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Preparation and Reactivity of Monomeric (Tolylimido)molybdenum(V) Complexes and Structure of *mer*-Trichloro-*trans*-bis(ethyldiphenylphosphine)-(*p*-tolylimido)molybdenum(V), $Mo(Ntol)Cl_3(EtPh_2P)_2$

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The reaction of the (*p*-tolylimido)molybdenum(VI) complex $Mo(Ntol)Cl_4(THF)$ with various tertiary phosphine ligands L affords monomeric (*p*-tolylimido)molybdenum(V) complexes of the form $Mo(Ntol)Cl_3L_2$ ($L = Ph_3P, EtPh_2P, Me_3P; L_2 = Ph_2PC_2H_4PPh_2$). In the solid state, these paramagnetic complexes are relatively stable in air and display magnetic moments close to the spin-only value. In solution, these species show strong ESR signals at room temperature. Reaction of $Mo(Ntol)Cl_3(EtPh_2P)_2$ with ethyldiphenylphosphine oxide affords $Mo(Ntol)Cl_3(OPEtPh_2)_2$. In toluene solution, $Mo(Ntol)Cl_3(EtPh_2P)_2$ reacts with O_2 and adventitious H_2O to ultimately yield *p*-toluidine, $EtPh_2PO$, and the dioxo Mo(VI) species $[MoO_2Cl_2(OPEtPh_2)\cdot{}^1/_2C_6H_5CH_3]$. A plausible mechanism for this process is presented. Reduction of $Mo(Ntol)Cl_3(Me_3P)_2$ by sodium amalgam in toluene in the presence of PMe_3 proceeds smoothly to yield the (*p*-tolylimido)molybdenum(IV) complex *cis,mer*-$Mo(Ntol)Cl_2(Me_3P)_3$. The structure of $Mo(Ntol)Cl_3(EtPh_2P)_2$ has been determined. The complex crystallizes in space group $P\bar{1}$ with $a = 12.988$ (4) Å, $b = 12.346$ (3) Å, $c = 11.789$ (3) Å, $\alpha = 73.58$ (1)°, $\beta = 103.97$ (1)°, $\gamma = 83.50$ (1)°, and $Z = 2$. The pseudooctahedral structure displays a meridional arrangement of the chlorine atoms and a trans disposition of the phosphine ligands. The Mo–Cl bond trans to the tolylimido ligand is lengthened by 0.1 Å compared to those in the cis positions. Comparisons to related structures are made.

Introduction

Transition-metal organoimido complexes,[3] $L_nM(NR)$, have been known for approximately 30 years but only lately has their chemistry begun to flourish. In part, this increased activity reflects a growing awareness of the importance of these species in diverse areas. Thus, organoimido complexes have recently been studied as models for both industrial[4] and metabolic[5] processes. In synthetic applications, organoimido complexes are useful reagents for the stereospecific oxyamination[6] and diamination[7] of olefins and have been implicated as the active catalysts in studies of olefin metathesis[8] and aziridination.[9]

As part of our continuing investigations of transition-metal organoimido species,[10-13] we report herein the preparation and properties of a series of paramagnetic (*p*-tolylimido)molybdenum(V) complexes of the type $Mo(Ntol)Cl_3L_2$ (L = tertiary phosphine). Aspects of the reactivity of the species are discussed, and the molecular structure of $Mo(Ntol)Cl_3(EtPh_2P)_2$ is presented. A portion of this work has appeared in a preliminary form.[11]

Results and Discussion

Preparation and Properties. When the (*p*-tolylimido)molybdenum(VI) complex $Mo(Ntol)Cl_4(THF)$[11] is treated with tertiary phosphines L in toluene or 1,2-dichloroethane solution at 40–50 °C, reduction of the metal occurs to produce (*p*-tolylimido)molybdenum(V) complexes of the type $Mo(Ntol)Cl_3L_2$, as shown in eq 1. Although the fate of the chlorine atom lost from the

$$Mo(Ntol)Cl_4(THF) + 2L \rightarrow Mo(Ntol)Cl_3L_2 \qquad (1)$$

$$L = Ph_3P,\ EtPh_2P,\ Me_3P;\ L_2 = Ph_2PC_2H_4PPh_2$$

Mo(VI) starting material is not known, many examples of similar reductions of high-oxidation-state halide complexes induced by phosphorus or nitrogen donor ligands have been documented in the literature,[14] including the corresponding reactions of $MoOCl_4$ with various Lewis bases.[15] All of the complexes shown in eq 1 are stable to air in the solid state, and all are orange to red-orange with the exception of the diphos compound, $Mo(Ntol)Cl_3(Ph_2PC_2H_4PPh_2)$, which is a golden color. While at this point we cannot be sure of the origin of this difference, it may reflect the fact in the diphos complex the phosphorus atoms are constrained to occupy cis positions, while in the bis(phosphine) complexes, the phosphorus ligands are free to adopt the less crowded trans disposition.

Table I. ESR Data[a] for $Mo(Ntol)Cl_3L_2$ Complexes

complex	g	$A(^{95,97}Mo)$, G	$A(^{31}P)$, G
$Mo(Ntol)Cl_3(PEtPh_2)_2$[b]	1.980	22.4	24.6
$Mo(Ntol)Cl_3(PMe_3)_2$[b]	1.981	21.9	25.1
$Mo(Ntol)Cl_3(PPh_3)_2$[b]	1.976	21.4	27.1
$Mo(Ntol)Cl_3(diphos)$[c]	1.968	25.8	28.3
$Mo(Ntol)Cl_3(OPEtPh_2)_2$[b]	1.961	26.9	20.2

[a] Toluene solution; 23 °C. Abbreviations: tol = *p*-tolyl; Me = methyl; Et = ethyl; Ph = phenyl; diphos = 1,2-bis(diphenylphosphino)ethane. [b] Spectrum composed of a principal triplet. [c] Spectrum composed of a principal doublet.

