

Synthesis and Characterization of Nitrosyl[tris(3,5dimethylpyrazolyl)borato]molybdenum Complexes Containing Aryloxo, Arylamido and Arylciano Ligands

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The complexes $[\text{MoTp}^*(\text{NO})\text{X}(\text{ZC}_6\text{H}_4\text{CN}-p)]$ [$\text{Tp}^* = 3,5\text{-dimethylpyrazolyl}$; $\text{X} = \text{Cl}$, $\text{Z} = \text{O}$ and NH ; $\text{X} = \text{I}$, $\text{Z} = \text{CN}$] were prepared and characterized using $^1\text{H-NMR}$, IR, FAB mass spectroscopy and micro analysis.

Key Words: Molybdenum complexes, Tris(3,5-dimethylpyrazolyl)borate, Molybdenum tris(3,5-dimethylpyrazolyl)borate complexes, Nitrosyl complexes.

Introduction

Tp^* , [tris(3,5-dimethylpyrazolyl)borate], is a bulky ligand which was first synthesized by Trofimenko¹ and has assumed an important role in modern coordination chemistry². Due to their tripodal nature, the tris(pyrazolyl)borates can act as passive co-ligands occupying 3 facial coordination sites on a metal atom. It has been shown that there are strong analogies between the behavior of metal complexes containing trispyrazolborato anions, and those containing a $\eta^5\text{-cyclopentadienyl}$ ligand. This ligand system has been widely used in inorganic and organometallic chemistry¹.

$[\text{MoTp}^*(\text{NO})\text{X}_2]$ ($\text{X} = \text{Cl}$ or I) is a monomer having a 16-electron, 6- coordinate molybdenum center³. The metal atom in $[\text{MoTp}^*(\text{NO})\text{X}_2]$ may be thought of as formally coordinatively unsaturated, having a 16- valence electron configuration. This, when combined with coordination of the strong $\pi\text{-acceptor}$ NO, means that the metal is relatively “electron deficient”. The overall effect of this particular ligand grouping around the molybdenum makes the $\{\text{Mo}(\text{NO})\text{Tp}^*\}^{2+}$ group strongly electronegative. This compound is known to react readily with primary alcohols^{3,4}, amines^{4,5}, or thiols⁶ to produce the air stable 16-electron complexes $[\text{MoTp}^*(\text{NO})\text{X}(\text{Y})]$ ($\text{Y} = \text{alkoxide}$, amide or thiolate). The related bis-alkoxide compounds

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[MoTp*(NO)(OR)₂], (R = Me, Et, Prⁿ, Buⁿ) were prepared by the reaction of the amido compound, [MoTp*(NO)Cl(NH₂)], with ROH⁷. The stability of these 16-electron species was ought to be due mainly to the protective nature of the Tp* ligand, the methyl groups adjacent to the metal (at the 3-positions on the pyrazolyl rings) providing a “screen” over the metal⁴.

There has been growing interest in the synthesis and development of molecular materials with second-order non-linear optical (NLO) properties. Although most effort has focused on organic molecules because of their capacity to yield large NLO responses, metal-organic compounds also have considerable NLO potential⁸. The addition of a metal to an otherwise organic material can result in interesting redox, magnetic and structural properties⁹. Metal complexes based on molybdenum moieties, stabilized by Tp* [tris(3,5-dimethylpyrazolyl)borate] and attached to phenolato and anilido groups are strongly polarizing and could act as electron acceptor termini of dipolar complexes for designing species having second-order NLO properties. In the case of compounds containing the {Mo(NO)}³⁺ core this leads to formal co-ordinative unsaturation and electron deficiency at the metal center⁸.

A particular advantage of the {M(NO)Tp*XY} fragment is that most of the components can be relatively easily varied. For example, compounds containing (M = Mo, X = halide, Y = phenoate, anilide, or pyridyl)^{10–12} were previously reported and employed as electron acceptor groups for designing materials with potential second-order NLO properties¹³.

