

complexes are usually very similar in their reactions, only the $O_2/HClO_4$ oxidation was carried out. In this case pale yellow, diamagnetic *trans*-[WH(CO)₂(DPM)₂]ClO₄ was isolated. Anal. Calcd: C, 53.6; P, 11.2; H, 4.1; Cl, 3.2. Found: C, 55.2; P, 10.9; H, 4.3; Cl, 3.4.

The NMR spectrum for the tungsten hydride was similar to that for the molybdenum hydride. It consisted of a phenyl region centered at τ 2.59, a triplet in the methylene region at τ 5.08 with $J_{P-H} = 8$ Hz, and a triplet of triplets centered at τ 11.54 with $J_{P-H} = 66$ Hz and $J_{P-H} = 14$ Hz (536 scans).

trans-[W(CO)₂(DPM)₂]⁺ was identified as an intermediate in the reaction by ESR monitoring. The ESR spectrum of this complex is not well defined as is the case with the DPE complex. The respective *g* values are 1.92 (DPM) and 2.08 (DPE).

The same hydride was isolated using hydrofluoric acid instead of perchloric acid.

Conclusions

The reactions of the DPM complexes demonstrated electrochemical predictions, based on E° values, that the DPM complexes would be easier to oxidize than the DPE complexes. In oxidation state II, six-coordinate species such as [M(CO)₂(DPM)₂]²⁺ are unstable and the oxidation state II complexes isolated are seven-coordinate hydrides. In oxidation state I, six-coordinate species such as [M(CO)₂(DPM)₂]⁺ do exist with *cis* complexes rapidly isomerizing to the *trans* form in good agreement with electrochemical data.

One distinct difference between the Cr and the other two metals is the stability of its oxidation state I complexes. This presumably reflects kinetic differences noted previously.²

Acknowledgment. The authors thank Mr. Max Beyer for recording ESR spectra, Colin Rix for helpful discussion, and M. R. Snow for the DPE complexes.

Registry No. *cis*-Cr(CO)₂(DPM)₂, 53092-55-0; *cis*-Mo(CO)₂(DPM)₂, 53152-36-6; *cis*-W(CO)₂(DPM)₂, 53092-56-1; *trans*-[Cr(CO)₂(DPM)₂]₃, 56210-39-0; *trans*-[Cr(CO)₂(DPM)₂]PF₆, 56210-40-3; *trans*-[Cr(CO)₂(DPM)₂]ClO₄, 56210-41-4; *trans*-[CrH(CO)₂(DPM)₂]ClO₄, 56210-43-6; *trans*-[Mo(CO)₂(DPM)₂]ClO₄, 56210-44-7; *cis*-[MoI(CO)₂(DPM)₂]₃, 56210-46-9; *trans*-[MoI(CO)₂(DPM)₂]₃, 56210-48-1; *cis*-[MoBr(CO)₂(DPM)₂]₃, 56271-06-8; *trans*-[MoBr(CO)₂(DPM)₂]₃, 56271-08-0; *trans*-[MoH(CO)₂(DPM)₂]ClO₄, 56210-50-5; *trans*-[WH(CO)₂(DPM)₂]ClO₄, 56210-52-7.

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Preparation and Properties of Dinitrogen-Molybdenum Complexes.

II.¹ Dinitrogen(organonitrile) Complexes of Molybdenum

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Received October 22, 1974

AIC407261

Various para-substituted benzonitriles have been shown to react with the bis(dinitrogen) complex *trans*-Mo(N₂)₂(DPE)₂ [DPE = 1,2-bis(diphenylphosphino)ethane] to form a new series of mono(dinitrogen)molybdenum complexes *trans*-Mo(N₂)(4-XC₆H₄CN)(DPE)₂, where X = NH₂, CH₃O, CH₃, H, Cl, and COCH₃. A good correlation is observed between the N₂ stretching vibration in the ir spectra of these complexes and the Hammett substitution parameter, σ_p . Analogous mono(dinitrogen) complexes of organonitriles are obtained by the reaction of the bis(dinitrogen) complex with 2-methylbenzonitrile, acetonitrile, and propionitrile. In all the complexes the CN stretching frequency of a coordinated organonitrile shows a decrease from the free ligand value. These mono(dinitrogen) complexes of para-substituted benzonitriles are assigned *trans* configuration on the basis of the ir and ³¹P NMR spectra. The benzoylazo complex MoCl(N₂COPh)(DPE)₂ is prepared by the reaction of the bis(dinitrogen) and mono(dinitrogen) complexes with benzoyl chloride. These reactions are shown to be remarkably affected by the coordinated organonitriles. Reaction of the benzoylazo complex with hydrochloric acid yields MoCl₂(N₂HCOPh)(DPE)₂, and the reaction is reversed by addition of triethylamine.

Introduction

Acetylene, organonitriles, organoisonitriles, dinitrogen oxide, and azide ion, as well as dinitrogen, are reducible by nitrogenase. The correlation between the relative affinity of these various ligands, including carbon monoxide, which is an inhibitor to nitrogenase, for nitrogenase and for ruthenium,² osmium,³ and cobalt⁴ complexes that bind dinitrogen indicates that these dinitrogen complexes may be valid models for biological nitrogen fixation. In view of the key role of molybdenum in biological nitrogen fixation, we have previously reported the preparation and properties of the first molybdenum-dinitrogen complexes.¹ In order to gain further knowledge of the character of this dinitrogen binding site, we have now studied the reaction of organonitriles with *trans*-Mo(N₂)₂(DPE)₂ [DPE = 1,2-bis(diphenylphosphino)ethane]

and prepared a new series of mono(dinitrogen) complexes of the type Mo(N₂)(RCN)(DPE)₂, where R is a substituted aryl or alkyl group. The electronic effect of the organonitrile as the coligand to the ligating dinitrogen was also investigated, since there have been few such systematic studies except those including cobalt,⁵ osmium,⁶ and rhenium⁷ dinitrogen complexes.

