

**Figure 3.**  $E_{1/2}$  vs.  $n$ , the number of isocyanide ligands, for the processes  $[\text{Mn}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n]^{n+} \rightleftharpoons [\text{Mn}(\text{CO})_{6-n}(\text{CNC}_6\text{H}_5)_n]^{(n+1)+} + e^-$  ( $M = \text{Mn}$  for processes  $\text{Mn}^+ \rightarrow \text{Mn}^{2+}$ ,  $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$ ;  $M = \text{Cr}$  for processes  $\text{Cr}^0 \rightarrow \text{Cr}^+$ ,  $\text{Cr}^+ \rightarrow \text{Cr}^{2+}$ ) in  $\text{CH}_2\text{Cl}_2$ .

$\text{O}(\text{CNC}_6\text{H}_5)_5$ ,  $E_{1/2}$  values at 0.13 and 0.80 V correspond to oxidation processes for  $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4$ , and the  $E_{1/2}$  values of 1.23 and 1.60 V are similar to the second oxidations of *fac*- $\text{Cr}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3$  and *cis*- $\text{Cr}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2$ . We are quite confident of the purity of the starting materials in these systems; they are crystalline products having clean melting points and no spurious  $\nu(\text{CO})$  or  $\nu(\text{CN})$  infrared absorptions. Thus we are led to the conclusion that upon oxidation these compounds must undergo a rapid exchange of ligands to generate the products observed by the CV ex-

periment in solution. We are currently trying to test out this hypothesis.

**Registry No.** *cis*- $[\text{Mn}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2]\text{PF}_6$ , 70800-83-8; *mer*- $[\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]\text{PF}_6$ , 70877-81-5; *fac*- $[\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]\text{PF}_6$ , 70800-85-0; *cis*- $[\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]\text{PF}_6$ , 70800-87-2; *trans*- $[\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]\text{PF}_6$ , 70831-77-5; *cis*- $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4$ , 70800-88-3;  $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5$ , 70800-89-4; *cis*- $[\text{Mn}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2]^{2+}$ , 70800-90-7; *mer*- $[\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]^{2+}$ , 70800-91-8; *fac*- $[\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3]^{2+}$ , 70831-78-6; *cis*- $[\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]^{2+}$ , 70897-65-3; *trans*- $[\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4]^{2+}$ , 70800-92-9;  $[\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_5]\text{PF}_6$ , 38889-71-3;  $[\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_5]^{2+}$ , 70800-93-0;  $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{PF}_6$ , 36786-48-8;  $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]^{2+}$ , 47873-90-5;  $\text{Cr}(\text{CO})_6^+$ , 54404-20-5;  $\text{Cr}(\text{CO})_5(\text{CNC}_6\text{H}_5)^+$ , 70800-94-1; *cis*- $\text{Cr}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2$ , 70831-79-7; *cis*- $\text{Cr}(\text{CO})_4(\text{CNC}_6\text{H}_5)_2^+$ , 70800-95-2; *fac*- $\text{Cr}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3$ , 70831-80-0; *fac*- $\text{Cr}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3^+$ , 70800-96-3; *cis*- $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4^+$ , 70800-97-4; *cis*- $\text{Cr}(\text{CO})_2(\text{CNC}_6\text{H}_5)_4^{2+}$ , 70800-98-5;  $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5^+$ , 70800-99-6;  $\text{Cr}(\text{CO})(\text{CNC}_6\text{H}_5)_5^{2+}$ , 70801-00-2;  $\text{Cr}(\text{CNC}_6\text{H}_5)_6^+$ , 57016-32-7;  $\text{Cr}(\text{CNC}_6\text{H}_5)_6^{2+}$ , 57016-35-0;  $\text{Cr}(\text{CNC}_6\text{H}_5)_6^{3+}$ , 70801-01-3; *fac*- $\text{Mn}(\text{CO})_3(\text{CNC}_6\text{H}_5)_3\text{Br}$ , 52730-08-2; *mer*-*cis*- $\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_5)_3\text{Br}$ , 70831-81-1;  $\text{Mn}(\text{C}-\text{O})_5\text{Br}$ , 14516-54-2;  $\text{Mn}(\text{CO})(\text{CNC}_6\text{H}_5)_5\text{Br}$ , 31392-78-6;  $\text{Cr}(\text{CNC}_6\text{H}_5)_6$ , 17375-15-4;  $\text{Cr}(\text{CO})_6$ , 13007-92-6;  $\text{Cr}(\text{CO})_5(\text{CNC}_6\text{H}_5)$ , 14782-94-6;  $\text{Cr}(\text{CNC}_6\text{H}_5)_6^-$ , 61506-06-7.

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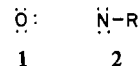
## Complexes of (Arylimido)molybdenum(VI)

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The reaction of an aryl azide with either  $\text{Mo}(\text{CO})_2(\text{Et}_2\text{dtc})_2$  or  $\text{MoO}(\text{Et}_2\text{dtc})_2$  yields  $\text{Mo}(\text{NR})_2(\text{Et}_2\text{dtc})_2$  and  $\text{MoO}(\text{NR})(\text{Et}_2\text{dtc})_2$ , respectively. The reaction of  $\text{Mo}(\text{NR})_2(\text{Et}_2\text{dtc})_2$  with  $\text{HCl}$  gives  $\text{Mo}(\text{NR})\text{Cl}_2(\text{Et}_2\text{dtc})_2$ , and the reaction with  $\text{CH}_3\text{Br}$  results in  $\text{Mo}(\text{NR})\text{Br}_2(\text{Et}_2\text{dtc})_2$ . While the reaction of  $\text{MoO}(\text{NPh})(\text{Et}_2\text{dtc})_2$  with  $\text{HCl}$  gives  $\text{Mo}(\text{NPh})\text{Cl}_2(\text{Et}_2\text{dtc})_2$ , the corresponding reaction with  $\text{MoO}(\text{NPhNO}_2)(\text{Et}_2\text{dtc})_2$  ( $\text{PhNO}_2 = p\text{-C}_6\text{H}_4\text{NO}_2$ ) leads to  $\text{MoOCl}_2(\text{Et}_2\text{dtc})_2$ . The metathesis of  $\text{Mo}(\text{NR})\text{Cl}_2(\text{Et}_2\text{dtc})_2$  and  $\text{Et}_2\text{dtc}^-$  gives  $\text{Mo}(\text{NR})(\text{Et}_2\text{dtc})_3^+$ . The oxo analogue of this complex was prepared from the reaction of  $\text{MoO}_2(\text{Et}_2\text{dtc})_2$  with  $\text{HBF}_4$ . A plausible mechanism for protonation of complexes containing the  $\text{MoO}_2$ ,  $\text{MoO}(\text{NR})$ , and  $\text{Mo}(\text{NR})_2$  fragments is suggested.