McCleverty et.al. reported^{13–17} that bimetallic molybdenum complexes of the type, [{MoTp*(NO)X}₂(ZC₆H₄Z)] (X = Cl or I; Z = NH or OH), in which 2 molybdenum moieties {MoTp*(NO)XY} were attached by anilido or phenolato groups, could be prepared by the reaction of [MoTp*(NO)X₂] with *p*-bifunctionalized aromatic ligands. These complexes have been of interest because of their remarkable magnetic and optical properties¹⁸.

This paper reports the preparation and spectroscopic characterization of 3 new complexes of the type [MoTp*(NO)X(Y)] (X = Cl, Y = ZC₆H₄CN, Z = O and NH; X = I, Y = CNC₆H₄CN-*p*).

Experimental

All preparations and manipulations were carried out using Schlenk techniques under an oxygen-free nitrogen atmosphere. All glassware was oven-dried at 120 °C. Solvents were dried using standard procedures, distilled and kept under nitrogen over 4 Å molecular sieves.

The compounds [MoTp*(NO)Cl₂]¹⁹ and [MoTp*(NO)I₂]²⁰ were prepared as previously described. *p*-hydroxybenzonnitrile, *p*-aminobenzonnitrile, *p*-cyanobenzonnitrile were used as purchased.

Infrared spectra were recorded on a Magna IR spectrophotometer as pressed KBr disks. ¹H-NMR spectra were recorded in CDCl₃ on 400 MHz High Performance Digital f.t.-NMR at The Scientific and Technical Research Council of Turkey (TÜBİTAK). Mass spectra analyses were performed on a Jeol AX505 FAB device using Xe at 3kV as a positive ion and a matrix m-NBA (meta-nitrobenzyl alcohol). Elemental analyses were carried out using a LECO CHNS 932 instrument.

Preparation of [MoTp*(NO)Cl(OC₆H₄CN-p)]

A mixture of [MoTp*(NO)Cl₂] (0.4 g, 0.81 mmol) and *p*-hydroxybenzotrile (0.09 g, 0.81 mmol) was stirred in toluene (20 cm³) overnight at room temperature. The red solution was cooled and evaporated to dryness in vacuo and the arylammonium salt produced was filtered off. The residue was purified using column chromatography on silica using CH₂Cl₂/n-hexane (1:1).

The major red-brown band was collected and evaporated to dryness to yield the compound [MoTp*(NO)I(OC₆H₄CN-p)] as red-brown microcrystals (0.28 g, 62%).

Preparation of [MoTp*(NO)Cl(NHC₆H₄CN-p)]

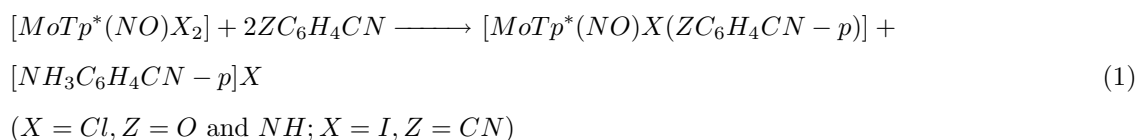
A mixture of [MoTp*(NO)Cl₂] (0.4 g, 0.81 mmol) and *p*-aminobenzotrile (0.09 g, 0.81 mmol) was refluxed in toluene (20 cm³) for 6 h. The brown solution was cooled and evaporated to dryness in vacuo and the arylammonium salt produced was filtered off. The components of the residue were purified by column chromatography on silica using CH₂Cl₂/n-hexane (1:3). The major red-brown band was collected and evaporated to dryness to yield the compound [MoTp*(NO)I(NHC₆H₄CN-p)] as brown microcrystals (26 g, 56 %).

Preparation of [MoTp*(NO)Cl(CNC₆H₄CN-p)]

[MoTp*(NO)I₂] (0.4 g, 0.59 mmol), dissolved in dichloromethane (20 cm³), was treated with *p*-cyanobenzotrile (0.076 g, 0.59 mmol). The mixture was stirred at room temperature for 2 days to produce a brown solution and was filtered through kieselguhr. The filtrate was then removed in vacuo, and the brown solid was purified using column chromatography on silica using CH₂Cl₂/n-hexane (3:7). Removal of solvent in vacuo gave the dark-brown microcrystals of [MoTp*(NO)I(CNC₆H₄CN-p)] (0.23 g, 49 %).