Molecular weight determinations establish that these 17-electron (d^1) species are monomeric in solution, while magnetic susceptibility data (along with the structural determination) indicate that they are also monomeric in the solid state. Monomeric imidomolybdenum(V) species are presently quite rare, especially in comparison to the numerous oxomolybdenum(V) complexes:[14,16] the only examples previously reported are two (pentachloroethyl)imido species, $(RCCl_2N)MoCl_3(RCN)_2$[17] and $[AsPh_4][Mo(NCCl_2R)Cl_4]$[18] ($R = Cl_3C$), and the diethyl dithiophosphate complexes $Mo(NR)(S_2P(OEt)_2)_2Cl$ and $Mo(NR)(S_2P(OEt)_2)_3$ (R = phenyl or *p*-tolyl).[19,20] The bonding in the $Mo(Ntol)Cl_3(PR_3)_2$ complexes is dominated by the effects of strong π-donation from nitrogen (p_x, p_y) to molybdenum (d_{xz}, d_{yz}), leading to the formation of a formal Mo≡Ntol triple bond. Thus, the electronic

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(1) Kansas State University.
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(3) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.
(4) Chan, D. M.-T.; Fultz, W. C.; Nugent, W. A.; Roe, D. C.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 251.
(5) Mansuy, D.; Battioni, P.; Mahy, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 4487.
(6) Patrick, D. W.; Truesdale, L. K.; Biller, S. A.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2628.
(7) Chong, A. O.; Oshima, K.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 3420.
(8) Kress, J.; Wesolek, M.; Le Ny, J.-P.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 1039.
(9) (a) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073. (b) Mansuy, D.; Mahy, J.-P.; Dureault, A.; Bedi, G.; Battioni, P. *J. Chem. Soc., Chem. Commun.* **1984**, 1161.
(10) Maatta, E. A. *Inorg. Chem.* **1984**, *23*, 2560.
(11) Chou, C. Y.; Huffman, J. C.; Maatta, E. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1184.
(12) Devore, D. D.; Maatta, E. A. *Inorg. Chem.* **1985**, *24*, 2846.
(13) Devore, D. D.; Takusagawa, F.; Maatta, E. A. *Inorg. Chim. Acta* **1986**, *112*, 87.
(14) Walton, R. A. *Prog. Inorg. Chem.* **1972**, *16*, 1.
(15) Larson, M. L.; Moore, F. W. *Inorg. Chem.* **1966**, *5*, 801.
(16) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.
(17) Fowles, G. W. A.; Moss, K. C.; Rice, D. A.; Rolfe, N. *J. Chem. Soc., Dalton Trans.* **1973**, 1871.
(18) Dehnicke, K.; Weiher, U. *Z. Anorg. Allg. Chem.* **1980**, *469*, 45.
(19) Edelblut, A. W.; Wentworth, R. A. D. *Inorg. Chem.* **1980**, *19*, 1110.
(20) Noble, M. E.; Huffman, J. C.; Wentworth, R. A. D. *Inorg. Chem.* **1982**, *21*, 2101.

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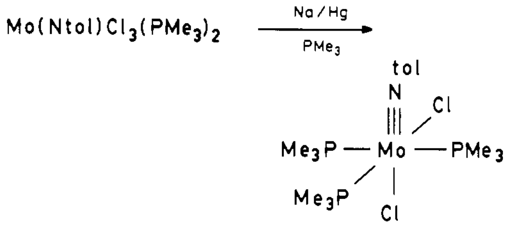
structures of these species will be qualitatively similar to that of the isoelectronic $[\mathrm{MoOCl_5}]^{2-}$ system as studied by Gray and co-workers[21] and the unpaired electron is expected to reside in the formally nonbonding Mo d_{xy} orbital. Our results are consistent with this description. All of the present complexes display solid-state magnetic moments close to the spin-only value of 1.73 μ_B, consistent with the unpaired electron occupying a nondegenerate orbital. Similarly, all of the $\mathrm{Mo(Ntol)Cl_3L_2}$ complexes display sharp ESR spectra at room temperature with g values near the free-electron value (Table I). Each of the ESR spectra displays hyperfine coupling to ^{95,97}Mo with $A(^{95,97}\mathrm{Mo}) \approx 24$ G as well as superhyperfine coupling to ^{31}P. Note however that the spectrum of the chelating diphos compound $\mathrm{Mo(Ntol)Cl_3(Ph_2PC_2H_4PPh_2)}$ is unique in that it shows strong coupling to only one ^{31}P nucleus, whereas the remaining spectra display superhyperfine coupling to two equivalent ^{31}P nuclei. On the basis of this information, we assign a cis,mer configuration for the structure of $\mathrm{Mo(Ntol)Cl_3(Ph_2PC_2H_4PPh_2)}$. Additional superhyperfine coupling is manifest in the spectra of the complexes in Table I; however, we refrain from making any further assignments until more detailed low-temperature studies are performed.

We have examined a few reactions of these (p-tolylimido)molybdenum(V) species. The phosphine ligands in $\mathrm{Mo(Ntol)Cl_3(EtPh_2P)_2}$ can be substituted by phosphine oxide in toluene solution, as shown in eq 2. The yellow $\mathrm{Mo(Ntol)Cl_3(OPEtPh_2)_2}$

$$\mathrm{Mo(Ntol)Cl_3(PEtPh_2)_2 + 2OPEtPh_2 \rightarrow Mo(Ntol)Cl_3(OPEtPh_2)_2 + 2PEtPh_2} \tag{2}$$

product is paramagnetic ($\mu_{\mathrm{eff}} = 1.85\ \mu_B$) and air-stable in the solid state and monomeric in solution. $\mathrm{Mo(Ntol)Cl_3(PMe_3)_2}$ can be cleanly reduced by sodium amalgam in toluene solution in the presence of $\mathrm{PMe_3}$ to afford a green, crystalline, diamagnetic (p-tolylimido)molybdenum(IV) complex, $\mathrm{Mo(Ntol)Cl_2(PMe_3)_3}$ (eq 3). The cis,mer configuration illustrated in eq 3 is assigned to the complex on the basis of a single-crystal X-ray diffraction study.[22] The ^{1}H NMR spectrum of $\mathrm{Mo(Ntol)Cl_2(PMe_3)_3}$ is consistent with this geometry being maintained in solution: the methyl protons of the $\mathrm{PMe_3}$ ligands appear as a triplet (δ 1.42; $J_{\mathrm{H-P}} = 3.6$ Hz) and a doublet (δ 1.28; $J_{\mathrm{H-P}} = 7.8$ Hz) in a ratio of 2:1.