Complexes of molybdenum containing imido (nitrene) ligands constitute a small but growing area of investigation. Like the oxo ligand, a species which pervades the complexes of molybdenum when that metal is in one of its higher oxidation states, imido ligands have been found in either bridging or terminal positions. Occupancy of a bridging site occurs in  $\text{Mo}_2\text{O}_3(\text{NH})(\text{Et}_2\text{dtp})_2$ ,<sup>1,2</sup> while terminal sites are occupied in  $\text{Mo}(\text{NH})\text{X}(\text{dppe})_2^+$  ( $\text{X} = \text{halogen}$ ),<sup>1,3</sup>  $\text{Mo}(\text{NMe})(\text{Et}_2\text{dtc})_3^+$ ,<sup>1,4</sup>  $\text{Mo}(\text{NPh})_2(\text{Et}_2\text{dtc})_2$ ,<sup>1,5</sup>  $\text{Mo}(\text{NR})(\text{Et}_2\text{dtp})_3$ , and  $\text{Mo}(\text{NR})\text{Cl}(\text{Et}_2\text{dtp})_2$  ( $\text{R} = \text{aryl}$ ).<sup>6</sup> We have also postulated<sup>7</sup> the transient existence of  $\text{MoO}(\text{NH})(\text{Et}_2\text{dtc})_2$  during the oxidation of  $\text{MoO}(\text{Et}_2\text{dtc})_2$  with  $\text{HN}_3$ . Although we have previously recognized<sup>2,7</sup> that the oxo and NH ligands are isoelectronic, a more useful view results from the recognition<sup>5</sup> that both the oxygen atom (1) and a nitrene (2) can serve as either two- or



four-electron donors in the sense of the EAN rule. The amphoteric character of these ligands allows each of these complexes to conform to that rule. Moreover, a homologous series of complexes might be expected and can be found in certain instances. The oxo analogues of the mononuclear complexes listed above are  $\text{MoOX}(\text{dppe})_2^+$ ,<sup>8</sup>  $\text{MoO}(\text{Et}_2\text{dtc})_3^+$ ,<sup>9</sup> well-known  $\text{MoO}_2(\text{Et}_2\text{dtc})_2$ ,  $\text{MoO}(\text{Et}_2\text{dtp})_3$ ,<sup>10</sup> and  $\text{MoOCl}(\text{Et}_2\text{dtp})_2$ ,<sup>10</sup> respectively. While the direct analogue of  $\text{Mo}_2\text{O}_3(\text{NH})(\text{Et}_2\text{dtp})_2$  is unknown, a closely related series of compounds is found in  $\text{Mo}_2\text{O}_4(\text{R}_2\text{dtc})_2$ . Similar analogies can be found with complexes of rhenium<sup>11</sup> and osmium.<sup>12</sup>

The purpose of this paper is to demonstrate the existence

of the first complete homologous series<sup>12</sup> designated by  $\text{MoO}_{2-n}(\text{NR})_n(\text{Et}_2\text{dtc})_2$  ( $R = \text{aryl}$ ) and to compare the reactivities of this series of compounds toward protonation as well as alkylation.

### Experimental Section

All reactions were performed either in vacuo or under an argon atmosphere with standard Schlenk techniques. Solvents were dried and distilled immediately prior to use.  $\text{MoO}_2(\text{Et}_2\text{dtc})_2$ ,  $\text{MoO}(\text{Et}_2\text{dtc})_2$ , and  $\text{Mo}(\text{CO})_2(\text{Et}_2\text{dtc})_2$ <sup>13-15</sup> were synthesized according to published procedures. Phenyl azide and *p*-tolyl azide were synthesized from the corresponding diazonium salts and sodium azide. The crude azides were dried over  $\text{MgSO}_4$ , distilled under argon at reduced pressure (phenyl azide, 51 °C at 11 torr, and *p*-tolyl azide, 53 °C at 3 torr), and made to approximately 2 M with cyclopentane. *p*-Nitrophenyl azide was synthesized from *p*-nitrophenylhydrazine and nitrous acid. The product was washed with a minimum quantity of ether and dried.

Infrared spectra were recorded as KBr pellets with a Perkin-Elmer Model 283 spectrophotometer, and <sup>1</sup>H NMR spectra were obtained at 220 MHz with a Varian HR-220 spectrometer. Mass spectra were recorded with a Varian CH-7 spectrometer. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

**Preparation of  $\text{Mo}(\text{NPh})_2(\text{Et}_2\text{dtc})_2$ .** This compound was prepared by a modification of our previous synthesis.<sup>5</sup> A sample of  $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNEt}_2)_2$  (4.5 mmol) was placed in a side arm attached to an evacuable flask containing 10 mmol of phenyl azide in cyclopentane. The system was evacuated via freeze-thaw cycles, and 35 mL of dry  $\text{CH}_2\text{Cl}_2$  was introduced by distillation. The dicarbonyl was added at room temperature, and the solution was stirred for 36 h, filtered, and taken to near dryness, yielding an intensely red-brown oil. The oil was washed with dry hexane (2 × 30 mL) to yield a red-brown powder which was dried under vacuum. The infrared and NMR spectra of the material obtained in this manner were identical with those of our previous preparation. Typical recovered yields were about 80%.

**Preparation of  $\text{Mo}(\text{Ntol})_2(\text{Et}_2\text{dtc})_2$ .** An analogous procedure using *p*-tolyl azide yielded  $\text{Mo}(\text{Ntol})_2(\text{Et}_2\text{dtc})_2$  as a deep red-black powder. This material is extremely soluble in most common organic solvents and could not be crystallized. Anal. Calcd for  $\text{Mo}(\text{Ntol})_2(\text{Et}_2\text{dtc})_2$ : C, 47.8; H, 5.7; N, 9.3. Found: C, 46.3; H, 5.7; N, 9.1.