Results and Discussion**Synthetic Studies**

The reaction of [MoTp*(NO)Cl₂] with an excess of HOC₆H₄CN-*p* and H₂NC₆H₄CN-*p* in toluene at reflux temperature afforded the monometallic compounds [MoTp*(NO)Cl(OC₆H₄CN-*p*)] and [MoTp*(NO)Cl(NHC₆H₄CN-*p*)] respectively. Similarly the compound [MoTp*(NO)I(CNC₆H₄CN)] was prepared by the reaction of [MoTp*(NO)I₂] with CNC₆H₄CN-*p* in toluene at room temperature for 2 days. In these reactions an excess of amine is desirable since it facilitates the removal of HX produced during the reaction. A 1:2 mol ratio is usually a sufficient excess to produce a reasonable yield. No trace of any bimetallic compound was observed in any of these reactions.



This procedure is identical to that followed for the analogous mono-alkylamido species^{3,10,11} and the previously reported¹⁰ similar compounds [MoTp*(NO)I(ZC₆H₄CN-*p*)] (Z = O and NH). Similarly

the previously reported²¹ compound $[\text{MoTp}^*(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_2-p)]$ was prepared by the reaction of $[\text{MoTp}^*(\text{NO})\text{Cl}_2]$ with $\text{HOC}_6\text{H}_4\text{PPh}_2-p$ in toluene.

The new compounds are red-brown in solution and remarkably soluble in many common organic solvents. They are all air- and moisture-stable. The metal in these compounds enjoys considerable steric protection, and, the existence of 6-coordinate species of this type, and even their apparent stability towards hydrolysis and oxidation, can be attributed to the tight ligand packing caused by the very bulky Tp^* ligand. Characterization data for the new complexes are given in Table 1.

Table 1. Characterization data for the complexes $[\text{MoTp}^*(\text{NO})\text{X}(\text{ZC}_6\text{H}_4\text{CN}-p)]$.

X	Z	Color	Yield (%)	Elemental analytical data (calc) (%)			FAB-MS ^c
				C	H	N	
Cl	O	red-brown	50	45.81 (45.11)	4.54 (5.23)	19.40 (18.66)	576.6
Cl	NH	red-brown	55	45.89 (46.72)	4.72 (4.01)	21.89 (21.22)	575.7
I	CN	dark brown	42	41.53 (41.5)	3.94 (3.86)	18.90 (18.58)	665.1

The new compounds were separated from the reaction mixture by crystallization from a dichloromethane/hexane mixture (V:V). The micro analyses of the new compounds are in good agreement with the suggested formulation shown in Figure.

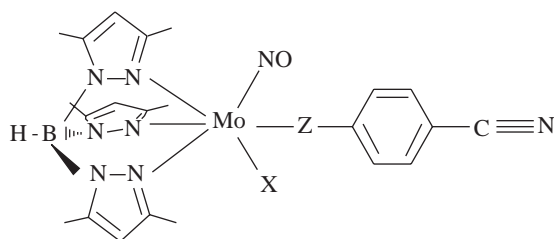


Figure. The proposed structure of the compounds $[\text{MoTp}^*(\text{NO})\text{X}(\text{ZC}_6\text{H}_4\text{CN}-p)]$ ($\text{X} = \text{Cl}$, $\text{Z} = \text{O}$ and NH ; $\text{X} = \text{I}$, $\text{Z} = \text{CN}$).

Spectroscopic Studies

Molecular ion peaks (Table 1) in the mass spectra are consistent with the suggested formulation of the new complexes.