(3)

When a toluene solution of $\mathrm{Mo(Ntol)Cl_3(PEtPh_2)_2}$ is exposed to air, its color slowly changes from orange to yellow, and after ca. 48 h, pale yellow acicular crystals of the Mo(VI) species $[\mathrm{MoO_2Cl_2(OPEtPh_2)\cdot{}^1/_2C_6H_5CH_3}]$ are deposited in high yield. Analysis of the mother liquor by GC/MS reveals the presence of p-toluidine and ethyldiphenylphosphine oxide. A similar reaction using $\mathrm{Mo(Ntol)Cl_3(OPEtPh_2)_2}$ proceeds more rapidly to give identical products. The overall reaction involves both oxidation and hydrolysis and can be expressed as in eq 4.

$$\mathrm{Mo(Ntol)Cl_3(PEtPh_2)_2 + {}^3/_2O_2 + H_2O \rightarrow MoO_2Cl_2(OPEtPh_2) + EtPh_2PO + tolNH_2 + Cl\cdot} \tag{4}$$

The deliberate addition of $\mathrm{H_2O}$ to solutions of $\mathrm{Mo(Ntol)Cl_3(EtPh_2P)_2}$ under an $\mathrm{N_2}$ atmosphere does not induce any reaction. However, if a toluene solution of $\mathrm{Mo(Ntol)Cl_3(EtPh_2P)_2}$ is exposed to an atmosphere of $\mathrm{O_2}$ using scrupulously dried reagents, reaction does occur and an orange-yellow solid can be isolated. The IR spectrum of this material displays a peak at 972 cm^{-1} attributable to a Mo–O vibration and a peak at 814 cm^{-1} (characteristic of a bound p-tolylimido ligand), as well as bands characteristic of the dioxo Mo(VI) species (ν(MoO) = 947, 904 cm^{-1}). Further aerobic reaction of this material proceeds with diminution of the 972- and 814-cm^{-1} features and concomitant production of the dioxo species. These observations are consistent with the presence of an intermediate complex of the form $\mathrm{MoO(Ntol)Cl_2(OPEtPh_2)_2}$, which suffers hydrolysis yielding p-toluidine and the dioxo compound. It is noteworthy that an analogous complex, $\mathrm{MoO(NH)Cl_2(OPEtPh_2)_2}$, displays a similar value of ν(MoO) and is also readily hydrolyzed to $\mathrm{MoO_2Cl_2(OPEtPh_2)_2}$.[23] A plausible sequence of reactions that accounts for the above observations is given in eq 5–11 (L = $\mathrm{PEtPh_2}$; R = p-tolyl).

$$\mathrm{2Mo^{V}(NR)Cl_3L_2 + O_2 \rightarrow L_2Cl_3(RN)Mo^{VI}\text{–}O\text{–}O\text{–}Mo^{VI}(NR)Cl_3L_2} \tag{5}$$

$$\mathrm{L_2Cl_3(RN)Mo^{VI}\text{–}O\text{–}O\text{–}Mo^{VI}(NR)Cl_3L_2 \rightarrow 2Mo^{VI}O(NR)Cl_2L_2 + 2Cl\cdot} \tag{6}$$

$$\mathrm{Mo^{VI}O(NR)Cl_2L_2 \rightarrow Mo^{IV}(NR)Cl_2(OL)L} \tag{7}$$

$$\mathrm{Mo^{IV}(NR)Cl_2(OL)L + {}^1/_2O_2 \rightarrow Mo^{VI}O(NR)Cl_2(OL)L} \tag{8}$$

$$\mathrm{Mo^{VI}O(NR)Cl_2(OL)L \rightarrow Mo^{IV}(NR)Cl_2(OL)_2} \tag{9}$$

$$\mathrm{Mo^{IV}(NR)Cl_2(OL)_2 + {}^1/_2O_2 \rightarrow Mo^{VI}O(NR)Cl_2(OL)_2} \tag{10}$$

$$\mathrm{Mo^{VI}O(NR)Cl_2(OL)_2 + H_2O \rightarrow Mo^{VI}O_2Cl_2(OL)_2 + RNH_2} \tag{11}$$

Each of the above steps has precedence in the literature. Thus, formation of the (μ-peroxo)dimolybdenum(VI) species of eq 5 is analogous to the synthesis of a Mo(VI)–$\mathrm{O_2}$–Co(III) complex obtained by the reaction of $\mathrm{O_2}$ with an aqueous solution of Mo(V) and Co(II),[24] while the overall one-electron oxidation of Mo(V) to Mo(VI) with accompanying substitution of oxygen for chlorine (eq 5 and 6) has been observed by Garner and co-workers (eq 12).[25] The sequence of eq 7–10, in which $\mathrm{PR_3}$ is oxidized by $\mathrm{O_2}$

$$\mathrm{MoOCl_3(OPPh_3)_2 + NO_3^- \rightarrow MoO_2Cl_2(OPPh_3)_2 + NO_2 + Cl^-} \tag{12}$$

to $\mathrm{OPR_3}$ as mediated by a Mo(VI)–Mo(IV) couple, is well-known in oxomolybdenum chemistry[26] and has recently been demonstrated in an analogous imidomolybdenum system.[12]

Our isolation of the monophosphine oxide adduct $[\mathrm{MoO_2Cl_2(OPEtPh_2)\cdot{}^1/_2C_6H_5CH_3}]$ is somewhat unusual but, again, not without precedent. While the coordination chemistry of $\mathrm{MoO_2Cl_2}$ is dominated by the formation of six-coordinate bisadducts of the type $\mathrm{MoO_2Cl_2L_2}$[15,27] (L = two-electron-donor Lewis base ligand), the ligands L in these complexes are invariably bound trans to the oxo ligands and thus the Mo–L bonds are lengthened and weakened by the strong trans influence of the oxo ligand. Monoadducts $\mathrm{MoO_2Cl_2L}$ have been reported,[27d] and in one structurally characterized complex, $\mathrm{MoO_2Cl_2(OPCl_3)}$, the molecules

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[21] (a) Gray, H. B.; Hare, C. R. *Inorg. Chem.* **1962**, *1*, 363. (b) Hare, C. R.; Bernal, I.; Gray, H. B. *Ibid.* **1962**, *1*, 831.