**Preparation of  $\text{MoO}(\text{NPh})(\text{Et}_2\text{dtc})_2$ .** A sample of  $\text{MoO}(\text{Et}_2\text{dtc})_2$  (3.9 mmol) was dissolved in 20 mL of dry, degassed  $\text{CH}_2\text{Cl}_2$ . A cyclopentane solution of phenyl azide (3.9 mmol) in 10 mL of dry  $\text{CH}_2\text{Cl}_2$  was evacuated during several freeze-thaw cycles and added to the stirred  $\text{Mo}(\text{IV})$  solution. The result was the evolution of  $\text{N}_2$  and an intensely purple solution. After stirring at room temperature for 15 min, the reaction mixture had become red-brown. The solution was evaporated to near dryness, and hexane (25 mL) was introduced by distillation to triturate the residue. The powdery solid which formed was filtered, washed with hexane, and dried under vacuum to give the burnt orange product. Anal. Calcd for  $\text{MoO}(\text{NPh})(\text{Et}_2\text{dtc})_2$ : C, 38.5; H, 5.0; N, 8.4; S, 25.7. Found: C, 37.5; H, 4.9; N, 8.1; S, 24.8. Although these analyses are not particularly good, no contaminants were found in the <sup>1</sup>H NMR spectrum.

If the reaction was allowed to occur for 18 h, bright yellow  $\text{Mo}_2\text{O}_4(\text{NPh})(\text{Et}_2\text{dtc})_2$  could be filtered from the solution. Anal. Calcd for  $\text{Mo}_2\text{O}_4(\text{NPh})(\text{Et}_2\text{dtc})_2$ : C, 29.9; H, 3.9; N, 6.5; S, 19.9. Found: C, 29.7; H, 4.0; N, 6.5; S, 19.7.

**Preparation of  $\text{MoO}(\text{NPhNO}_2)(\text{Et}_2\text{dtc})_2$ .** Samples of  $\text{MoO}(\text{Et}_2\text{dtc})_2$  (1.25 mmol) and *p*-nitrophenyl azide (1.25 mmol) were placed in a side arm of a flask. After 15 mL of  $\text{CH}_2\text{Cl}_2$  was introduced into the flask by distillation, the solids were added to give an intense red-violet solution with gas evolution. After about 90 min, the solution had acquired a slight orange cast. The volume was reduced to about 3 mL, and 15 mL of hexane was introduced by distillation. Initially, a dark red oil was produced, but, on further stirring, a red-brown solid was deposited. The supernatant liquid was decanted, leaving a red-brown product which was dried under a vacuum. Anal. Calcd for  $\text{MoO}(\text{NPhNO}_2)(\text{Et}_2\text{dtc})_2$ : C, 35.3; H, 4.4; N, 10.3; S, 23.6. Found: C, 35.5; H, 4.7; N, 10.1; S, 23.2.

**Reaction of  $\text{Mo}(\text{NR})_2(\text{Et}_2\text{dtc})_2$  ( $R = \text{Ph or tol}$ ) with HCl.** A sample of  $\text{Mo}(\text{NPh})_2(\text{Et}_2\text{dtc})_2$  (0.5 mmol) was dissolved in benzene (25 mL), and gaseous HCl was bubbled through the solution for approximately 5 s. The color of the solution immediately changed from red-brown to bright yellow, and a flocculent white precipitate was formed. This

material was separated by filtration and dried in air. The infrared and mass spectra of this material revealed it to be aniline hydrochloride (verified by comparison with those of an authentic sample). The yellow solution was evaporated to dryness, and the product was recrystallized from chloroform-hexane. Elemental analysis, as well as a subsequent single-crystal X-ray crystallographic study,<sup>16</sup> indicated that the compound is  $\text{Mo}(\text{NPh})\text{Cl}_2(\text{Et}_2\text{dtc})_2 \cdot \text{CHCl}_3$ . Anal. Calcd for  $\text{Mo}(\text{NPh})\text{Cl}_2(\text{Et}_2\text{dtc})_2 \cdot \text{CHCl}_3$ : C, 30.3; H, 3.9; N, 6.2. Found: C, 30.2; H, 3.9; N, 6.2.

An analogous procedure utilizing  $\text{Mo}(\text{Ntol})_2(\text{Et}_2\text{dtc})_2$  yielded *p*-toluidine hydrochloride (confirmed by comparison of the infrared and mass spectra with those of an authentic sample) and the bright yellow  $\text{CHCl}_3$  solvate of  $\text{Mo}(\text{Ntol})\text{Cl}_2(\text{Et}_2\text{dtc})_2$ . Anal. Calcd for  $\text{Mo}(\text{Ntol})\text{Cl}_2(\text{Et}_2\text{dtc})_2 \cdot \text{CHCl}_3$ : C, 31.4; H, 4.1; N, 6.1. Found: C, 31.5; H, 4.2; N, 6.4.

**Reaction of  $\text{Mo}(\text{NPh})_2(\text{Et}_2\text{dtc})_2$  with  $\text{CH}_3\text{Br}$ .** A portion of  $\text{Mo}(\text{NPh})_2(\text{Et}_2\text{dtc})_2$  (1.74 mmol) was dissolved in 15 mL of dry  $\text{CH}_2\text{Cl}_2$  under an argon blanket.  $\text{CH}_3\text{Br}$  was bubbled through the solution for 15 min, and the solution was then stirred for 24 h. After that time the solution was orange-yellow and contained a suspended white solid. The solid was filtered, washed with a small amount of cold  $\text{CH}_2\text{Cl}_2$ , and dried in air. The infrared and mass spectra of this material indicated it to be phenyltrimethylammonium bromide which was substantiated by comparison with an authentic sample. Hexane was added to the reaction solution, and, after it was chilled to 10 °C, a golden brown solid was deposited. This material was recrystallized from  $\text{CHCl}_3$  to give the bright yellow  $\text{CHCl}_3$  solvate of  $\text{Mo}(\text{NPh})\text{Br}_2(\text{Et}_2\text{dtc})_2$ . Anal. Calcd for  $\text{Mo}(\text{NPh})\text{Br}_2(\text{Et}_2\text{dtc})_2 \cdot \text{CHCl}_3$ : C, 26.8; H, 3.4; N, 5.5. Found: C, 26.8; H, 3.5; N, 5.5.