Chatt et al. recently obtained complexes of the type WCl₂(N₂HCOR)(DPE)₂ and WCl(N₂COR)(DPE)₂ from *trans*-W(N₂)₂(DPE)₂ and organic acid chlorides and briefly commented that *trans*-Mo(N₂)₂(DPE)₂ reacted analogously with organic acid chlorides.⁸ We have now found that these mono(dinitrogen)molybdenum complexes obtained react with benzoyl chloride to afford the benzoylazo complex MoCl(N₂COPh)(DPE)₂, from which MoCl₂(N₂HCOPh)(DPE)₂

can be prepared by addition of HCl. The result of preliminary X-ray analysis of the former complex is also described.

Experimental Section

All reactions were carried out under an atmosphere of pure nitrogen or argon. Solvents were dried and distilled under nitrogen. The commercially obtained organonitriles were used without further purification except that liquid nitriles were distilled over phosphorus(V) pentoxide. Benzoyl chloride and triethylamine were used as purchased. *trans*-Mo(N₂)₂(DPE)₂ was obtained by the method described in the previous paper,¹ from which the ¹⁵N₂ analog was prepared by exchange with ¹⁵N₂. ³¹P (40.5 MHz) and ¹H (100 MHz) spectra were recorded on a computer-assisted JEOL PS-100 spectrometer. Conductivity was measured with a Radiometer conductivity bridge.

Preparation of Mo(N₂)(PhCN)(DPE)₂. To a suspension of 0.100 g (0.105 mmol) of *trans*-Mo(N₂)₂(DPE)₂ in 10 ml of toluene was added 33 μl (0.32 mmol) of benzonitrile. The mixture was stirred at ambient temperature for 18 hr. After the solution turned dark green, a dark green solid precipitated. Addition of *n*-hexane to the mixture deposited an additional quantity of the complex. The precipitate was filtered, washed with *n*-hexane, crystallized from toluene/*n*-hexane and dried in vacuo to yield dark green crystals of the product (0.080 g, 74%). Anal. Calcd for C₅₉H₅₃N₃P₄Mo: C, 69.2; H, 5.2; N, 4.1. Found: C, 68.9; H, 5.4; N, 4.2.

Preparation of Mo(N₂)(4-CH₃OC₆H₄CN)(DPE)₂. A suspension of 0.100 g (0.105 mmol) of *trans*-Mo(N₂)₂(DPE)₂ and 42 mg (0.32 mmol) of 4-methoxybenzonitrile in 5 ml of toluene was stirred at ambient temperature for 18 hr. The mixture turned dark brown and became homogeneous. *n*-Hexane was added to precipitate dark brown crystals. The crystals were filtered, washed with *n*-hexane and ether, and dried in vacuo (0.083 g, 75%). Anal. Calcd for C₆₀H₅₅N₃OP₄Mo: C, 68.4; H, 5.3; N, 4.0. Found: C, 68.7; H, 5.5; N, 3.9.

The following complexes were prepared in a similar manner with exceptions as noted below. In the case of the 4-aminobenzonitrile complex tetrahydrofuran was used as the solvent and 0.53 mmol of the nitrile was added. In the case of the complexes of 4-chloro- and 4-acetylbenzonitrile and 1,4-dicyanobenzene, 0.105 mmol of the nitrile was added. In the case of the aliphatic nitrile complexes 0.53 mmol of the nitrile was added.

Mo(N₂)(4-NH₂C₆H₄CN)(DPE)₂. Obtained as maroon crystals in 60% yield. Anal. Calcd for C₅₉H₅₄N₄P₄Mo: C, 68.2; H, 5.2; N, 5.4. Found: C, 67.4; H, 5.4; N, 5.3.

Mo(N₂)(4-CH₃C₆H₄CN)(DPE)₂. Obtained as dark green crystals in 71% yield. Anal. Calcd for C₆₀H₅₅N₃P₄Mo: C, 69.4; H, 5.3; N, 4.1. Found: C, 69.4; H, 5.7; N, 4.3.

Mo(N₂)(4-ClC₆H₄CN)(DPE)₂. Obtained as dark green crystals in 48% yield. Anal. Calcd for C₅₉H₅₂N₃P₄ClMo: C, 67.0; H, 5.0; N, 4.0. Found: C, 66.5; H, 5.3; N, 3.6.

Mo(N₂)(4-CH₃COC₆H₄CN)(DPE)₂. Obtained as olive green crystals in 20% yield. Anal. Calcd for C₆₁H₅₅N₃OP₄Mo: C, 68.7; H, 5.2; N, 3.9. Found: C, 67.4; H, 5.4; N, 3.3. Prolonged standing of the reaction mixture affords an ill-defined violet complex.

Mo(N₂)(2-CH₃C₆H₄CN)(DPE)₂. Obtained as dark green crystals in 56% yield. Anal. Calcd for C₆₀H₅₅N₃P₄Mo: C, 69.4; H, 5.3; N, 4.1. Found: C, 68.6; H, 5.7; N, 4.3.

