



Synthesis and Characterization of A. New Mono-Molybdenated Metallo-Ligand [Mo{HB(3, 5-Me₂C₃HN₂)₃} (NO)Cl(OC₆H₄PPh₂-p)]

Isil Topaloglu & Jon A. McCleverty

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**SYNTHESIS AND CHARACTERIZATION OF A NEW
MONO-MOLYBDENATED METALLO-LIGAND
[Mo{HB(3,5-Me₂C₃HN₂)₃}(NO)Cl(OC₆H₄PPh₂-p)]**

Işıl Topaloğlu*

Department of Chemistry, Faculty of Science, Izmir Institute of
Technology, Izmir, Turkey

Jon A. McCleverty

School of Chemistry, University of Bristol, Bristol, England

ABSTRACT

The "metallo-ligands" can be considered effectively as a modified triphenylphosphine ligand, and used to generate novel transition metal complexes in which electron-transfer and magnetism is embedded within the stable ligand framework. A new mono-molybdenated metallo-ligand was synthesized and characterized by NMR (¹H and ³¹P-¹H}), IR and mass spectroscopy techniques as a starting material in the search for designing novel bimetallic complexes exhibiting optoelectronic properties and development of non-linear optical materials that possess commercial device applications.

INTRODUCTION

One of the most exciting developments in contemporary materials science has been the exploitation of molecular inorganic solids in the construction of materials with remarkable physical properties.¹ Their great utility rests largely on the chemist's ability to manipulate the structural and internal electronic properties of molecules in such a way as to have profound influence to the bulk properties of the solid material. Two sub-areas of materials science in which the molecular approach has been demonstrated to be particularly effective are non-linear optics and molecular magnetism. An important molecular design feature in these sub-areas has been the creation of bimetallic compounds in which two metals are held in close proximity to each other, not directly bonded but linked by bridging groups which are easily polarised by the metal centres. Using this design, it has been possible to make very effective frequency doublers, by combining electron-deficient molybdenum nitrosyls with electron-rich ferrocene², and to deliberately create ferromagnetic interactions, albeit weak, within bi-metallic molybdenum species.

The all-important bridging ligands in these bimetallic species have been based on N-heterocycles and phenols, or on combinations of them. It might be possible to include tertiary phosphines in such bridging groups, for example by linking PPh₂ groups to pyridine or phenols giving, for example, the functional ligands *p*-NC₅H₄PPh₂ and *p*-HOC₆H₄PPh₂. For these ligands, using tried and tested methods⁵, it will be possible to make the mono-molybdenated "metallo-ligands".

The preference of a molybdenum nitrosyl centre for the "hard" N or O atoms is based on very well-understood stereochemistry⁶. These

mono-molybdenated metallo-ligands are expected to be paramagnetic (the Mo centre has 17 valence electrons) and capable of one-electron reduction and oxidation behaviour, detectable by electrochemical techniques.

This work was carried out in an attempt to prepare the new mono-molybdenated "metallo-ligand" $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_{2-p})]$ as the starting material in the search for designing novel bimetallic species which will have optoelectronic properties, expecting that the species will be dipolar (e.g., an electron-deficient Mo centre linked to an electron-rich centre like Pt(0) by readily polarisable benzene ring) and should exhibit strong, first-order hyperpolarisability (β) in solution. This paper deals only with the synthesis and the spectroscopic characterization of the mono-molybdenated "metallo-ligand" $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_{2-p})]$.

RESULTS AND DISCUSSION

Synthetic Studies

The mono-molybdenated compound $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_{2-p})]$ was obtained by refluxing of $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}_2]$ with $(p\text{-HOC}_6\text{H}_4\text{PPh}_2)^{\ominus}$ in the presence of triethylamine in toluene for ca. 12 h. In this reaction it was essential to use an excess of triethylamine since in the absence of this base the completion of the reaction and the isolation of the product could not be achieved cleanly, even after prolonged reaction times. The reaction mixture was

refluxed from 12 h up to 24 h and product formation was always accompanied by some decomposition.

The compound $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_{2-p})]$ was obtained as purple-red crystals and the yield of the reaction ranged from 51-64 %, lower than hoped for because of competing side reactions which produced, *inter alia*, significant amounts of the green oxo-bridged bimetallic molybdenum nitrosyl complex $[\{\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}\}_2\text{O}]^9$, because the starting material, $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}_2]$, has a tendency to react with traces of air and/or moisture. Besides this oxo species, other side products could not be identified.

The elemental analyses of the new mono-molybdenated compound are in good agreement with the expected formulation in Fig.1.

Spectroscopic Studies

Electron-impact (EI) mass spectroscopy results showed the ion of highest m/z at 735.0 which is consistent with the calculated value (735.8) (Table I).

The IR spectrum of the complex $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_{2-p})]$ contains a band at 2553 cm^{-1} attributable to the presence of the BH group in the $\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}$ ligand together with a strong nitrosyl band at 1690 cm^{-1} (Table II).

The ^1H NMR spectrum of the new mono-molybdenated compound is in agreement with the suggested formulation proposed for a monomeric structure.