**Reactions of  $\text{MoO}(\text{NPh})(\text{Et}_2\text{dtc})_2$  with HX ( $X = \text{Cl or Br}$ ).** Gaseous HCl was bubbled through a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{MoO}(\text{NPh})(\text{Et}_2\text{dtc})_2$  for 5 s, resulting in a bright yellow solution. After evaporation to dryness, the product was recrystallized from  $\text{CHCl}_3$  to give  $\text{Mo}(\text{NPh})\text{Cl}_2(\text{Et}_2\text{dtc})_2 \cdot \text{CHCl}_3$ . A similar reaction with HBr led to  $\text{Mo}(\text{NPh})\text{Br}_2(\text{Et}_2\text{dtc})_2 \cdot \text{CHCl}_3$ . Anal. Found for  $\text{Mo}(\text{NPh})\text{Cl}_2(\text{Et}_2\text{dtc})_2 \cdot \text{CHCl}_3$ : C, 30.3; H, 3.9; N, 6.2. Found for  $\text{Mo}(\text{NPh})\text{Br}_2(\text{Et}_2\text{dtc})_2 \cdot \text{CHCl}_3$ : C, 26.9; H, 3.4; N, 5.5. The infrared spectra of these compounds were identical with those obtained from the compounds which were prepared by the methods described above.

**Reaction of  $\text{MoO}(\text{NPhNO}_2)(\text{Et}_2\text{dtc})_2$  with HCl.** An analogous procedure led to the initial separation of (*p*-nitrophenyl)ammonium chloride (confirmed by comparison of the infrared and mass spectra with those of an authentic sample). Evaporation of the supernatant liquid led to the recovery of  $\text{MoOCl}_2(\text{Et}_2\text{dtc})_2$  after recrystallization from  $\text{CHCl}_3$ . The nature of the compound was verified by comparing its infrared spectrum to that of an authentic sample.

**Reaction of  $\text{MoO}_2(\text{Et}_2\text{dtc})_2$  with  $\text{HBF}_4$ .** A sample of  $\text{MoO}_2(\text{Et}_2\text{dtc})_2$  (0.25 g) was dissolved in benzene (25 mL), and several drops of 48%  $\text{HBF}_4$  were added to the stirred solution. Within a few minutes, a flocculent orange-yellow precipitate appeared. After the solution was stirred for 1 h, the benzene was evaporated under vacuum, yielding a tacky orange solid. This material was taken up in ethanol, and ether was added. Upon standing at room temperature, this solution yielded bright orange rodlike crystals of  $[\text{MoO}(\text{Et}_2\text{dtc})_3]\text{BF}_4$ . This compound was removed by filtration and dried under vacuum. Anal. Calcd for  $[\text{MoO}(\text{Et}_2\text{dtc})_3]\text{BF}_4$ : C, 28.0; H, 4.7; N, 6.5; S, 29.9. Found: C, 28.3; H, 4.8; N, 6.4; S, 29.5.

**Preparation of  $[\text{Mo}(\text{NPh})(\text{Et}_2\text{dtc})_3]\text{PF}_6$ .** A portion of  $\text{Mo}(\text{NPh})\text{Cl}_2(\text{S}_2\text{CNEt}_2)_2$  (0.3 mmol) and  $\text{Na}[\text{S}_2\text{CNEt}_2] \cdot 3\text{H}_2\text{O}$  (1.1 mmol) were added to 25 mL of absolute EtOH. Although the reaction at this stage was virtually heterogenous, the original yellow color of the molybdenum compound was rapidly discharged in favor of a burnt orange hue. After 15 min, 5 drops of 65%  $\text{HPF}_6$  were added, causing a darkening of the solution. After the mixture was stirred for 1 h, a small amount of a dark solid was removed by filtration, and the orange solution was concentrated in vacuo to 15 mL. After 6 h, the bright yellow precipitate which had formed was collected by filtration, washed with ether, and dried under vacuum. Anal. Calcd for  $[\text{Mo}(\text{NPh})(\text{Et}_2\text{dtc})_3]\text{PF}_6$ : C, 32.5; H, 4.5; N, 7.2; S, 24.8. Found: C, 32.2; H, 4.7; N, 7.1; S, 24.6.

### Discussion of Results

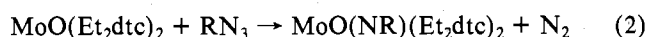
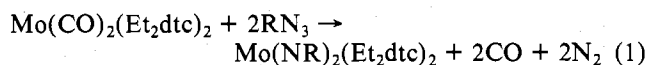
**Reactions.** The preparation of  $\text{Mo}(\text{NR})_2(\text{Et}_2\text{dtc})_2$  ( $R = \text{Ph or tol}$ ) was accomplished according to our published procedure<sup>5</sup> which is shown in eq 1 while the synthesis of  $\text{MoO}(\text{NR})-$

Table I. <sup>1</sup>H NMR Spectra of (Arylimido)molybdenum(VI) Complexes in CDCl<sub>3</sub><sup>a</sup>