Mo(N₂)(CH₃CN)(DPE)₂. Obtained as vermilion crystals in 58% yield. Anal. Calcd for C₅₄H₅₁N₃P₄Mo: C, 67.4; H, 5.3; N, 4.4. Found: C, 66.8; H, 5.5; N, 4.3.

Mo(N₂)(C₂H₅CN)(DPE)₂. Obtained as brick red crystals in 62% yield. Anal. Calcd for C₅₅H₅₃N₃P₄Mo: C, 67.7; H, 5.5; N, 4.3. Found: C, 67.0; H, 5.7; N, 3.8.

[Mo(N₂)(DPE)₂]₂(1,4-NCC₆H₄CN). Obtained as an olive green solid in 30% yield. The complex was too insoluble for recrystallization. Anal. Calcd for C₁₁₂H₁₀₀N₆P₈Mo₂: C, 68.3; H, 5.1; N, 4.3. Found: C, 66.8; H, 4.9; N, 4.0.

Reactions of the Mono(dinitrogen) Complexes with Nitrogen. Nitrogen gas was bubbled into a solution of 0.040 g (0.042 mmol) of Mo(N₂)(CH₃CN)(DPE)₂ in 5 ml of toluene at ambient temperature for 6 hr. Addition of 10 ml of *n*-hexane gave 0.030 g (76%) of *trans*-Mo(N₂)₂(DPE)₂, which was identified by its ir spectrum. The band at 1910 cm⁻¹ assigned to ν(N₂) of the starting material completely disappeared. Mo(N₂)(C₂H₅CN)(DPE)₂ was similarly converted into *trans*-Mo(N₂)₂(DPE)₂ (71%). All the other complexes when treated with nitrogen in a similar manner were unaffected.

Reaction of *trans*-Mo(N₂)₂(DPE)₂ with Benzoyl Chloride. A suspension of 0.200 g (0.211 mmol) of *trans*-Mo(N₂)₂(DPE)₂ and

3.0 ml (26 mmol) of benzoyl chloride in 10 ml of benzene was stirred for 12 hr at ambient temperature. The mixture turned reddish brown and became homogeneous. The solution was concentrated to a volume of ca. 5 ml in vacuo. Addition of 10 ml of *n*-hexane deposited orange-red crystals, which were filtered and washed with *n*-hexane and ether. A small quantity of a yellow-brown powder containing MoCl₂(N₂HCOPh)(DPE)₂ was also obtained, from which HCl can be removed by triethylamine to produce an additional amount of the same orange-red crystals, which were washed with methanol, ether, and *n*-hexane. The combined crystals were recrystallized from toluene/*n*-hexane to yield 0.120 g (53%) of MoCl(N₂COPh)(DPE)₂. Anal. Calcd for C₅₉H₅₃N₂OP₄ClMo: C, 66.8; H, 5.0; N, 2.6. Found: C, 66.8; H, 5.0; N, 2.5.

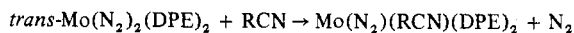
Reactions of the Mono(dinitrogen) Complexes with Benzoyl Chloride. The reactions were carried out as above and continued until the color of the solution showed that the reaction was completed. The yield of MoCl(N₂COPh)(DPE)₂ from Mo(N₂)(4-XC₆H₄CN)(DPE)₂ (X = CH₃O, CH₃, H, Cl, and COCH₃) was 56 (12), 46 (12), 22 (30), 10 (48), and 0% (6), respectively, where the number in parentheses represents the reaction time (hr). The yield of MoCl(N₂COPh)(DPE)₂ from Mo(N₂)(CH₃CN)(DPE)₂ and Mo(N₂)(C₂H₅CN)(DPE)₂ was 3 and 5% (12 hr).

Reaction of MoCl(N₂COPh)(DPE)₂ with Hydrogen Chloride. Aqueous hydrogen chloride (0.7 ml, 35% solution) was added to 0.200 g (0.188 mmol) of MoCl(N₂COPh)(DPE)₂ in 10 ml of tetrahydrofuran. Immediate reaction took place and the resultant wine red solution was stirred for 4 hr. The solution was taken to dryness in vacuo, and the light purple residue was washed with water and ether and crystallized from dichloromethane (3 ml)/ether (10 ml) to yield 0.158 g (77%) of MoCl₂(N₂HCOPh)(DPE)₂. Anal. Calcd for C₅₉H₅₄N₂P₄OCl₂Mo: C, 64.5; H, 4.9; N, 2.6. Found: C, 63.9; H, 4.9; N, 2.4. The analogs shown in Table III were similarly prepared.

Reaction of MoCl₂(N₂HCOPh)(DPE)₂ with Triethylamine. To a suspension of 0.040 g (0.036 mmol) of MoCl₂(N₂HCOPh)(DPE)₂ in 5 ml of tetrahydrofuran was added 0.05 ml (0.36 mmol) of triethylamine and the mixture was stirred for 10 min. The resulting orange-red solution was concentrated to a volume of 2 ml in vacuo, and 5 ml of *n*-hexane was added to precipitate orange-red crystals. The crystals contaminated with [NEt₃H]Cl (ir) were washed with methanol and dried to give 0.027 g (70%) of MoCl(N₂COPh)(DPE)₂.