[22] Chou, C. Y.; Devore, D. D.; Huckett, S. C.; Maatta, E. A.; Huffman, J. C.; Takusagawa, F. *Polyhedron*, in press.

[23] (a) Chatt, J.; Choukroun, R.; Dilworth, J. R.; Hyde, J.; Vella, P.; Zubieta, J. *Transition Met. Chem.* (*Weinheim, Ger.*) **1979**, *4*, 59. (b) Dilworth, J. R., personal communication.

[24] (a) Arzoumanian, H.; Alvarez, R. L.; Kowalek, A. D.; Metzger, J. *J. Am. Chem. Soc.* **1977**, *99*, 5175. (b) Arzoumanian, H.; Lai, R.; Alvarez, R. L.; Petrignani, J.-F; Metzger, J.; Fuhrhop, J. *Ibid.* **1980**, *102*, 845.

[25] Garner, C. D.; Hyde, M. R.; Mabbs, F. E.; Routledge, V. I. *J. Chem. Soc., Dalton Trans.* **1975**, 1180.

[26] Reynolds, M. S.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 3057 and references therein.

[27] (a) Krauss, H. L.; Huber, W. *Chem. Ber.* **1961**, *94*, 2864. (b) Horner, S. M.; Tyree, S. Y., Jr. *Inorg. Chem.* **1962**, *1*, 122. (c) Feenan, K.; Fowles, G. W. A. *Inorg. Chem.* **1965**, *4*, 310. (d) Carmichael, W. M.; Edwards, D. A.; Fowles, G. W. A.; Marshall, P. R. *Inorg. Chim. Acta* **1967**, *1*, 93. (e) Florian, L. R.; Corey, E. R. *Inorg. Chem.* **1968**, *7*, 722. (f) Butcher, R. J.; Penfold, B. R.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1979**, 668.

Table II. Crystal Data for $Mo(Ntol)Cl_3(EtPh_2P)_2$

formula	$MoC_{35}H_{37}Cl_3NP_2$
mol wt	735.94
cryst dimens, mm	0.13 × 0.14 × 0.23
space group	$P\bar{1}$
cell dimens (20 °C; 30 reflcns)	
a, Å	12.988 (4)
b, Å	12.346 (3)
c, Å	11.789 (3)
α, deg	73.58 (1)
β, deg	103.97 (1)
γ, deg	83.50 (1)
Z	2
V, Å^3	1726.04
calcd density, g/cm^3	1.416
λ, Å	0.71069
μ, cm^{-1}	7.205
2θ range, deg	6–45
no. of unique data	4531
no. of unique data with $F > 3.00\sigma(F)$	4169
$R(F)$	0.0627
$R_w(F)$	0.0691
goodness of fit for last cycle	1.456
max Δ/σ for last cycle	0.05

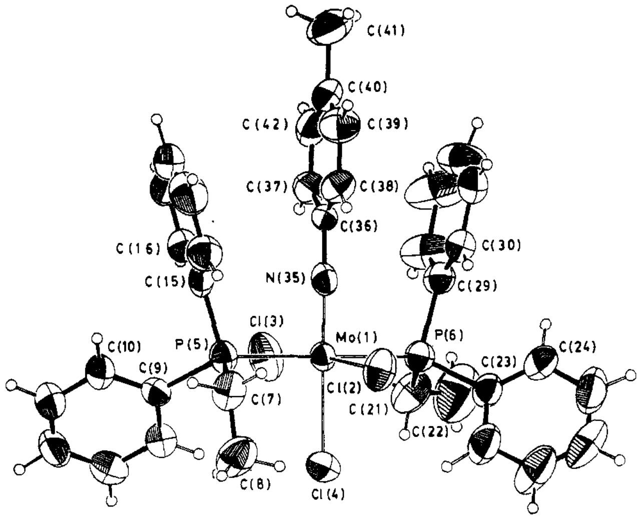

Figure 1. ORTEP view of the $Mo(Ntol)Cl_3(EtPh_2P)_2$ molecule. Carbon atoms of the phenyl rings are numbered sequentially from those shown.

are linked together by weak, asymmetric oxo bridges.[28] A similar solid-state structure may be found for $[MoO_2Cl_2(OPEtPh_2)\cdot{}^1/_2C_6H_5CH_3]$, but in solution, the complex is monomeric.

Molecular Structure of $Mo(Ntol)Cl_3(EtPh_2P)_2$. Crystal data are summarized in Table II, and a listing of fractional coordinates and isotropic thermal parameters is presented in Table III. An ORTEP drawing of the molecule is shown in Figure 1 while selected interatomic distances and angles are given in Table IV. The pseudooctahedral coordination geometry displays a meridional arrangement of the chlorine atoms and a trans disposition of the two ethyldiphenylphosphine ligands, leading to virtual C_{2v} local symmetry about the Mo atom. A similar trans,mer configuration has been established in three d^2 complexes of the form $Re(NR)Cl_3(PR_3)_2$[29,30] as well as in the analogous d^1 species $W(NPh)Cl_3(PPh_3)_2$.[31] Interestingly, d^0 imido Ta(V) complexes of related stoichiometry appear to favor the cis,mer configuration as seen in the structures of $Ta(NPh)Cl_3(THF)(PEt_3)$[32] and $[Cl_3(THF)_2Ta(NCMe{=}CMeN)TaCl_3(THF)_2]$, a species containing a bridging bis(imido) ligand.[33] A cis,mer configuration has also been proposed for the structures of $Ta(NR)Cl_3L_2$ (L = THF, R = Me, Ph, *t*-Bu; L = PMe$_3$, R = Ph), but the complex $Ta(NPh)Cl_3(PEt_3)_2$ seems to display the trans,mer configuration.[34]