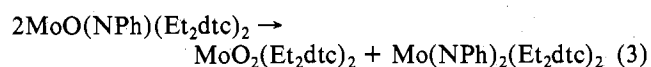
	Et <sub>2</sub> dtc		aryl	
	CH <sub>3</sub>	CH <sub>2</sub>	H	CH <sub>3</sub>
Mo(NPh) <sub>2</sub> (Et <sub>2</sub> dtc) <sub>2</sub> <sup>b</sup>	1.24 t	3.74 q (4) 3.77 q (4)	~7.0 m	
Mo(Ntol) <sub>2</sub> (Et <sub>2</sub> dtc) <sub>2</sub>	1.24 t	3.74 q	6.99 q	2.27 s
Mo(NPh)Cl <sub>2</sub> (Et <sub>2</sub> dtc) <sub>2</sub> <sup>c</sup>	1.33 t	3.75 q	~7.3 m	
Mo(NPh)Br <sub>2</sub> (Et <sub>2</sub> dtc) <sub>2</sub> <sup>c</sup>	1.30 t	3.74 q	~7.4 m	
Mo(Ntol)Cl <sub>2</sub> (Et <sub>2</sub> dtc) <sub>2</sub> <sup>c</sup>	1.30 t	~3.7 m	7.19 q	2.33 s
MoO(NPh)(Et <sub>2</sub> dtc) <sub>2</sub>	1.26 t	3.74 q	~7.3 m	
MoO(NPhNO <sub>2</sub> )(Et <sub>2</sub> dtc) <sub>2</sub>	1.28 t	3.75 q	6.99 q	
[Mo(NPh)(Et <sub>2</sub> dtc) <sub>3</sub> ]PF <sub>6</sub>	1.20 t (3) 1.34 m (15)	~3.8 m	7.32 s	

<sup>a</sup> s = singlet, t = triplet, q = quartet, and m = multiplet; chemical shifts given as δ values. <sup>b</sup> Measured in CD<sub>2</sub>Cl<sub>2</sub>; data from ref 5. <sup>c</sup> The solvate-free compounds were used because of solubility.

(Et<sub>2</sub>dtc)<sub>2</sub> (R = Ph or PhNO<sub>2</sub>) was achieved by the reaction of MoO(Et<sub>2</sub>dtc)<sub>2</sub> and RN<sub>3</sub> as shown in eq 2. The mixed-



ligand complex is easily obtained with R = PhNO<sub>2</sub>, but the reaction time is very important with R = Ph. While the desired product can be obtained by using a short reaction time, if the reaction is allowed to progress, yellow Mo<sub>2</sub>O<sub>4</sub>(NPh)(Et<sub>2</sub>dtc)<sub>2</sub> will precipitate from solution. Other products which result from the obvious scrambling are not known at present. Although the spectroscopic data which are listed in Table I do not provide sufficient information to specify the geometry of the desired compounds, the known structures of Mo(NPh)<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub><sup>5</sup> and MoO<sub>2</sub>(Pr<sub>2</sub>dtc)<sub>2</sub><sup>17</sup> lead us to believe that each has the cis configuration. This configuration should lead to greater stability than that available to a trans isomer since maximum utilization of the metal's d<sub>xy</sub> orbitals will result.<sup>18</sup> The mass spectrum of MoO(NPh)(Et<sub>2</sub>dtc)<sub>2</sub> showed ions corresponding to both Mo(NPh)<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub> and MoO<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub>, which indicates that the disproportionation shown in eq 3



appears to occur in the gas phase. However, the infrared spectrum of MoO(NPh)(Et<sub>2</sub>dtc)<sub>2</sub> clearly rules out the possibility that this material is an equimolar mixture of disproportionation products in the solid state. Similarly, appreciable disproportionation in solution is ruled out because the <sup>1</sup>H NMR spectrum is unique and definitely not a superposition of the spectra of MoO<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub> and Mo(NPh)<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub>. This conclusion has been confirmed in a separate experiment involving equimolar quantities of these materials.

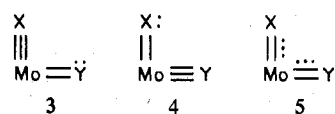
The reaction of Mo(NR)<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub> (R = Ph or tol) with HCl results in the removal of one and only one NR ligand and yields Mo(NR)Cl<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub> and the corresponding arylammonium salt. The latter was isolated and identified in both cases. Similarly, alkylation with CH<sub>3</sub>Br results in the formation of Mo(NR)Br<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub> and the trimethylarylammonium salt. Again, the latter was isolated and identified. The oxo analogues MoOX<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub> (X = Cl or Br) have been previously prepared<sup>20</sup> by the reaction of MoO<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub> with HX. Thus, oxo and imido ligands are both susceptible to protonation and removal when present in complexes containing either MoO<sub>2</sub> or Mo(NR)<sub>2</sub> fragments. Consequently, the reaction of a complex containing a MoO(NR) fragment should delineate the relative basicities of these ligands. While the reaction of MoO(NPh)(Et<sub>2</sub>dtc)<sub>2</sub> with HX (X = Cl or Br) results in the formation of Mo(NPh)X<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub>, the reaction of MoO(NPhNO<sub>2</sub>)(Et<sub>2</sub>dtc)<sub>2</sub> with HCl leads to the removal

of the imido ligand and the formation of MoOCl<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub>. Once again, the arylammonium salt was isolated and identified.

Although protonation of the oxo or imido ligands is clearly important in these reactions, the nucleophilicity of the conjugate base of the acid plays an important role in determining the final product. When MoO<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub> is treated with HBF<sub>4</sub>, the result is [MoO(Et<sub>2</sub>dtc)<sub>3</sub>]BF<sub>4</sub>. This cation was obtained previously<sup>9</sup> by treating MoO<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub> with HF. Although we were unable to obtain Mo(NPh)(Et<sub>2</sub>dtc)<sub>3</sub><sup>+</sup> in pure form by the reaction of Mo(NPh)<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub> with HBF<sub>4</sub>, this cation was obtained by the reaction of Mo(NPh)Cl<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub> with Et<sub>2</sub>dtc<sup>-</sup> and precipitated as its PF<sub>6</sub><sup>-</sup> salt.

The structures of the 18-electron complexes Mo(NR)X<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub> (X = Cl or Br) and Mo(NR)(Et<sub>2</sub>dtc)<sub>3</sub><sup>+</sup> can be assumed to mimic the structures of their 18-electron oxo analogues. Seven-coordination and a geometry consisting of a distorted pentagonal bipyramid with an apical oxo ligand have been found in each of these compounds.<sup>9,19</sup> Indeed, a recent X-ray structural study<sup>16</sup> involving Mo(NPh)Cl<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub>CHCl<sub>3</sub> indicated the presence of this geometry. Furthermore, one of the halogens is found in the equatorial plane while the other occupies an apical site in exact mimicry of its oxo analogue.