Results and Discussion

Treatment of *trans*-Mo(N₂)₂(DPE)₂ with molar excesses of substituted benzonitriles, acetonitrile, or propionitrile in toluene or tetrahydrofuran caused displacement of one molecule of ligating dinitrogen by the organonitriles to afford the corresponding dinitrogen(organonitrile)molybdenum complex, Mo(N₂)(RCN)(DPE)₂ [R = 4-XC₆H₄ (X = NH₂, CH₃O,



CH₃, Cl, or COCH₃), 2-CH₃C₆H₄CN, C₆H₅, CH₃, or C₂H₅] in good yields. The presence of an excess of the organonitrile favored the isolation of pure product except the benzonitriles substituted with electron-withdrawing groups, which caused the replacement of the second dinitrogen to afford ill-defined complexes. It is interesting to note that carbon monoxide displaced two molecules of dinitrogen of the bis(dinitrogen) complex to produce *cis*-Mo(CO)₂(DPE)₂.^{1,9}

In the case of the mono(dinitrogen) complexes of acetonitrile and propionitrile the reaction was reversible; treatment of these complexes with bubbled nitrogen gas re-formed the bis(dinitrogen) complex. In contrast the complexes of substituted benzonitriles were recovered quantitatively after bubbling nitrogen gas through a toluene solution for 6 hr. George and Siebold found that no dinitrogen complexes were formed when MoCl₄(RCN)₂ was reduced in the presence of phosphine ligand and suggested that the nitrile must be inhibiting the uptake of dinitrogen.¹⁰ This finding is interesting in light of the dinitrogen(organonitrile)molybdenum complexes prepared in this report. It is noteworthy that *trans*-Mo(N₂)₂(DPE)₂ is stable in acetonitrile at room temperature (7 days) as already reported,¹⁰ while the complex reacts smoothly with acetonitrile in toluene to give Mo(N₂)(CH₃CN)(DPE)₂. The lack of

Table I. Selected Infrared Absorptions (cm^{-1}) of Mono(dinitrogen) Complexes of Organonitriles^a

Compd	$\nu(\text{N}\equiv\text{N})$	$\nu(\text{C}\equiv\text{N})$		$\Delta\nu(\text{CN})^b$
		Coordinated	Free	
$\text{Mo}(\text{N}_2)(4\text{-NH}_2\text{C}_6\text{H}_4\text{CN})(\text{DPE})_2$	1930	2153	2216	-63
$\text{Mo}(\text{N}_2)(4\text{-CH}_3\text{OC}_6\text{H}_4\text{CN})(\text{DPE})_2$	1931	2142	2217	-84
$\text{Mo}(\text{N}_2)(4\text{-CH}_3\text{C}_6\text{H}_4\text{CN})(\text{DPE})_2$	1940	2143	2230	-87
$\text{Mo}(\text{N}_2)(\text{C}_6\text{H}_5\text{CN})(\text{DPE})_2$	1945	2134	2231 ^c	-96
$\text{Mo}(\text{N}_2)(4\text{-ClC}_6\text{H}_4\text{CN})(\text{DPE})_2$	1954	2116	2227	-114
$\text{Mo}(\text{N}_2)(4\text{-CH}_3\text{COC}_6\text{H}_4\text{CN})(\text{DPE})_2$	1965	2103	2228	-125
$\text{Mo}(\text{N}_2)(2\text{-CH}_3\text{C}_6\text{H}_4\text{CN})(\text{DPE})_2$	1928	2138	2230 ^c	-92
$\text{Mo}(\text{N}_2)(\text{CH}_3\text{CN})(\text{DPE})_2$	1910	2212	2254 ^c	-42
$\text{Mo}(\text{N}_2)(\text{C}_2\text{H}_5\text{CN})(\text{DPE})_2$	1915	2191	2249 ^c	-58
$[\text{Mo}(\text{N}_2)(\text{DPE})_2]_2(1,4\text{-NCC}_6\text{H}_4\text{CN})$	1938	2119	2232	-113

^a All spectra taken as KBr pellets unless noted. ^b Change in $\nu(\text{CN})$ on coordination. ^c Neat.

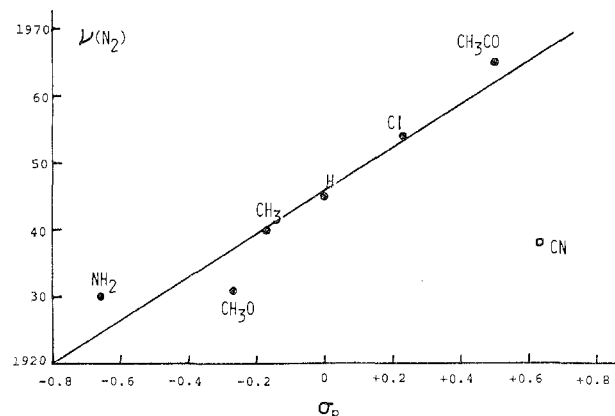


Figure 1. Hammett σ_p vs. $\nu(\text{N}_2)$ for $\text{MoN}_2(4\text{-XC}_6\text{H}_4\text{CN})(\text{DPE})_2$ (●) and $[\text{MoN}_2(\text{DPE})_2]_2(1,4\text{-NCC}_6\text{H}_4\text{CN})$ (○).

reactivity of the bis(dinitrogen) complex with neat acetonitrile is probably due to its poor solubility in acetonitrile.