IR spectra data for the new complexes are given in Table 2. All complexes exhibit the expected absorptions due to the Tp^* ligand (ca. 2500 cm^{-1} due to $\nu_{(\text{BH})}$ and 1400 cm^{-1} associated with the pyrazolyl ring) as well as characteristic group frequencies associated with the aromatic ring substituents. All the compounds exhibited a nitrosyl group absorption in the range 1660 to 1698 cm^{-1} . The compound $[\text{MoTp}^*(\text{NO})\text{Cl}(\text{NHC}_6\text{H}_4\text{CN}-p)]$ exhibited $\nu_{(\text{NO})}$ at 1660 cm^{-1} . This value is lower than the comparable $\nu_{(\text{NO})}$ value 1681 cm^{-1} observed for the compound $[\text{MoTp}^*(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{CN}-p)]$, presumably because $\text{OC}_6\text{H}_4\text{CN}-p$ is a poorer donor than $\text{NHC}_6\text{H}_4\text{CN}-p$. This observation was in accord with the previously reported¹⁰ $\nu_{(\text{NO})}$ values, 1686 and 1666 cm^{-1} , for $[\text{MoTp}^*(\text{NO})\text{I}(\text{OC}_6\text{H}_4\text{CN}-p)]$ and $[\text{MoTp}^*(\text{NO})\text{I}(\text{NHC}_6\text{H}_4\text{CN}-p)]$ respectively, whereas the compound $[\text{MoTp}^*(\text{NO})\text{Cl}(\text{CNC}_6\text{H}_4\text{CN}-p)]$ exhibited $\nu_{(\text{NO})}$ at 1698 cm^{-1} .

The compound [MoTp*(NO)Cl(HNC₆H₄CN-*p*)] also exhibited a single $\nu_{(NH)}$ at 3257 cm⁻¹, confirming the existence of a NH group that is close to the value of 3227 cm⁻¹ for the related compound [MoTp*(NO)I(NHC₆H₄CN-*p*)]¹⁰.

Table 2. Key IR bands (cm⁻¹) for the compounds [MoTp*(NO)X(ZC₆H₄CN-*p*)].

X	Z	ν_{BH}	ν_{NO}	ν_{CN}	ν_{NH}
Cl	NH	2559 br	1677 s	2229 s	3257 s
Cl	O	2557 br	1664 s	2227 s	—
I	CN	2563 br	1698 s	2223 s	—
				2271 m	

Table 3. ¹H NMR data for the compounds [MoTp*(NO)X(ZCC₆H₄CN-*p*)].

X	Z	δ	$H(A)^a/ppm$	Multiplicity and Assignments ^b
Cl	O	7.30		4H, A ₂ B ₂ , $\delta(A)$ 7.22, $\delta(B)$ 7.38, J(AB) 9.0 Hz, OC ₆ H ₄ CN
		5.90		s, 1H, Me ₂ C ₃ HN ₂
		5.81		s, 1H, Me ₂ C ₃ HN ₂
		5.70		s 1H, Me ₂ C ₃ HN ₂
		2.89		s, 3H, Me ₂ C ₃ HN ₂
		2.74		s, 3H, Me ₂ C ₃ HN ₂
		2.60		s, 3H, Me ₂ C ₃ HN ₂
		2.46		s, 3H, Me ₂ C ₃ HN ₂
		2.31		s, 3H, Me ₂ C ₃ HN ₂
		2.17		s, 3H, Me ₂ C ₃ HN ₂
Cl	NH	12.18		s, 1H, NHC ₆ H ₄ CN
		7.65		4H, A ₂ B ₂ , $\delta(A)$ 7.80, $\delta(B)$ 7.50, J(AB) 9.0 Hz, NHC ₆ H ₄ CN
		5.98		s, 1H, Me ₂ C ₃ HN ₂
		5.85		s, 1H, Me ₂ C ₃ HN ₂
		5.77		s, 1H, Me ₂ C ₃ HN ₂
		2.94		s, 3H, Me ₂ C ₃ HN ₂
		2.86		s, 3H, Me ₂ C ₃ HN ₂
		2.71		s, 3H, Me ₂ C ₃ HN ₂
		2.57		s, 3H, Me ₂ C ₃ HN ₂
		2.33		s, 3H, Me ₂ C ₃ HN ₂
2.11		s, 3H, Me ₂ C ₃ HN ₂		
I	CN	7.73		4H, A ₂ B ₂ , $\delta(A)$ 7.82, $\delta(B)$ 7.64, J(AB) 7 Hz, CNC ₆ H ₄ CN
		6.16		s, 2H, Me ₂ C ₃ HN ₂
		5.86		s, 1H, Me ₂ C ₃ HN ₂
		2.66		s, 3H, Me ₂ C ₃ HN ₂
		2.61		s, 3H, Me ₂ C ₃ HN ₂
		2.59		s, 3H, Me ₂ C ₃ HN ₂
		2.55		s, 3H, Me ₂ C ₃ HN ₂
		2.45		s, 3H, Me ₂ C ₃ HN ₂
		2.18		s, 3H, Me ₂ C ₃ HN ₂