Table III. Fractional Coordinates and Isotropic Thermal Parameters for $Mo(Ntol)Cl_3(EtPh_2P)_2$[a]

atom	*x*	*y*	*z*	B_{iso}
Mo(1)	2339.5 (4)	2185.8 (5)	9532.4 (5)	32
Cl(2)	4198 (1)	2191 (2)	9661 (2)	54
Cl(3)	432 (2)	2446 (2)	9255 (2)	65
Cl(4)	2001 (2)	4269 (2)	8343 (2)	59
P(5)	2074 (1)	1613 (2)	7529 (2)	39
P(6)	2552 (2)	2774 (2)	11505 (2)	40
C(7)	3111 (6)	1911 (7)	6712 (7)	51
C(8)	3038 (8)	3171 (8)	6089 (9)	71
C(9)	800 (5)	2193 (6)	6292 (6)	39
C(10)	439 (6)	1589 (6)	5512 (7)	50
C(11)	−471 (7)	2059 (8)	4527 (7)	58
C(12)	−1035 (7)	3123 (8)	4312 (7)	61
C(13)	−694 (7)	3739 (7)	5077 (8)	62
C(14)	219 (6)	3285 (7)	6084 (7)	51
C(15)	2162 (6)	63 (6)	7936 (6)	41
C(16)	1368 (6)	−412 (6)	8356 (6)	47
C(17)	1403 (8)	−1580 (8)	8716 (8)	58
C(18)	2247 (9)	−2302 (8)	8657 (8)	67
C(19)	3065 (8)	−1859 (9)	8277 (9)	71
C(20)	3034 (6)	−679 (6)	7905 (7)	53
C(21)	1363 (7)	3749 (7)	11469 (8)	60
C(22)	1286 (10)	4093 (11)	12499 (12)	113
C(23)	3682 (6)	3455 (6)	11997 (7)	45
C(24)	4298 (8)	3136 (7)	13192 (8)	63
C(25)	5185 (9)	3681 (9)	13506 (11)	90
C(26)	5385 (9)	4537 (10)	12642 (14)	86
C(27)	4805 (10)	4842 (10)	11506 (11)	87
C(28)	3942 (8)	4304 (8)	11142 (8)	64
C(29)	2734 (7)	1455 (6)	12792 (6)	48
C(30)	3704 (7)	694 (7)	13174 (7)	58
C(31)	3880 (10)	−366 (8)	14102 (9)	86
C(32)	3085 (15)	−628 (9)	14567 (9)	114
C(33)	2101 (14)	85 (10)	14182 (12)	118
C(34)	1916 (10)	1169 (8)	13261 (9)	77
N(35)	2554 (5)	751 (5)	10387 (5)	40
C(36)	2676 (5)	−386 (5)	11098 (5)	36
C(37)	1843 (6)	−742 (6)	11562 (7)	46
C(38)	3608 (6)	−1155 (6)	11307 (7)	48
C(39)	3726 (7)	−2284 (7)	12030 (8)	57
C(40)	2919 (7)	−2643 (6)	12539 (7)	53
C(41)	3065 (10)	−3885 (8)	13358 (10)	84
C(42)	1976 (7)	−1860 (7)	12284 (7)	55

[a] Fractional coordinates are ×10^4. B_{iso} values are ×10.

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) in $Mo(Ntol)Cl_3(EtPh_2P)_2$

	Distances		
Mo(1)–Cl(2)	2.3830 (21)	P(5)–C(7)	1.847 (7)
Mo(1)–Cl(3)	2.3908 (22)	P(5)–C(9)	1.832 (7)
Mo(1)–Cl(4)	2.4861 (22)	P(5)–C(15)	1.819 (7)
Mo(1)–P(5)	2.6092 (20)	P(6)–C(21)	1.831 (8)
Mo(1)–P(6)	2.5891 (20)	P(6)–C(23)	1.828 (7)
Mo(1)–N(35)	1.725 (6)	P(6)–C(29)	1.831 (7)
N(35)–C(36)	1.385 (8)		

	Angles		
Mo(1)–N(35)–C(36)	176.7 (5)	Cl(3)–Mo(1)–P(6)	88.58 (7)
Cl(2)–Mo(1)–Cl(3)	172.43 (9)	Cl(3)–Mo(1)–N(35)	92.82 (20)
Cl(2)–Mo(1)–Cl(4)	86.28 (8)	Cl(4)–Mo(1)–P(5)	91.98 (7)
Cl(2)–Mo(1)–P(5)	90.31 (7)	Cl(4)–Mo(1)–P(6)	87.58 (7)
Cl(2)–Mo(1)–P(6)	91.00 (7)	Cl(4)–Mo(1)–N(35)	178.28 (19)
Cl(2)–Mo(1)–N(35)	94.75 (20)	P(5)–Mo(1)–P(6)	178.59 (7)
Cl(3)–Mo(1)–Cl(4)	86.15 (9)	P(5)–Mo(1)–N(35)	89.38 (18)
Cl(3)–Mo(1)–P(5)	90.05 (7)	P(6)–Mo(1)–N(35)	91.03 (18)

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(28) Beyendorff-Gulba, G.; Strahle, J.; Liebelt, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1981**, *483*, 26.

(29) Bright, D.; Ibers, J. A. *Inorg. Chem.* **1968**, *78* 1099.

(30) Bright, D.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 703.

(31) Bradley, D. C. Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2651.

(32) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 223.

(33) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1978**, *17*, 3525.

The bonding of the tolylimido ligand in $Mo(Ntol)Cl_3(EtPh_2P)_2$ is characterized by a short Mo–N distance (1.725 (6) Å) and a near-linear Mo–N–C angle (176.7 (5)°); these values are consistent with the presence of an sp-hybridized nitrogen atom and a formal Mo≡Ntol triple bond. The Cl–Mo–P angles in the equatorial plane comprised of Cl(2), Cl(3), and P(5), and P(6) are all nearly 90°, with values ranging from 88.58 (7) to 91.00 (7)°. Both chlorine atoms are distorted away from the tolylimido ligand with angles N(35)–Mo–Cl(2) = 94.75 (20)° and N(35)–Mo–Cl(3) = 92.82 (20)°. However, only one of the phosphorus atoms is similarly displaced: while the angle N(35)–Mo–P(6) is slightly obtuse at 91.03 (18)°, the angle N(35)–Mo–P(5) is slightly acute at 89.38 (18)°. Analogous distortions are observed in the structure of $Ta(NPh)Cl_3(PEt_3)(THF)$ in which all three chlorides and the PEt_3 ligand are cis to the phenylimido ligand: all three N–Ta–Cl angles are obtuse while the N–Ta–P angle is slightly acute.[32]

The two molybdenum–ethyldiphenylphosphine distances are similar (Mo–P(5) = 2.609 (2) Å; Mo–P(6) = 2.589 (2) Å), as are the two equatorial Mo–Cl distances (Mo–Cl(2) = 2.383 (2) Å; Mo–Cl(3) = 2.391 (2) Å). These Mo–Cl distances are ca. 0.04 Å longer than the corresponding values observed in the Mo(VI) parent complex $Mo(Ntol)Cl_4(THF)$ (average Mo–Cl = 2.34 Å)[11] and may reflect both the lower oxidation state and the increased equatorial crowding in $Mo(Ntol)Cl_3(EtPh_2P)_2$.