The ir spectra of the mono(dinitrogen) complexes of organonitriles show a very strong absorption in the range of 1910–1965 cm^{-1} assignable to $\nu(\text{N}_2)$ of coordinated dinitrogen and a sharp absorption in the range of 2103–2212 cm^{-1} assignable to $\nu(\text{CN})$ of coordinated organonitriles. Pertinent ir data are presented in Table I. Table I shows that the $\nu(\text{N}_2)$ vibration is sensitive to the nature of the para substituent associated with the $\text{XC}_6\text{H}_4\text{CN}$ moiety in the complexes. A plot of $\nu(\text{N}_2)$ vs. the Hammett substituent parameter, σ_p , is shown in Figure 1.¹¹ The linearity of this plot indicates that there is a clear correlation between these quantities. An electron-releasing substituent of benzonitriles would be expected to increase the electron density at molybdenum, resulting in an increase in the amount of back-donation from the metal to the dinitrogen ligand. This would be reflected by a lowering of $\nu(\text{N}_2)$ and vice versa for an electron-withdrawing substituent.

Attempts were made to prepare other mono(dinitrogen)-molybdenum complexes of organonitriles by the above routes, e.g., where $\text{R} = 4\text{-NCC}_6\text{H}_4$, $4\text{-O}_2\text{NC}_6\text{H}_4$, and $\text{CH}_2=\text{CH}$. Only when 1,4-dicyanobenzene was employed, the product showed a peak assignable to $\nu(\text{N}_2)$. Its analysis was close to that expected for $[\text{Mo}(\text{N}_2)(\text{DPE})_2]_2(1,4\text{-NCC}_6\text{H}_4\text{CN})$. This formulation would be supported by its poor solubility and deviation from the straight line of Figure 1. The complexes of propionitrile and acetonitrile have low values for $\nu(\text{N}_2)$, reflecting the electron-releasing effect of the alkyl groups.

In general, organonitrile coordination to metals through its nitrogen atom results in an increase in $\nu(\text{CN})$. The ir spectrum of $\text{Mo}(\text{N}_2)(\text{C}_6\text{H}_5\text{CN})(\text{DPE})_2$, however, shows a sharp absorption at 2134 cm^{-1} assignable to $\nu(\text{CN})$, which is 96 cm^{-1} lower than that of free benzonitrile. This pattern of frequency shift was observed for the entire series of the mono(dinitrogen) complexes of organonitriles investigated. The data presented

Table II. Phosphorus-31 MNR Data

Compd	δ^a	Solvent
$\text{Mo}(\text{N}_2)(4\text{-NH}_2\text{C}_6\text{H}_4\text{CN})(\text{DPE})_2$	-72 s	THF ^b
$\text{Mo}(\text{N}_2)(4\text{-CH}_3\text{OC}_6\text{H}_4\text{CN})(\text{DPE})_2$	-73 s	Toluene
$\text{Mo}(\text{N}_2)(4\text{-CH}_3\text{C}_6\text{H}_4\text{CN})(\text{DPE})_2$	-73 s	Toluene
$\text{Mo}(\text{N}_2)_2(\text{DPE})_2$	-72 s	Toluene
DPE	7	Toluene

^a Ppm relative to PPh_3 ; s = singlet. ^b Tetrahydrofuran.

in Table I show the value of $\nu(\text{CN})$ and $\Delta\nu(\text{CN})$, where $\Delta\nu(\text{CN})$ is the change in $\nu(\text{CN})$ on coordination. These spectral features are evidence of an unusually strong release of electrons from the filled nonbonding d orbitals of molybdenum into the antibonding π^* orbitals on the ligand. Metal electron back-bonding is expected to be accelerated by the electron-withdrawing substituent of benzonitriles. In fact the $\Delta\nu(\text{CN})$ differences among the various substituted benzonitrile series show a clear trend toward more negative $\Delta\nu(\text{CN})$'s with the more electron-withdrawing substituents.

Three examples are known in which $\nu(\text{CN})$ of coordinated organonitriles shows a decrease from the free ligand value. They are all analogs of dinitrogen complexes, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$,^{2a} $\text{OsCl}_2(\text{N}_2)(\text{PMe}_2\text{Ph})_3$,³ and $\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$,^{4a} as is the case for the molybdenum complexes obtained here. The $\nu(\text{CN})$ decrease of $\text{Mo}(\text{N}_2)(\text{RCN})(\text{DPE})_2$ is remarkably larger than those observed for the Ru(II) or Os(II) species; i.e., $\Delta\nu(\text{CN})$ of benzonitrile for the Mo, Ru, and Os complexes is -96, -37, and -39 cm^{-1} , respectively. Thus the back-donation ability of the $\text{Mo}(\text{N}_2)(\text{DPE})_2$ moiety is stronger than that of the $\text{Ru}(\text{NH}_3)_5^{2+}$ or $\text{OsCl}_2(\text{PMe}_2\text{Ph})_3$ moiety. Analogous tendency was observed from the $\nu(\text{N}_2)$'s of a series of the corresponding dinitrogen complexes.

As described above, the mono(dinitrogen) complexes of substituted benzonitriles could not be reconvered to the bis(dinitrogen) complex *trans*- $\text{Mo}(\text{N}_2)_2(\text{DPE})_2$. The irreversibility may be due to the strong M-NCR bonds as reflected in the large decrease in $\nu(\text{CN})$, compared with the complexes of aliphatic nitriles. But the reversibility observed in the acetonitrile and propionitrile complexes may be interpreted in terms of the equilibrium shift to the formation of the bis(dinitrogen) complex since these nitriles are volatile and removable in a stream of nitrogen.