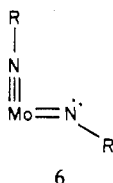
**A Possible Mechanism.** If π bonding to the remainder of the ligating atoms is ignored, there are three general structures (3, 4, and 5) which pertain to the cis isomers of complexes



containing the MoO<sub>2</sub>, Mo(NR)<sub>2</sub>, and MoO(NR) fragments. The group designated by X serves as a four-electron donor in 3 while Y is a two-electron donor. The roles of these groups are reversed in 4. An additional lone pair of electrons is also present on the ligands when X or Y is the oxygen atom. The electron density in either of these forms will be polarized toward the group which is linked to the metal by a double bond. Polarization will not occur in 5 which can be considered as a hybrid of 3 and 4.

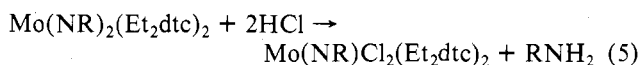
The identical MoO bond lengths of 1.696 (5) Å in MoO<sub>2</sub>(Pr<sub>2</sub>dtc)<sub>2</sub><sup>17</sup> indicate that 5 (X = Y = O) describes the true structure of this complex. Although the structures of MoO<sub>2</sub>(acac)<sub>2</sub><sup>20</sup> and MoO<sub>2</sub>Br<sub>2</sub>(bpy)<sup>21</sup> should be viewed with caution since they were obtained by film techniques, significantly different MoO bond lengths within each MoO<sub>2</sub> fragment have been cited. If true, the structure in the solid state is heavily weighted in favor of one of the equivalent polarized structures. One of the polarized forms is definitely favored with Mo(NPh)<sub>2</sub>(Et<sub>2</sub>dtc)<sub>2</sub> (X = Y = NPh) whose structure has been described previously.<sup>5</sup> Unequal MoN bond lengths of 1.754 (4) and 1.789 (4) Å and severe bending about one of the nitrogen atoms in the Mo(NPh)<sub>2</sub> fragment suggests

that the true structure is described approximately by **6**. No structural data is currently available for  $\text{MoO}(\text{NR})(\text{Et}_2\text{dtc})_2$  ( $\text{X} = \text{O}$  and  $\text{Y} = \text{NR}$ ).

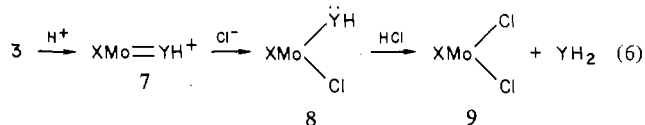


We have attempted to deduce the structure of the  $\text{Mo}(\text{NR})_2$  fragment within  $\text{Mo}(\text{Ntol})_2(\text{Et}_2\text{dtc})_2$  in solution by examining the  $^1\text{H}$  NMR spectrum at temperatures ranging from 16 to  $-40^\circ\text{C}$ . Only a single sharp resonance due to the hydrogen atoms of the methyl groups attached to the aryl rings can be observed throughout this temperature range. With the assumption that accidental degeneracy is not occurring, these results suggest that the structure in solution can be described either by **5** or by the supposition that there is a rapid equilibration given by  $3 \rightleftharpoons 5 \rightleftharpoons 4$ . In any event, the implication from the collective evidence is that the energies of **3** or **4** are not very different from that of **5** since one of the polarized forms is found in the solid state<sup>5</sup> while **5** is apparently present in solution to some extent. A similar situation may exist for complexes containing the  $\text{MoO}_2$  fragment, but it would be difficult to detect.

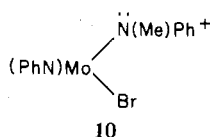
Although the subtle differences in  $\pi$  bonding within  $\text{MoO}_2(\text{Et}_2\text{dtc})_2$  and  $\text{Mo}(\text{NR})_2(\text{Et}_2\text{dtc})_2$  which are observed in the solid state may or may not persist in solution, the reactions of these complexes with  $\text{HCl}$  proceed along identical pathways as shown in eq 4 and 5. An adequate description of this  $\text{MoO}_2(\text{Et}_2\text{dtc})_2 + 2\text{HCl} \rightarrow \text{MoOCl}_2(\text{Et}_2\text{dtc})_2 + \text{H}_2\text{O}$  (4)



pathway is shown in eq 6 ( $\text{X} = \text{Y} = \text{O}$  or  $\text{NR}$ ) wherein **9**



corresponds to the observed product containing molybdenum. Protonation of **3** should occur on the electron-rich  $\text{Y}$  group, leading to **7**, in which the 18-electron count persists. The subsequent inclusion of  $\text{Cl}^-$  in the metal's coordination sphere (**8**) requires that the  $\text{YH}$  ligand will serve as a one-electron donor providing  $\text{X}$  remains a four-electron donor. With this provision, the lone pair of electrons which is localized on the  $\text{YH}$  ligand allows  $\text{HCl}$  to attack once again to give the observed products. A similar mechanism probably also applies to the alkylation of  $\text{Mo}(\text{NPh})_2(\text{Et}_2\text{dtc})_2$  with the nucleophilic nitrogen atom in **6** attacking the carbon atom of  $\text{CH}_3\text{Br}$ . Displacement of  $\text{Br}^-$  and the formation of a  $\text{MoBr}$  bond would cause the appearance of **10** which would then react with  $\text{CH}_3\text{Br}$  once again to give the observed products.



Since the reaction of  $\text{MoO}(\text{NPh})(\text{Et}_2\text{dtc})_2$  with  $\text{HCl}$  gives  $\text{Mo}(\text{NPh})\text{Cl}_2(\text{Et}_2\text{dtc})_2$  exclusively, **3** must be considerably stabilized with respect to **4** ( $\text{X} = \text{NPh}$  and  $\text{Y} = \text{O}$ ) so that protonation only occurs at  $\text{Y}$ . However, the reaction of  $\text{MoO}(\text{NPhNO}_2)(\text{Et}_2\text{dtc})_2$  with the same reagent results in the exclusive formation of  $\text{MoOCl}_2(\text{Et}_2\text{dtc})_2$ . The electron-

withdrawing group on the aryl ring must effectively stabilize **4** with respect to **3** ( $\text{X} = \text{NPhNO}_2$  and  $\text{Y} = \text{O}$ ). Protonation then occurs only at  $\text{X}$ .