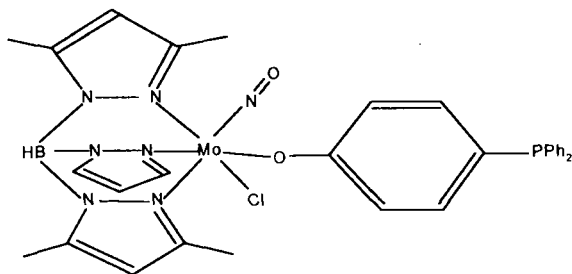


Figure 1. The Structural Formula of the Compound $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_2\text{-}p)]$

Table I. Mass Spectrometric Data for the Complex $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_2\text{-}p)]$

M^{+a}	$\{\text{M}-\text{Cl}\}^+$	$\{\text{M}-[\text{OC}_6\text{H}_4\text{PPh}_2]\}^+$	$\{\text{M}-[\text{MoTp}^+\text{Cl}(\text{NO})]\}^+$
735 (100.00) ^b	700 (32.79)	534 (13.50)	275 (25.81)

^aPosition of the ion of highest m/z in the EI mass spectrum. ^bThe values given in parenthesis are the relative intensities.

The protons of the C₆H₄ and phenyl group in $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_2\text{-}p)]$ resonate in the range 7.28-7.18 ppm and 7.63-7.53 ppm as two doublets and 7.63-7.53 ppm as a multiplet, respectively, whereas these resonances in the free ligand appeared in the range 6.84-6.80 as two doublets and in the range 7.32-7.25 ppm as a multiplet, respectively (Table II).

Table II. ^1H , $^{31}\text{P}\{-\text{H}\}$ NMR and IR Spectroscopic Data for the Complex $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_2\text{-}p)]$

^1H NMR ^a δ (ppm)	$^{31}\text{P}\{-\text{H}\}$	IR ^c	
	NMR ^{a,b} δ (ppm)	$\nu(\text{NO})$	$\nu(\text{BH})$
7.63-7.53 (m, 10H, Ph); 7.28 [2H, d, $J(\text{HH}) = 8.6$, C_6H_4] 7.18 [2H, d, $J(\text{HH}) = 8.6$, C_6H_4] 5.85 (1H, s, $\text{Me}_2\text{C}_3\text{HN}_2$) 5.81 (1H, s, $\text{Me}_2\text{C}_3\text{HN}_2$) 5.68 (1H, s, $\text{Me}_2\text{C}_3\text{HN}_2$) 2.48 (3H, s, $3\text{Me}_2\text{C}_3\text{HN}_2$) 2.34 (3H, s, $3\text{Me}_2\text{C}_3\text{HN}_2$) 2.33 (3H, s, $3\text{Me}_2\text{C}_3\text{HN}_2$) 2.31 (3H, s, $3\text{Me}_2\text{C}_3\text{HN}_2$) 2.12 (3H, s, $3\text{Me}_2\text{C}_3\text{HN}_2$) 1.98 (3H, s, $3\text{Me}_2\text{C}_3\text{HN}_2$)	-5.43	1690	2553

^ain CDCl_3 . ^bchemical shifts are positive to high frequency, relative to external 85 % H_3PO_4 , coupling constants are in Hz. ^c cm^{-1} , in CH_2Cl_2 solution.

The signals due to the three pyrazol 4-protons appeared in the range 5.85-5.68 ppm as three singlets and the 3- or 5-methyl protons in the pyrazolyl ligand revealed themselves as six discrete signals in the region 2.48-1.98, as expected for an octahedral complex of this ligand with three different substituents bonded to the metal¹⁰. The $^{31}\text{P}\{-\text{H}\}$ NMR

spectrum of the complex $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_2\text{-}p)]$ showed a singlet at -5.43 ppm due the PPh_2 group of the $\text{OC}_6\text{H}_4\text{PPh}_2$ ligand whereas this resonance in the free ligand was observed at -6.92 ppm.

EXPERIMENTAL

The complex $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_2\text{-}p)]$ was prepared adopting a described general procedure⁷. The compound $p\text{-HOC}_6\text{H}_4\text{PPh}_2$ was synthesised according to the literature method⁸. Triethylamine was dried over sodium and stored over activated alumina. Solvents were of the highest grade commercially available and were used as received. Reactions were carried out under nitrogen but purification procedures were carried out in air. Silica gel 60 (70-230 mesh) was used for column chromatography.

The IR spectrum was measured using a PE 1600 IR spectrometer, ^1H , and $^{31}\text{P}\{-\text{H}\}$ NMR spectra were obtained using a JEOL GX400 spectrometer. Elemental analyses were carried out by the Microanalytical Laboratories of the School of Chemistry at the University of Bristol. The electron-impact spectrum was recorded on a VG-Autospec instrument.

Preparation of the Complex $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_2\text{-}p)]$

A mixture of $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}_2]$ (0.2 g, 0.42 mmol) and $p\text{-HOC}_6\text{H}_4\text{PPh}_2$ (0.12 g, 0.42 mmol) was stirred under reflux in

toluene (30 mL) in the presence of triethylamine ((0.2 mL, 0.14 mmol)) for ca. 12 h. The purple-red solution was allowed to cool and evaporated to dryness *in vacuo*. The solid residue was purified by column chromatography over silica. Initially, elution with dichloromethane/n-hexane (4:1) removed unreacted starting material (orange) and the by-product $[\{\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}\}_2(\mu\text{-O})]$ (pale green). The solvent polarity was then increased and pure dichloromethane was used to separate the major purple band which was then crystallised from dichloromethane/n-hexane (1:4) to afford the compound $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{Cl}(\text{OC}_6\text{H}_4\text{PPh}_2\text{-}p)]$, as purple-red microcrystals, m.p. 169°C (decomp.); yield 0.19 g (64%). *Anal.* Found: C, 54.5; H, 4.85; N, 13.8 %. Calcd. for $\text{C}_{33}\text{H}_{36}\text{N}_7\text{O}_2\text{BCIPMo}$ (735.8): C, 53.9; H, 4.93; N, 13.3 %.

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