The proton-decoupled ³¹P NMR data of the dinitrogen-molybdenum complexes are presented in Table II. The complex of 4-methoxybenzonitrile exhibits a sharp singlet at -73 ppm (relative to PPh_3) assigned to four equivalent phosphorus nuclei in *trans*- $\text{Mo}(\text{N}_2)(4\text{-CH}_3\text{OC}_6\text{H}_4\text{CN})(\text{DPE})_2$. This represents a coordination shift of 80 ppm down field from free DPE. Similar NMR spectra were observed for the complexes of 4-amino- and 4-methylbenzonitriles and the bis(dinitrogen) complex. Therefore the apical ligand of the complexes seems to have little effect on the ³¹P chemical shift. Although ³¹P NMR spectra of other mono(dinitrogen) complexes of para-substituted benzonitriles were not examined,

Table III. Selected Infrared Absorptions (cm^{-1}) of $\text{MoCl}(\text{N}_2\text{COPh})(\text{DPE})_2$ and Its Derivatives^a

Compd	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{N=N})$
$\text{MoCl}(\text{N}_2\text{COPh})(\text{DPE})_2$ ^b		1565 m	1356 m
$\text{MoCl}({}^{15}\text{N}_2\text{COPh})(\text{DPE})_2$ ^b		1565 m	1305 m
$\text{MoCl}_2(\text{N}_2\text{HCOPh})(\text{DPE})_2$ ^c	2600 br, w	1660 m	
$\text{MoCl}_2(\text{N}_2\text{-}^2\text{HCOPh})(\text{DPE})_2$ ^c	2050 br, w	1660 m	
$\text{MoCl}_2({}^{15}\text{N}_2\text{HCOPh})(\text{DPE})_2$ ^c	2590 br, w	1660 m	

^a br = broad; w = weak; m = medium. ^b KBr pellets. ^c Nujol mull.

they are also assumed to have trans configuration, since the plot of $\nu(\text{N}_2)$ vs. Hammett parameter, σ_p , (Figure 1) is found to be linear.

Chatt et al. reported that organic acid chlorides reacted with *trans*- $\text{W}(\text{N}_2)_2(\text{DPE})_2$ to produce complexes $\text{WCl}_2(\text{N}_2\text{HCOR})(\text{DPE})_2$ from which HCl can be removed to form acyl-azo and aroyl-azo complexes.⁸ They also briefly commented that *trans*- $\text{Mo}(\text{N}_2)_2(\text{DPE})_2$ reacted analogously with organic acid chlorides. We obtained a benzoylazo complex $\text{MoCl}(\text{N}_2\text{COPh})(\text{DPE})_2$ directly by the reaction of *trans*- $\text{Mo}(\text{N}_2)_2(\text{DPE})_2$ or $\text{Mo}(\text{N}_2)(\text{RCN})(\text{DPE})_2$ ($\text{R} = 4\text{-CH}_3\text{OC}_6\text{H}_4$, $4\text{-CH}_3\text{C}_6\text{H}_4$, C_6H_5 , $4\text{-ClC}_6\text{H}_4$, CH_3 , or C_2H_5) with an excess of benzoyl chloride in benzene. The complex obtained as orange-red crystals by the recrystallization from toluene/*n*-hexane is protonated by an excess of aqueous hydrogen chloride to give $\text{MoCl}_2(\text{N}_2\text{HCOPh})(\text{DPE})_2$. Treatment of the protonated complex with triethylamine gives

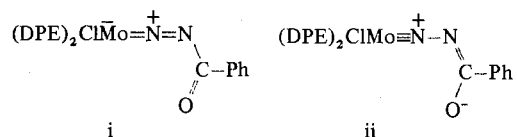


back the original benzoylazo complex.

Pertinent ir data of these complexes as well as ^{15}N - and ^2H -labeled derivatives are shown in Table III. The spectrum of the benzoylazo complex shows a band at 1565 cm^{-1} assignable to $\nu(\text{CO})$. There are also a very strong broad band at 1255 cm^{-1} and two medium intensity bands at 1356 and 1305 cm^{-1} . The ^{15}N -labeled derivative shows bands at 1305 and 1245 cm^{-1} . It is probably reasonable to consider that by ^{15}N labeling the band at 1356 cm^{-1} assignable to $\nu(\text{NN})$ is shifted accidentally to 1305 cm^{-1} and that the original band at 1305 cm^{-1} is shifted and masked by the broad band at 1245 cm^{-1} . The band at 1255 cm^{-1} may be assigned to the vibration of the benzoyl group, slightly coupled with that of the azo group, since Chatt et al. have noted the presence of a strong band at ca. 1220 cm^{-1} in the related species of the type $\text{ReCl}_2(\text{N}_2\text{COPh})\text{L}_3$ ($\text{L} =$ tertiary phosphine) and assigned this to the vibration of the benzoyl group.¹² The absorption at 1305 cm^{-1} may be attributable to the stretching vibration of the C-N bond with considerable double-bond character (vide infra).

Preliminary X-ray analysis of the benzoylazo complex $\text{MoCl}(\text{N}_2\text{COPh})(\text{DPE})_2$ showed that the complex has a trans structure; the bond angles are $\text{Mo-N-N} = 171.7^\circ$, $\text{N-N-C} = 116.9^\circ$, and $\text{N-C-O} = 125.2^\circ$, and the bond lengths are $\text{Mo-N} = 1.81\text{ \AA}$, $\text{N-N} = 1.24\text{ \AA}$, $\text{N-C} = 1.38\text{ \AA}$, and $\text{C-O} = 1.24\text{ \AA}$.¹³ These results indicate that the Mo-N-N linkage is essentially linear and the azo ligand is not chelating through the carbonyl oxygen to the metal, although Chatt et al. suggested the coordination of the carbonyl oxygen in the analogous tungsten complexes from their ir spectra.⁸ The value of 1565 cm^{-1} for $\nu(\text{CO})$ in the uncoordinated organic carbonyl is exceedingly low. This is, however, compatible with the observed C-O bond length 1.24 \AA which is considerably longer than an ordinary double bond. Accompanying the elongation of the C-O bond, the C-N bond possesses significant double-bond character due to its resonance with the carbonyl group. The N-N bond length indicates a bond order of ca. 2.0 and the Mo-N bond length is consistent with considerable multiple-bond character between the metal and the nitrogen

atom. From these facts the two resonance structures can be considered, where the contribution of structure i would be more important.