Although we have attempted to isolate complexes containing **7**, we have met with notable failure. Since the reaction of  $\text{MoO}_2(\text{Et}_2\text{dtc})_2$  with  $\text{HBF}_4$ , an acid whose conjugate base is a very poor nucleophile, gave  $\text{MoO}(\text{Et}_2\text{dtc})_3^+$  instead of a complex corresponding to **7**, we conclude that **7** is necessarily highly unstable and capable of only transient existence. In the absence of a good nucleophilic reagent, **7** scavenges the sulfur-containing bidentate ligand from another complex. Unfortunately, other products have not been identified.

The general mechanism shown in eq 6 suggests that the EAN rule is important in determining the pathways of the reactions shown in eq 4 and 5. Similarly, the EAN rule would appear to have a marked influence on the stability of the imido group in  $\text{Mo}(\text{NR})\text{X}_2(\text{Et}_2\text{dtc})_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) toward protonation. Simple bonding arguments suggest that the  $\text{MoN}$  bond order in these compounds should be 3 if  $\pi$  bonding between the metal and other ligating atoms is neglected. The recent crystal structure of the  $\text{CHCl}_3$  solvate of  $\text{Mo}(\text{NPh})\text{Cl}_2(\text{Et}_2\text{dtc})_2$  has provided confirmation of that expectation.<sup>16</sup> Although the idealized symmetry of  $C_s$  indicates that the bonding orbitals will belong to different representations, these orbitals will be approximately degenerate. Since all of the valence electrons which formally belong to the nitrogen atom are found in bonding orbitals, little tendency for protonation should exist. Furthermore, protonation and removal of the imido group may be prevented because of the lack of a stable product. Removal of the imido group by protonation would lead to either  $\text{MoCl}_4(\text{Et}_2\text{dtc})_2$  or an ionic variant of that complex, and none of these satisfies the EAN rule. Although not widely appreciated, most  $\text{Mo}(\text{VI})$  complexes conform to this rule, and ligand-replacement reactions generally give rise to other  $\text{Mo}(\text{VI})$  compounds which also conform to the rule. These explanations may also account for the robust nature of the imido ligand in  $\text{Re}(\text{NR})\text{X}_3(\text{PPh}_3)_2$ .<sup>11</sup>

The lack of a stable product would also explain the inability to remove the oxo ligand in  $\text{MoOX}_2(\text{Et}_2\text{dtc})_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ). However, the bonding arguments which were applied to the imido group to explain its lack of basicity require some modification when applied to the oxo analogues. Although the  $\text{MoO}$  bond distance of  $1.656$  (**5**)  $\text{\AA}$ <sup>19</sup> in  $\text{MoOBr}_2(\text{Et}_2\text{dtc})_2$  is in accord<sup>22</sup> with a bond order of 3, the corresponding distance in  $\text{MoOCl}_2(\text{Et}_2\text{dtc})_2$  has increased to  $1.701$  (**4**)  $\text{\AA}$ <sup>19</sup> which suggests of bond order of approximately 2.5.<sup>22</sup> Nevertheless, infrared and  $^{17}\text{O}$  NMR studies<sup>22</sup> indicate that the bond orders are identical when these complexes are in solution and that the bond order is probably slightly greater than 2.5. These results imply that the other ligating atoms participate in  $\pi$  bonding to some extent. Although the two  $\pi$ -bonding interactions can not be equivalent when these additional bonding interactions are included, four of the valence electrons of the oxo ligand are nonetheless expected to be in bonding orbitals. The remaining pair of electrons would be usually described as a lone pair. However, these electrons occupy an orbital whose symmetry will allow weak bonding interactions with the metal's  $\sigma$  orbitals. We have previously suggested<sup>5</sup> that the magnitude of this interaction will be important in determining the magnitude of the trans effect. Since the structures<sup>19</sup> of  $\text{MoOX}_2(\text{Et}_2\text{dtc})_2$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) indicate a substantial trans effect, the formal description of this pair of electrons as a lone pair may not be very appropriate. Thus, the lack of basicity of the oxo ligand in these complexes becomes explicable.

**Infrared Studies.** Special attention was given to the infrared spectra of all of these compounds since a definite assignment of  $\nu(\text{MoN})$  has proved elusive in previous studies of imido

Table II. Selected Infrared Absorptions ( $\nu$  in  $\text{cm}^{-1}$ )<sup>a</sup>

$\text{Mo}(\text{NPh})\text{Cl}_2(\text{Et}_2\text{dtc})_2 \cdot \text{CHCl}_3$ <sup>b</sup>	985 w, 915 w, 852 m
$\text{Mo}(\text{NPh})\text{Br}_2(\text{Et}_2\text{dtc})_2 \cdot \text{CHCl}_3$ <sup>b</sup>	980 m, br, 915 w, 849 m
$\text{Mo}(\text{Ntol})\text{Cl}_2(\text{Et}_2\text{dtc})_2 \cdot \text{CHCl}_3$ <sup>b</sup>	990 w, 920 w, 851 m
$[\text{Mo}(\text{NPh})(\text{Et}_2\text{dtc})_3]\text{PF}_6$ <sup>c</sup>	992 w, br, 911 w, 840 s
$\text{Mo}(\text{NPh})_2(\text{Et}_2\text{dtc})_2$	1000 w, 950 m, 914 w, 847 m
$\text{Mo}(\text{Ntol})_2(\text{Et}_2\text{dtc})_2$	998 m, 960 m, 911 w, 842 m
$\text{MoO}(\text{NPh})(\text{Et}_2\text{dtc})_2$	1000 m, 963 w, 913 m, 865 s, 846 m
$\text{MoO}(\text{NPhNO}_2)(\text{Et}_2\text{dtc})_2$	997 m, 962 m, 915 m, 883 s, 846 sh, 840 s

<sup>a</sup> Obtained in KBr disks. Abbreviations are w = weak, m = medium, s = strong, sh = shoulder, and br = broad. <sup>b</sup> A strong, broad band at  $750 \text{ cm}^{-1}$  due to  $\text{CHCl}_3$  is also observed. <sup>c</sup> A strong band at  $561 \text{ cm}^{-1}$  due to  $\text{PF}_6^-$  is also found. The band at  $840 \text{ cm}^{-1}$  is a composite of bands due to  $\text{PF}_6^-$  as well as the bidentate ligand.