^aIn CDCl₃; A = relative intensity. ^bJ values in Hz

The C≡N stretching vibration in the IR spectra of the compounds [MoTp*(NO)Cl(ZC₆H₄CN-*p*)] (Z = O, HN, CN) is also an informative spectroscopic tool for the characterization of the new species. The C≡N group bonded in *p*-position on (ZC₆H₄CN-*p*) (Z = O, NH, CN) revealed itself at ca. 2223 cm⁻¹ as reported²¹ for similar compounds. The $\nu_{(CN)}$ for the C≡N group bonded to the molybdenum atom in the compound [MoTp*(NO)Cl(CNCC₆H₄CN-*p*)] shifted to a higher wave number (2282 cm⁻¹). This observation resembles the data found for other transition metal complexes reported²¹ previously.

The ¹H NMR data (Table 3) of the new complexes were consistent with the proposed structures and internally consistent with each other. Thus all species exhibited 6 methyl proton signals due to the methyl groups of the 3 inequivalent pyrazole rings in the range δ 2.0 to 3.0 ppm. Signals due to the C(4) proton of the pyrazole group generally occur in the range δ 5.0 to 6.0 ppm, and when X \neq Y in [MoTp*(NO)XY] they usually occur as 3 singlets because of the absence of a plane of symmetry in these 6-coordinate compounds. The compounds [MoTp*(NO)Cl(ZC₆H₄CN-*p*)] (Z = O and NH) revealed 3 signals as expected. However, for [MoTp*(NO)I(CNC₆H₄CN-*p*)] C(4) protons of the pyrazole ring appeared as 2 resonances of intensity ratio 2:1 at δ 6.16 and 5.86 ppm. This could be attributed to the accidental overlap of 2 of the 3 expected signals, a phenomenon reported¹⁰ previously.

The number and form of signals due to the aromatic group in the new compounds are as expected, and appear as A₂B₂-type spectra. The proton in [MoTp*(NO)Cl(HNC₆H₄CN-*p*)] appeared as a sharp singlet at δ 12.18 ppm. These data are in agreement with the previously reported molybdenum compounds containing aryloxo and arylamido ligands^{4,7,10-12,22}.

Conclusion

This study was carried out in order to prepare aryloxo, arylamido and arylcyano complexes of nitrosyl[tris(3,5-dimethylpyrazolyl)borato]molybdenum. The monometallic complexes of the type [MoTp*(NO)X(ZCC₆H₄CN-*p*)] (X = Cl, Z = O, NH; X = I, Z = CN) were obtained as a result of the reaction of [MoTp*(NO)X₂] with ZC₆H₄CN-*p*. The spectroscopic data and elemental analysis of the new complexes are consistent with the suggested formulation of the new species. In these compounds the electron deficiency of the formally 16-electron molybdenum center is thought to be relieved to some extent by N p _{π} \rightarrow Mo d _{π} charge donation. The importance of these monometallic species arises from their possible employment as electron acceptor termini of dipolar compounds for designing new materials with potential applications in molecular electronic and electro-optic devices.

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