The ir spectrum of the complex $\text{MoCl}_2(\text{N}_2\text{HCOPh})(\text{DPE})_2$ shows a broad band at 2600 cm^{-1} , characteristic of protonic N-H, which is shifted to 2040 cm^{-1} in the ^2H -labeled derivative. The ^1H NMR spectrum shows the N-H resonance, integrating for one proton, centered at $\delta 14.1$ ppm. Sellman has pointed out that the H atom attached to a nitrogen atom adjacent to a transition metal ion has a ^1H NMR resonance at much lower field than 6 ppm.¹⁴ He observed it at 14.27 ppm in the complex *trans*- $[\text{Ph}(\text{CO})_2\text{MnNH}=\text{NHMn}(\text{CO})_2\text{Ph}]$. These facts suggested that in our complexes, the N_2HCOPh might have a structure $\text{Mo}(\text{NH}=\text{NCOPh})$.

In the complex $\text{MoCl}_2(\text{N}_2\text{HCOPh})(\text{DPE})_2$ $\nu(\text{CO})$ is 1660 cm^{-1} , but no band assignable to $\nu(\text{NN})$ is observed. There are also a strong band at 1265 cm^{-1} and weak bands at 1510 and 1310 cm^{-1} . The latter two bands are not shifted upon ^{15}N substitution but the former shifts to 1260 cm^{-1} . Therefore it probably corresponds to the band at 1255 cm^{-1} in the benzoylazo complex. Since the band at 1310 cm^{-1} is shifted to 1290 cm^{-1} upon deuteration, it may contain a small contribution from the N-H deformation mode.

The molar conductivity of $\text{MoCl}_2(\text{N}_2\text{HCOPh})(\text{DPE})_2$ in ca. 10^{-3} M nitromethane solution is observed to be 30, suggesting that one of the chlorine ligands is labile, and in nitromethane a six-coordinated species is formed to a considerable extent.

In the mono(dinitrogen) complexes of organonitriles the reactivity of the dinitrogen ligand to form the C-N bond was significantly affected by the nitrile ligand. We could observe that the mono(dinitrogen)-molybdenum complexes of benzonitriles having an electron-releasing substituent show a tendency to lead selectively to the formation of the benzoylazo complex. Treatment of $\text{Mo}(\text{N}_2)(4\text{-CH}_3\text{OC}_6\text{H}_4\text{CN})(\text{DPE})_2$ with benzoyl chloride afforded a reddish brown solution after 12 hr, indicating the formation of the benzoylazo complex. In contrast, the starting green solution of $\text{Mo}(\text{N}_2)(\text{C}_6\text{H}_5\text{CN})(\text{DPE})_2$ still remained after 12 hr, and reaction time longer than 1 day was necessary to complete the reaction. In the case of $\text{Mo}(\text{N}_2)(4\text{-ClC}_6\text{H}_4\text{CN})(\text{DPE})_2$ it took still longer for the starting green color to disappear. Moreover, the complexes of benzonitrile and 4-chlorobenzonitrile gave a brown powder as a by-product, the structure of which remains uncertain. There was no evidence of the formation of the benzoylazo complex from $\text{Mo}(\text{N}_2)(4\text{-CH}_3\text{COC}_6\text{H}_4\text{CN})(\text{DPE})_2$. That is, the tendency of the dinitrogen ligand of the substituted benzonitrile complexes to be aroylated increases as the $\nu(\text{N}_2)$ decreases. On the other hand, from the mono(dinitrogen) complexes of acetonitrile and propionitrile which have lower $\nu(\text{N}_2)$'s than $\text{Mo}(\text{N}_2)(4\text{-CH}_3\text{OC}_6\text{H}_4\text{CN})(\text{DPE})_2$, the benzoylazo complex was obtained in low yields. These results indicate that the reactivity of coordinated dinitrogen toward benzoyl chloride does not necessarily increase with a decrease in $\nu(\text{N}_2)$.

Acknowledgment. The authors are grateful to Associate Professor T. Mizorogi of Tokyo Institute of Technology for the measurement of the ^{31}P NMR spectra.

