **1984**, *3*, 1515.

(37) Bursten, B. E. *J. Am. Chem. Soc.* **1982**, *104*, 1299.

(38) Bursten, B. E., private communication.

itative MO treatment proposed by Bursten,[37] which compares the electronic properties of model complexes having two cis CO ligands with those having two trans CO ligands.[39] This scheme is shown in Figure 7; the two energy level diagrams represent the d_π orbitals for the isomers of $M(CO)_2L_4$, where M is a metal with six d electrons and L is a ligand with poorer π-acceptor ability than CO. This scheme is in agreement with the experimentally observed properties of $Mo(CO)_2(CNR)_2(PR'_3)_2$, that is, the trans CO isomers are easier to oxidize because the electron is removed from an orbital of higher energy than that of the cis isomer HOMO. The HOMO of the trans isomer has no stabilization from interaction with CO ligands, while all the orbitals of the cis isomer are stabilized to some extent by interaction with CO. The preference for one geometry over another depending on oxidation state is similarly explained: the cis isomer is stabilized the maximum amount by having 18 electrons, while the trans isomer is equally stable with 16, 17, or 18 electrons. The rapid isomerization to the trans isomer when an electron is removed from the cis isomer is nicely explained in this manner.[40]

Acknowledgment. Support of this research by the National Science Foundation (Grants CHE82-06117 and CHE85-06702) is gratefully acknowledged.

Supplementary Material Available: Tables giving homogeneous chemical rate constants for the cis–trans isomerization of $Mo(CO)_2(CNR)_2(PR'_3)_2$ (Table SI), IR spectral data for $[Mo(CO)_2(CNR)_2(PR'_3)]^+$ (Table SII), and electronic absorption spectral data for $Mo(CO)_2(CNR)_2(PR'_3)_2$ (Table SIII) and figures showing cyclic voltammograms of $Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(P\text{-}n\text{-}Pr_3)_2$ (Figure S1), the $^{31}P\{^1H\}$ NMR spectrum of $Mo(CO)_2(CNxylyl)_2(PEt_2Ph)_2$ (Figure S2), and the ESR spectrum of $[Mo(CO)_2(CN(t\text{-}Bu_3Ph))_2(P\text{-}n\text{-}Pr_3)_2]^+$ (Figure S3) (8 pages). Ordering information is given on any current masthead page.

---

[39] EHMO calculations on the model complexes $[Mo(CO)_2(PH_3)_4]^{+/0}$ show that the cis form is favored in 18-electron systems and the trans form in 17-electron systems; see: Mingos, M. P. *J. Organomet. Chem.* **1979**, *179*, C29.

[40] Measurements carried out on the tungsten complex $W(CO)_2(CNxylyl)_2(P\text{-}n\text{-}Pr_3)_2$ show that it behaves in a similar fashion to its molybdenum analogues; consequently a discussion of its properties is not given in the text. Its spectroscopic and electrochemical properties are summarized in Tables I–IV and SI–SIII. The complex was prepared as an orange powder by the reaction of $(\eta^3\text{-}C_3H_5)WCl(CO)_2(CNxylyl)_2$ with $P\text{-}n\text{-}Pr_3$ in CH_2Cl_2 solution (see procedure B.1. in the Experimental Section) and recrystallized from CH_2Cl_2/MeOH.

Contribution from the Department of Chemistry,
Michigan State University, East Lansing, Michigan 48824

NMR and Potentiometric Studies of Lithium Salts in 1-Butylpyridinium Chloride–Aluminum(III) Chloride Molten Systems

Rick R. Rhinebarger, John W. Rovang, and Alexander I. Popov*

Received March 20, 1986

Lithium-7 NMR and potentiometric measurements have been used to identify and characterize lithium chloro complexes of the lithium ion in the *n*-butylpyridinium chloride–aluminum chloride ($AlCl_3$–(BP)Cl) ambient temperature molten salt media. Concentration-dependent ^7Li chemical shift data have been fitted to a two-site fast-exchange model that assumes an equilibrium between the $LiCl_2^-$ monomer and the $Li_2Cl_4^{2-}$ dimer species (log K_d = 2.82 (±0.39) M^{-1}, K_d = dimerization constant). Potentiometric measurements on LiCl and $LiClO_4$ solutions in basic melt (45 mol % $AlCl_3$) confirm that two chloride ions are associated with each lithium ion.