complexes of molybdenum<sup>3</sup> and rhenium.<sup>11</sup> Since  $\nu(\text{CO})$  occurs near  $2140 \text{ cm}^{-1}$  in the spectrum of CO while  $\nu(\text{CN})$  occurs between  $2105$  and  $2130 \text{ cm}^{-1}$  in the spectra of aryl isocyanides,<sup>23</sup> one might expect that  $\nu(\text{MoO})$  and  $\nu(\text{MoN})$  in the spectra of compounds containing either the MoO fragment or the MoNR (R = aryl) fragments would be similar. The merit of this analogy depends strongly on the perturbation of  $\nu(\text{MoN})$  by the N-C(aryl) stretching motion. Certainly, the magnitude of this perturbation would be larger in the metal complexes than the corresponding perturbation in the aryl isocyanides.

The spectra of each of the seven-coordinate complexes,  $\text{MoOX}_2(\text{Et}_2\text{dtc})_2$  (X = Cl or Br) and  $\text{MoO}(\text{Et}_2\text{dtc})_3$ <sup>+</sup>, contain a strong band between  $930$  and  $960 \text{ cm}^{-1}$  which has been assigned to  $\nu(\text{MoO})$ .<sup>9,19</sup> These assignments have been substantiated by isotopic labeling studies.<sup>22</sup> In addition, there are bands due to the bidentate ligand near  $840$ ,  $920$ , and  $990 \text{ cm}^{-1}$ . While the latter are also present in the infrared spectra of the corresponding imido complexes, as shown in Table II, the remainder of this region is devoid of any other bands. Furthermore, the remainder of each spectrum shows only bands which can be attributed to intraligand or MoS vibrations. Similarly, the spectrum of  $\text{MoO}_2(\text{Et}_2\text{dtc})_2$  contains the bands due to the bidentate ligand as well as absorptions at  $877$  and  $908 \text{ cm}^{-1}$  due to the symmetric and antisymmetric stretching motions within the  $\text{MoO}_2$  fragment. Again, these assignments have been thoroughly substantiated by isotopic labeling.<sup>22</sup> The spectra of complexes containing the  $\text{Mo}(\text{NR})_2$  or  $\text{MoO}(\text{NR})$  fragments contain the bands which are characteristic of the bidentate ligand as well as a single band between  $945$  and  $965 \text{ cm}^{-1}$ . This absorption is possibly due to one of the two expected Mo-NR stretching frequencies in complexes containing the  $\text{Mo}(\text{NR})_2$  fragment. If so, we have been unable to locate its companion. Two stretching frequencies are also expected for complexes containing the  $\text{MoO}(\text{NR})$  fragment. In addition to the band at  $963 \text{ cm}^{-1}$ , there is also a strong absorption at  $865 \text{ cm}^{-1}$  in the spectrum of  $\text{MoO}(\text{NPh})(\text{Et}_2\text{dtc})_2$  which is absent in the spectrum of

$\text{Mo}(\text{NPh})_2(\text{Et}_2\text{dtc})_2$ . This band may arise from a vibration which is principally composed of a Mo-O stretching motion. A band at about  $850 \text{ cm}^{-1}$  in the spectra of  $\text{MoO}(\text{NPhNO}_2)_2(\text{Et}_2\text{dtc})_2$  has been previously assigned as  $\nu(\text{MoO})$ .<sup>4</sup> The spectrum of  $\text{MoO}(\text{NPhNO}_2)(\text{Et}_2\text{dtc})_2$  contains bands at  $883$  and  $840 \text{ cm}^{-1}$ . One of these is undoubtedly due to  $\nu(\text{CN})$  for the (aryl)C-NO<sub>2</sub> fragment<sup>23</sup> while the other may be due to  $\nu(\text{MoO})$ .

**Acknowledgment.** Support from NSF Grant No. CHE 75-08188-A01 and a grant-in-aid from Indiana University is acknowledged.

**Registry No.**  $\text{Mo}(\text{NPh})_2(\text{Et}_2\text{dtc})_2$ , 70415-02-0;  $\text{Mo}(\text{Ntol})_2(\text{Et}_2\text{dtc})_2$ , 70749-52-9;  $\text{Mo}(\text{NPh})\text{Cl}_2(\text{Et}_2\text{dtc})_2$ , 70749-53-0;  $\text{Mo}(\text{NPh})\text{Br}_2(\text{Et}_2\text{dtc})_2$ , 70749-54-1;  $\text{Mo}(\text{Ntol})\text{Cl}_2(\text{Et}_2\text{dtc})_2$ , 70749-55-2;  $\text{MoO}(\text{NPh})(\text{Et}_2\text{dtc})_2$ , 70749-56-3;  $\text{MoO}(\text{NPhNO}_2)(\text{Et}_2\text{dtc})_2$ , 70749-57-4;  $[\text{Mo}(\text{NPh})(\text{Et}_2\text{dtc})_3]\text{PF}_6$ , 70749-59-6;  $\text{Mo}_2\text{O}_4(\text{NPh})(\text{Et}_2\text{dtc})_2$ , 70749-60-9;  $[\text{MoO}(\text{Et}_2\text{dtc})_3]\text{BF}_4$ , 70788-19-1;  $\text{MoOCl}_2(\text{Et}_2\text{dtc})_2$ , 57146-54-0;  $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNEt}_2)_2$ , 18947-43-8;  $\text{MoO}(\text{Et}_2\text{dtc})_2$ , 25395-92-0;  $\text{MoO}_2(\text{Et}_2\text{dtc})_2$ , 19680-83-2.

## References and Notes

- (1) Abbreviations used herein are  $\text{R}_2\text{dtc} = \text{S}_2\text{CNR}_2$ ,  $\text{R}_2\text{dtp} = \text{S}_2\text{P}(\text{OR})_2$ ,  $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ,  $\text{Ph} = \text{C}_6\text{H}_5$ ,  $\text{tol} = p\text{-CH}_3\text{C}_6\text{H}_4$ , and  $\text{PhNO}_2 = p\text{-O}_2\text{NC}_6\text{H}_4$ .
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