Registry No. *trans*- $\text{Mo}(\text{N}_2)_2(\text{DPE})_2$, 25145-64-6; $\text{Mo}(\text{N}_2)(\text{PhCN})(\text{DPE})_2$, 56195-81-4; $\text{Mo}(\text{N}_2)(4\text{-CH}_3\text{OC}_6\text{H}_4\text{CN})(\text{DPE})_2$, 56195-82-5; $\text{Mo}(\text{N}_2)(4\text{-NH}_2\text{C}_6\text{H}_4\text{CN})(\text{DPE})_2$, 56195-83-6; $\text{Mo}(\text{N}_2)(4\text{-CH}_3\text{C}_6\text{H}_4\text{CN})(\text{DPE})_2$, 56195-84-7; $\text{Mo}(\text{N}_2)(4\text{-ClC}_6\text{H}_4\text{CN})(\text{DPE})_2$, 56195-85-8; $\text{Mo}(\text{N}_2)(4\text{-CH}_3\text{COC}_6\text{H}_4\text{CN})$ -

(DPE)₂, 56195-86-9; Mo(N₂)(2-CH₃C₆H₄CN)(DPE)₂, 56195-87-0; Mo(N₂)(CH₃CN)(DPE)₂, 56195-88-1; Mo(N₂)(C₂H₅CN)(DPE)₂, 56195-89-2; [Mo(N₂)(DPE)₂]₂(1,4-NCC₆H₄CN), 56195-90-5; MoCl(N₂COPh)(DPE)₂, 56210-38-9; MoCl₂(N₂HCOPh)(DPE)₂, 56271-04-6; benzoyl chloride, 98-88-4.

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Preparation and Properties of a Neutral, Chelated Four-Coordinate Organoaluminum–Nitrogen Derivative¹

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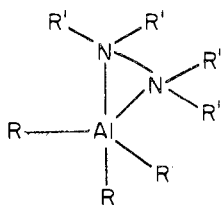
Received February 5, 1975

AIC50088J

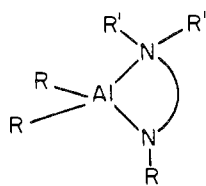
The new compound (CH₃)₂AlN(C₂H₅)C₂H₄N(CH₃)₂ has been prepared from trimethylalane and H(C₂H₅)NC₂H₄N(CH₃)₂ by pyrolysis at 100°. This compound represents the first example of a neutral four-coordinate organoaluminum–nitrogen derivative in which the nitrogen-containing ligand is chelated to the aluminum. The material has been thoroughly characterized according to its elemental analysis, cryoscopic molecular weight in benzene (+5°) and chlorobenzene (−46°), ¹H NMR spectrum, and infrared spectrum. All of our data are consistent with the hypothesis that (CH₃)₂AlN(C₂H₅)C₂H₄N(CH₃)₂ is a monomeric species in aromatic solvents. However, in aliphatic solvents such as cyclopentane, an equilibrium between the monomeric chelate and a dimeric species exists. This equilibrium is shifted toward the dimer at lowered temperatures. The reactions of the new compound as an acid and a base are also considered.

Introduction

There are very few examples of organo- or hydridoaluminum compounds containing chelated ligands. Those that have been reported can be described as five-coordinate adducts or four-coordinate derivatives. These two classes of chelated



five-coordinate adduct



four-coordinate derivative

compounds can be distinguished by the coordination number of the aluminum and the ligand atoms. In the case of an aluminum–nitrogen five-coordinate adduct, the aluminum is five-coordinate and both nitrogen atoms of the ligand are four-coordinate. For the classification “four-coordinate derivative” the aluminum is four-coordinate and one nitrogen of the chelating ligand is three-coordinate while the second nitrogen is four-coordinate. There are several good examples of five-coordinate adducts but there are no well-characterized four-coordinate chelated aluminum–nitrogen derivatives. The complexes² tetramethylmethylenediamine–alane (H₃Al·N(CH₃)₂CH₂N(CH₃)₂) and tetramethylpropanediamine–alane (H₃Al·N(CH₃)₂C₃H₆N(CH₃)₂) have been thoroughly characterized and represent five-coordinate aluminum species. Other compounds which have been reported to involve chelated ligands are the adducts of trimethylalane with tetramethylhydrazine,³ tetramethyltetrazine,⁴ and tetramethylmethylenediamine.⁵ However, the evidence for chelation in these

compounds is less complete. Prior to this research there were no known examples of neutral four-coordinate derivatives of aluminum involving chelated nitrogen ligands. This type of derivative is a possible product of the reaction between an alane and a dibasic ligand which contains one acidic hydrogen. The compound dimethylaluminum acetylacetonate^{6,7} might be included in the classification “four-coordinate derivative”, but both ends of the ligand are identical after chelation. Other attempts have been made to prepare chelated aluminum derivatives,⁸ but in all previous cases, association with dimer formation occurred rather than chelation. For example, dimethylaluminum 2-methoxyethoxide⁹ [(CH₃)₂AlOC₂H₄OCH₃]₂ forms a four-membered aluminum–oxygen ring and the methoxy oxygen is not coordinated.

In this paper we report the preparation of the first example of a neutral, chelated four-coordinate organoaluminum–nitrogen derivative, (CH₃)₂AlN(C₂H₅)C₂H₄N(CH₃)₂. This compound has been thoroughly characterized by cryoscopic molecular weight measurements in a variety of solvents and by low-temperature and concentration-dependent ¹H NMR data.

Experimental Section

All compounds described in this investigation were manipulated in a vacuum line or a purified nitrogen atmosphere. The solvents and reagents were purified by conventional means. Aluminum compounds were analyzed for aluminum by EDTA titration¹⁰ and for nitrogen by the standard Kjeldahl method and by hydrolyzable methyl content.

Preparation of (CH₃)₂AlN(C₂H₅)C₂H₄N(CH₃)₂. This compound was prepared by reaction of trimethylalane (10.0 mmol) with *N,N*-dimethyl-*N'*-ethylethylenediamine (10.0 mmol) without solvent in a sealed flask equipped with a break-seal side arm. The mixture was heated at 100° for 24 hr to allow complete reaction. The noncondensable gas produced was measured (9.82 mmol) and identified as