Introduction

The $AlCl_3$–*n*-butylpyridinium chloride ambient temperature molten salt system, first described by Osteryoung et al.,[1] has been shown to be a highly versatile anhydrous medium for many chemical applications and, in particular, for studies of various complexation equilibria.[2-6] Our interest in this system is focused primarily upon the interaction of alkali-metal cations with the components of these media as well as on the influence of those "nonaqueous solvents" on the formation of macrocyclic complexes of the alkali-metal ions.[7,8]

The purpose of this work was to characterize in greater detail the environment of the lithium ion in basic (mole fraction $AlCl_3$ < 0.50) and acidic (mole fraction of $AlCl_3$ > 0.50) melts, to identify various lithium species (chloro complexes and crown ether complexes), and to study their interactions in the melt. Lithium-7 chemical shifts, spin–lattice (T_1) relaxation measurements, and potentiometric titration methods have been used to obtain this information.

Experimental Section

n–Butylpyridinium chloride was prepared by the method of Osteryoung et al.[1] The salt was recrystallized twice from an acetonitrile–ethyl acetate mixture and dried under vacuum; it was then stored in vacuum-sealed ampules until used. Aluminum(III) chloride (Fluka) was distilled under vacuum in the presence of aluminum wire (Alfa). Lithium chloride and lithium bromide (Fisher), lithium nitrate (Mallinckrodt), and lithium perchlorate and lithium hexafluoroarsenate (Alfa) were dried for 3 days at 100 °C.

Preparation of all melts and solutions was carried out in a drybox under an inert-gas atmosphere with a combined $H_2O + O_2$ level of less than 10 ppm. All NMR samples were contained in 5 mm (Wilmad) vacuum-sealed NMR tubes.

Lithium-7 NMR measurements were made on a Bruker WH-180 spectrometer at the field of 42.28 kG and at a resonance frequency of 69.951 MHz. Except where otherwise indicated, NMR spectra were obtained at 40 (±1) °C. The instrument was locked on the deuterium signal of the primary external reference (0.015 M LiCl in D_2O) for all samples where the overlap with the ^7Li signal of the reference did not occur. Otherwise, a secondary reference (0.015 M LiCl in pyridine) was used, and spectra were obtained without lock. Chemical shifts (except those in acidic melt solutions) are corrected for differences in magnetic susceptibility between the melt and water. The uncertainties in chemical shift values are ±0.02 ppm. Downfield (paramagnetic) shifts are indicated as *positive*. The magnetic susceptibility of the 45:55 mol % $AlCl_3$–(BP)Cl melt was determined at 40 °C by using an SHE Corp. 800

---

(1) Gale, R. J.; Gilbert, B.; Osteryoung, R. A. *Inorg. Chem.* **1978**, *17*, 2728. Gale, R. J.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 1603.
(2) Pickup, P. G.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2294.
(3) Hussey, C. L.; King, L. A.; Wilkes, J. S. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *102*, 321.
(4) Schoebrechts, J. P.; Gilbert, B. P.; Duyckaerts, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *145*, 127.
(5) Fannin, A. A.; King, L. A.; Levisky, J. A.; Wilkes, J. S. *J. Phys. Chem.* **1984**, *88*, 2609.
(6) Lipsztajn, M.; Osteryoung, R. A. *Inorg. Chem.* **1985**, *24*, 716.
(7) Taulelle, F.; Popov, A. I. *Polyhedron*, **1983**, *2*, 889.
(8) Rhinebarger, R. R.; Rovang, J. W.; Popov, A. I. *Inorg. Chem.* **1984**, *23*, 2557.

0020-1669/86/1325-4430$01.50/0 © 1986 American Chemical Society