An interesting aspect of the present structure is the observation of a trans influence[35] exerted by the tolylimido ligand. The Mo–Cl(4) distance trans to the tolylimido ligand at 2.486 (2) Å is 0.10 Å longer than the average of the equatorial Mo–Cl distances. A similar trans lengthening of ca. 0.06 Å was observed by Bradley et al. in the structure of the analogous 17-electron (d^1) species $W(NPh)Cl_3(PPh_3)_2$.[31] Likewise, a trans lengthening is observed in the Mo(V) complex $Mo(Ntol)(\eta^2\text{-}S_2P(OEt)_2)_2(\eta^1\text{-}S_2P(OEt)_2)$,[20] although this system is somewhat more complicated because one of the chelating dithiophosphate ligands spans the axial and equatorial positions and thus may display an inherent axial lengthening due to the restricted "bite" of the ligand, as found for related dithiocarbamate ligands.[36] Nevertheless, if a reasonable allowance for this effect is made, the trans lengthening is again ca. 0.1 Å.

The magnitude of the trans influence exerted by a linear organoimido ligand in pseudooctahedral complexes is markedly dependent upon the electron configuration at the metal. Thus, large trans lengthenings are observed in 16-electron d^0 complexes as exemplified in the structure of $[Cl_3(THF)_2Ta(NCMe{=}CMeN)TaCl_3(THF)_2]$:[33] the Ta–O distance for the THF molecule cis to the imido ligand is 2.151 (5) Å while the Ta–O distance for the trans THF molecule is lengthened by 0.20 Å to 2.356 (6) Å. With the above Ta–THF distance of 2.15 Å as a benchmark, the Ta–O distance of 2.379 (4) Å found in $Ta(NPh)Cl_3(THF)(PEt_3)$[32] represents a trans lengthening of 0.23 Å. Likewise, a trans lengthening of similar magnitude is observed in the structure of $Mo(Ntol)Cl_4(THF)$.[11] In sharp contrast, 18-electron d^2 complexes show no trans lengthening whatsoever as documented in the structures of $Mo(Ntol)Cl_2(PMe_3)_3$,[22] $W(NPh)Cl_2(PMe_3)_3$,[31] and three $Re(NR)Cl_3(PR_3)_2$ species.[29,30] On the basis of the above data, the magnitude of the trans influence exerted by organoimido ligands in pseudooctahedral species thus decreases as follows: 16-electron d^0 (~0.20–0.25 Å) > 17-electron d^1 (~0.06–0.10 Å) > 18-electron d^2 (~0.00 Å).

Experimental Section

General Procedures and Instrumentation. All reactions were carried out either in vacuo or under atmospheres of dry nitrogen, except as noted. Solvents were dried over appropriate reagents, stored in vacuo, and distilled directly into the reaction vessels. PMe_3, $PEtPh_2$, and $OPEtPh_2$ were used as received from Strem Chemicals.

Infrared spectra were recorded as Nujol mulls by using a Perkin-Elmer 1330 spectrophotometer and were calibrated with the use of a polystyrene film. Magnetic susceptibilities at 23 °C were determined by the Faraday method. ^1H (400 MHz) and ^{31}P (162 MHz) NMR spectra were obtained on an IBM/Bruker WM-400 instrument and are referenced to internal Me_4Si and external 70% H_3PO_4, respectively. ESR spectra were recorded by using a Bruker ER200D spectrometer operating near 9.78 GHz and were calibrated by using DPPH as a field marker. Solution molecular weights were determined by the isopiestic method in a locally modified version of the Signer apparatus.[37] Elemental analyses were performed by Galbraith Laboratories.

Preparation of $Mo(Ntol)Cl_4(THF)$. A portion of *p*-tolyl azide (0.49 g; 3.7 mmol) was added to 50 mL of 1,2-dichloroethane containing $MoCl_4(THF)_2$ (1.27 g; 3.3 mmol). The stirred system was maintained at 40 °C for 16 h with the evolved N_2 being vented through a bubbler system. The red-brown solution was filtered, and the solvent was removed in vacuo, yielding a dark red-purple solid, which was washed with hexane (2 × 50 mL) and dried in vacuo. The yield is essentially quantitative. Anal. Calcd for $MoC_{11}H_{15}NOCl_4$: C, 31.84; H, 3.64; N, 3.38. Found: C, 32.00; H, 3.80; N, 3.46. ^1H NMR ($CDCl_3$): δ 7.58 (AB quartet, J_{AB} = 8 Hz, 4 H, $C_6\mathit{H}_4CH_3$), 4.73 (m, 4 H, $\overline{\mathrm{OC}\mathit{H}_2(\mathrm{CH}_2)_2\mathrm{C}}\mathit{H}_2$), 2.86 (s, 3 H, $C_6H_4C\mathit{H}_3$), 2.16 (m, 4 H, $\overline{\mathrm{OCH}_2(\mathrm{C}\mathit{H}_2)_2\mathrm{C}}\mathrm{H}_2$). IR: 1580 (m), 1327 (m), 1165 (s), 1008 (s), 845 (s), 811 (s), 444 (m), 340 (m) cm^{-1}.

Preparation of $Mo(Ntol)Cl_3(EtPh_2P)_2$. A portion of $EtPh_2P$ (1.57 g; 7.34 mmol) was added to a stirred solution of $Mo(Ntol)Cl_4(THF)$ (1.27 g; 3.06 mmol) in toluene (100 mL) at room temperature. After 14 h, the orange solution was evaporated and the residue was washed with hexane (2 × 50 mL). The red-orange powdery product was collected by filtration and dried in vacuo (2.19 g; 97% yield). Anal. Calcd for $MoC_{35}H_{37}Cl_3NP_2$: C, 57.12; H, 5.07; N, 1.90. Found: C, 56.90; H, 4.96; N, 1.88. Magnetic moment: 1.79 μ_B. IR: 1590 (w), 1435 (m), 1413 (m), 1101 (m), 1044 (m), 1030 (m), 821 (s), 762 (s), 732 (s), 715 (m), 700 (m), 502 (m), 433 (m) cm^{-1}.

Preparation of $Mo(Ntol)Cl_3(Ph_3P)_2$. A portion (0.65 g; 2.5 mmol) of Ph_3P was added to a solution of $Mo(Ntol)Cl_4(THF)$ (0.47 g; 1.1 mmol) in 1,2-dichloroethane (35 mL), and the solution was stirred at 50 °C for 2 h. The solution was filtered, and the filtrate was evaporated to half-volume. Addition of hexane (10 mL) precipitated an orange solid, which was collected by filtration, washed with hexane (2 × 30 mL), and dried in vacuo. The complex thus obtained contains one-half of a dichloroethane molecule of solvation. Anal. Calcd for $MoC_{44}H_{39}NCl_4P_2$: C, 59.95; H, 4.46; N, 1.59. Found: C, 59.06; H, 4.55; N, 1.76. Magnetic moment: 1.77 μ_B. IR: 1583 (w), 1570 (sh), 1435 (m), 1169 (m), 1112 (m), 1091 (m), 1030 (w), 1014 (w), 999 (m), 823 (s), 748 (s), 730 (s), 696 (s), 543 (m), 525 (s), 513 (m), 492 (m), 440 (w) cm^{-1}.

Preparation of $Mo(Ntol)Cl_3(Ph_2PC_2H_4PPh_2)$. A portion (0.82 g; 2.06 mmol) of 1,2-bis(diphenylphosphine)ethane was added to a solution of $Mo(Ntol)Cl_4(THF)$ (0.82 g; 1.97 mmol) in 1,2-dichloroethane (35 mL) and heated to 50 °C for 1 h. The golden-bronw solution was filtered and evaporated to dryness, yielding a golden solid, which was triturated with hexane (3 × 50 mL) and dried in vacuo. This material was then redissolved in 1,2-dichloroethane (30 mL), and the solution was slowly concentrated in vacuo, producing the golden-brown microcrystalline product, which was collected by filtration and dried in vacuo. The complex thus obtained is the hemi(dichloroethane) solvate. Anal. Calcd for $MoC_{34}H_{33}NCl_4P_2$: C, 54.06; H, 4.40; N, 1.85. Found: C, 53.33; H, 4.48; N, 1.79. Mol wt: calcd (unsolvated), 706; found (1,2-dichloroethane solution), 701. Magnetic moment: 1.69 μ_B. IR: 1585 (m), 1435 (s), 1408 (sh), 1170 (m), 1101 (m), 1030 (w), 1015 (w), 1001 (m), 869 (w), 822 (s), 742 (s), 692 (s), 513 (s), 500 (m), 438 (w) cm^{-1}.

Preparation of $Mo(Ntol)Cl_3(Me_3P)_2$. A portion (0.71 g; 9.37 mmol) of Me_3P was added to a stirred solution of $Mo(Ntol)Cl_4(THF)$ (1.62 g; 3.90 mmol) in toluene (50 mL) at room temperature. After 12 h, the solution was filtered and taken to dryness in vacuo. The red-orange solid product was washed with hexane (50 mL) and dried in vacuo. Mol wt: calcd for $MoC_{13}H_{25}NP_2Cl_3$, 460; found (1,2-dichloroethane solution, 434. Magnetic moment: 1.75 μ_B. IR: 1585 (w), 1412 (m), 1284 (s), 1173 (w), 1113 (w), 1103 (m), 1042 (w), 1019 (w), 949 (vs), 822 (s), 743 (s), 674 (w), 653 (w), 559 (s), 444 (s) cm^{-1}.

Preparation of $Mo(Ntol)Cl_3(OPEtPh_2)_2$. A portion (0.37 g; 1.61 mmol) of $OPEtPh_2$ was added to a stirred solution of $Mo(Ntol)Cl_3(EtPh_2P)_2$ (0.49 g; 0.67 mmol) in toluene (30 mL) at room temperature. After 16 h, the solution had acquired a greenish color and was filtered. The filtrate was evaporated to dryness, and the solid residue was washed with hexane (2 × 50 mL) and Et_2O (50 mL) to afford the yellow-green powdery product, which was dried in vacuo. Anal. Calcd for

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(34) (a) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7809. (b) *Ibid.* **1982**, *104*, 3077.

(35) Shustorovich, E. M.; Porai-Koshits, M. A.; Buslaev, Y. A. *Coord. Chem. Rev.* **1975**, *17*, 1.

(36) Tan, L. S.; Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1983**, *22*, 1744.

(37) Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820.

$MoC_{35}H_{37}NO_2P_2Cl_3$: C, 54.74; H, 4.86; N, 1.82. Found: C, 55.04; H, 5.22; N, 1.51. Mol wt: calcd, 768; found (toluene solution), 764. Magnetic moment: 1.85 μ_B. IR: 1590 (w), 1439 (m), 1143 (vs), 1126 (s), 1099 (s), 1073 (w), 1032 (w), 1021 (w), 1000 (m), 840 (w), 823 (m), 752 (s), 731 (s), 699 (s), 542 (s), 520 (s), 487 (m), 440 (m) cm^{-1}.

Preparation of [$MoO_2Cl_2(OPEtPh_2)\cdot{}^1/_2C_6H_5CH_3$]. Hexane was added to a solution of $Mo(Ntol)Cl_3(EtPh_2P)_2$ (0.97 g; 1.32 mmol) in toluene (30 mL) until the point of incipient precipitation. The red-orange solution was then allowed to stand undisturbed, exposed to the atmosphere, for 2 days. During this time, the color of the solution became yellow and large pale yellow acicular crystals were deposited. These crystals were collected by filtration, washed with hexane, and dried in vacuo. Analysis of the mother liquor by GC/MS revealed the presence of *p*-toluidine and ethyldiphenylphosphine oxide. Anal. Calcd for $MoC_{31.5}H_{34}O_4Cl_2P_2$: C, 44.23; H, 4.03. Found: C, 44.20; H, 3.97; N, 0.00. Mol wt: calcd, 475; found (CH_2Cl_2 solution), 462. IR: 1591 (w), 1441 (s), 1174 (vs), 1150 (vs), 1126 (s), 1103 (s), 1076 (m), 1033 (w), 1002 (w), 947 (vs), 904 (vs), 764 (m), 750 (s), 723 (s), 703 (s), 545 (s), 513 (m) cm^{-1}.

Preparation of *cis,mer*-$Mo(Ntol)Cl_2(Me_3P)_3$. A stirred solution of $Mo(Ntol)Cl_3(Me_3P)_2$ (0.99 g; 2.16 mmol) and Me_3P (0.60 g; 7.84 mmol) in toluene (75 mL) was treated with sodium amalgam (0.08 g of Na (3.5 mmol) in 10 g of Hg). Over a 3-h period, the color of the solution changed from dark orange to green to blue and finally to green-brown. After being stirred an additional 12 h, the solution was filtered and the filtrate was taken to dryness. The green powdery product was washed with pentane (3 × 30 mL) and dried in vacuo. Large, dark green crystals of this material were readily obtained by slow cooling of a warm (40 °C) saturated toluene solution. The identity of the complex has been established by a single-crystal X-ray diffraction study.[22] ^1H NMR (C_6D_6): δ 6.87 (AB quartet, J_{AB} = 8.2 Hz, 4 H, $C_6H_4CH_3$), 1.88 (s, 3 H, $C_6H_4CH_3$), 1.42 (t, J_{HP} = 3.6 Hz, 18 H, PMe_3), 1.29 (d, J_{HP} = 7.8 Hz, 9 H, PMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 5.38 (t, J_{PP} = 18.1 Hz, area 1), −7.32 (d, J_{PP} = 18.1 Hz, area 2). IR: 1593 (w), 1416 (m), 1330 (s), 1301 (m), 1275 (s), 1106 (m), 1017 (m), 951 (vs), 853 (s), 826 (s), 783 (s), 674 (s), 554 (m), 444 (m) cm^{-1}.

Crystallographic Study. General operating procedures have been previously described.[38] Repeated attempts to cool suitable crystals to low temperatures (between −165 and −30 °C) resulted in crystal fracture; thus, data were collected at 20 °C. there was no evidence of decomposition during the course of the data collection as monitored by four reflections chosen as standards.

A systematic search of a limited hemisphere of reciprocal space located no systematic absences or symmetry, leading to a triclinic space group. The structure was readily solved by a combination of direct methods and Fourier techniques and refined by full-matrix least squares. Hydrogen atoms were not visible in difference Fourier maps phased on the non-hydrogen atoms but were included in the final cycles of refinement as idealized fixed-atom contributors (d(C–H) = 0.95 Å; B_{iso} = 1.0 + B_{iso}(riding atom)). A final difference Fourier was featureless, the largest peak being 0.21 e/Å^3. ψ scans of three reflections near χ = 90° were flat, indicating no absorption correction was necessary.

The thermal parameters are rather large for some parts of the molecule, indicative of the relatively "unstable" room-temperature form. The fact that a phase transition occurs slightly below room temperature is in agreement with these observations.

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Supplementary Material Available: Complete listings of bond lengths, bond angles, anisotropic thermal parameters, and structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

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(38) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

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Electrochemical Generation and Study of Labile 19-Electron Dinitrosylmolybdenum Radicals

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Electrochemical reduction of dicationic, monocationic, and neutral dinitrosylmolybdenum complexes in acetonitrile are reported: $[Mo(NO)_2L_2L_2]^{2+}$, $[Mo(NO)_2L_2LCl]^+$, $[Mo(NO)_2L_2Cl_2]$; L = MeCN, L_2 = 2,2′-bipyridine. All of the compounds are reducible by one electron to yield stable 19-electron complexes. The radical complexes can be reduced by another electron to unstable 20-electron complexes. Cyclic voltammetry and controlled-potential coulometry have been used at several temperatures to characterize these processes. The dicationic complexes undergo a reversible one-electron reduction. IR, UV–vis, and ESR studies have shown that the unpaired electron is delocalized over both nitrosyl groups. One-electron transfer to the monochloro and dichloro complexes induces facile exchange of the chloro ligand in the 19-electron complexes with L = MeCN. The free Cl^- anions coordinate to the remaining 18-electron chloro complexes to give $[Mo(NO)_2Cl_3L]^-$ and $[Mo(NO)_2Cl_4]^{2-}$, which are more easily reduced than dichloro or monochloro complexes. The multiple-electrochemical-step system is therefore not catalytic, but is rather of the electroactivation type.

Substitution reactions involving the removal of halide ions from halo complexes such as dinitrosyl complexes and replacement by neutral two-electron-donor ligands such as phosphine, nitrile, olefin, or alkyne lead to useful cationic complexes.[1-4] In particular, cationic olefin complexes have been thoroughly investigated because of their applications in catalytic organic synthesis.[5-7] The conventional associative and dissociative mechanisms for ligand exchanges are usually considered to involve even-numbered 16- and 18-electron intermediates.[8] Recently, efficient chain mechanisms of ligand substitution in metal carbonyls involving odd-electron radical intermediates have been proposed.[9] Fur-

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(1) Regina, F. J.; Wojciki, A. *Inorg. Chem.* **1980**, *19*, 3803.

(2) Legzdins, P.; Nurse, C. R. *Inorg. Chem.* **1982**, *21*, 3110.

(3) Fisher, E. O.; Fichtel, K. *Chem. Ber.* **1962**, *94*, 1200.

(4) (a) Foxman, B. M.; Klemarczyk, P. T.; Liptrot, R. E.; Rosemblum, M. *J. Organomet. Chem.* **1980**, *187*, 253. (b) Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3155. (c) Davison, A.; Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3172. (d) Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186. (e) Ballivet-Tkatchenko, D.; Brēmard, C. *J. Chem. Soc., Dalton Trans.* **1983**, 1143 and references therein. See also: Johnson, B. F. G.; Khair, A.; Savory, C. G.; Walter, R. H.; Alobaidi, K. H.; Al Hassam, T. J. *Transition Met. Chem.* (*Weinheim, Ger.*) **1978**, *3*, 81.

(5) Lennon, P.; Rosen, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8476 and references therein.

0020-1669/86/1325-0826$01.50/0