

## $\mu$ -Coordination chemistry of NO ligands: Adducts of *trans*-Mo(dmpe)<sub>2</sub>(H)(NO) with lithium salts

Fupei Liang<sup>a</sup>, Helmut W. Schmalke<sup>b</sup>, Heinz Berke<sup>b,\*</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Guangxi Normal University, Guilin 541004, PR China

<sup>b</sup> Anorganisch-Chemisches Institut der Universität Zürich, Winterthurer strasse 190, CH-8057 Zürich, Switzerland

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### Abstract

Four adducts were formed by the reaction of *trans*-Mo(dmpe)<sub>2</sub>(H)(NO) (**1**) (dmpe = bis(dimethylphosphino)ethane) and a respective lithium reagent to afford, [Mo(dmpe)<sub>2</sub>(H)(NO)LiHBEt<sub>3</sub>]<sub>2</sub> (**2**), [Mo(dmpe)<sub>2</sub>(H)(NO)LiN(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**3**), [Mo(dmpe)<sub>2</sub>(H)(NO)]<sub>3</sub>(LiBH<sub>4</sub>)<sub>2</sub> (**4**), and {[Mo(dmpe)<sub>2</sub>(H)(NO)]<sub>2</sub>[LiBH<sub>4</sub>]<sub>5</sub>]<sub>*n*</sub> (**5**). Structures **2–5** were characterized by crystal X-ray diffraction analyses. Structures **2** and **3** revealed to be dimers of the 1:1 adduct of **1** and the lithium salt. The two nitrosyl oxygen atoms in **2** are  $\mu_2$ -bridged connecting two separate LiHB(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> moieties, whereas in **3** these oxygen atoms exhibit a terminal coordination mode binding to two lithium ions of the dimeric [LiN(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> unit. Structure **4** shows a discrete structure formed by two separate mononuclear LiBH<sub>4</sub> units being bridged by the nitrosyl oxygen atoms of three Mo(dmpe)<sub>2</sub>(H)(NO) moieties. Structure **5** displays a complicated chain structure with differently coordinated lithium centers, various types of bridging BH<sub>4</sub> and bridging nitrosyl groups.

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**Keywords:** Hydride; Nitrosyl binding; Molybdenum; Lithium; Adduct formation

### 1. Introduction

The Lewis basicity of coordinated carbonyl ligands has been well documented [1]. In contrast, studies on the interaction of bound NO acting as a Lewis base are relatively rare [2]. The first investigation on the Lewis basicity of the NO ligand was made by Legzdins and his coworkers. They studied the interaction of CpCr(NO)<sub>2</sub>Cl and CpM(CO)<sub>2</sub>(NO) (M = Cr, Mo, W) with R<sub>3</sub>Ln (R = Cp, Cp'; Ln = Sm, Er, Yb, Ho, Dy) in solution by IR and NMR spectroscopy [3]. The Lewis basicity of the nitrosyl was indicated by IR and <sup>1</sup>H NMR spectroscopic changes accompanied by lowering of the  $\nu$ (NO) frequencies, which occur upon adduct formation. Similar spectroscopic methods were used in the study of the interaction of Cp<sub>3</sub>Sm in solution with CpCr(CO)<sub>2</sub>(NO), [CpFe(NO)]<sub>2</sub> and Cp<sub>3</sub>Mn<sub>3</sub>(NO)<sub>4</sub> that stand for three kinds of ligation modes

of NO groups, namely, terminal,  $\mu_2$ -bridging and  $\mu_3$ -bridging, respectively. Based on the IR spectroscopic changes in the adduct formation, the Lewis basicity of the NO ligand was shown to have the order of terminal NO >  $\mu_2$ -NO >  $\mu_3$ -NO [4]. The MgI<sub>2</sub> complexes of CpM(NO)(CH<sub>2</sub>-SiMe<sub>3</sub>) have been isolated in analytically pure form with the compositions of [CpM(NO)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> · MgI<sub>2</sub> · Et<sub>2</sub>O (M = Mo, W) [5]. The existences of the isonitrosyl linkage (NO → Mg) in both complexes were manifested by IR spectroscopy and partially by X-ray crystallographic analyses of the complexes. The analogous complex CpMo(NO)I<sub>2</sub> · C<sub>4</sub>H<sub>6</sub>Mg · 1/2(Et<sub>2</sub>O) has also been isolated and characterized [6]. The crystal structure of the nitrosyl ligand/Lewis acid adduct CpRe(NO · BCl<sub>3</sub>)(PPh<sub>3</sub>)(SiMe<sub>2</sub>Cl) has been determined [7]. The Re–N bond is distinctly shortened and the N–O bond revealed lengthening upon the formation of the adduct. In dinitrosyl complexes Re(H)(NO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> (R = <sup>*i*</sup>Pr, Cy), one NO group was found to be capable of coordinating to one or two BF<sub>3</sub> molecules, and more interesting, the interaction of a second

\* Corresponding author. Tel.: +41 1 635 46 80; fax: +41 1 635 68 02.

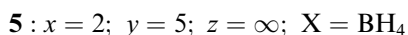
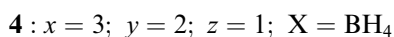
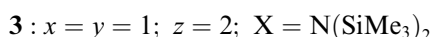
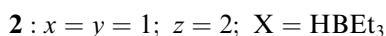
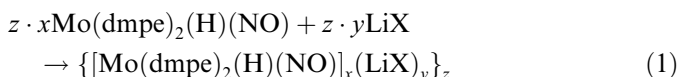
E-mail address: [hberke@aci.unizh.ch](mailto:hberke@aci.unizh.ch) (H. Berke).

BF<sub>3</sub> molecule caused bending of the NO group, thus providing a new coordination site in the metal sphere [8]. The coordination of the nitrosyl group to the lithium ions in the compounds [Cp\*Mo(NO)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>](=CHSiMe<sub>3</sub>)<sub>2</sub>[Li<sub>2</sub>(THF)<sub>3</sub>], [(η<sup>5</sup>,η<sup>1</sup>-C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>)Mo(NO)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>][Li(THF)<sub>3</sub>] and {[Cp\*Mo(NO)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>][Li(THF)]}<sub>2</sub> have been unambiguously confirmed by X-ray crystallographic analyses [9]. We have previously reported the structural characterizations of the compounds formed by the chloride *trans*-Mo(dmpe)<sub>2</sub>(Cl)(NO) (dmpe = bis(dimethylphosphino)ethane) and lithium reagents [10]. Extending these investigations, we present here structural characterizations of the adducts of the hydride *trans*-Mo(dmpe)<sub>2</sub>(H)(NO) (**1**) and various lithium salts.

## 2. Results and discussion

### 2.1. Preparation and characterization of complex 2–5

**Complex 2:** Treatment of **1** with equimolar lithium triethylborohydride in diethyl ether afforded the 1/LiHBEt<sub>3</sub> adduct [Mo(dmpe)<sub>2</sub>(H)(NO)LiHBEt<sub>3</sub>]<sub>2</sub> (**2**), which was isolated as well-defined crystals in 68% yield after diffusion of pentane into a concentrated toluene solution of the reaction mixture (Eq. (1)). The IR spectrum of **2** as a Nujol mull showed an ν(NO) absorption at 1520 cm<sup>-1</sup> of medium intensity. This NO stretching frequency is 23 cm<sup>-1</sup> lower than the corresponding one of the precursor **1** (1543 cm<sup>-1</sup> in Nujol), suggesting interaction of the lithium cation at the nitrosyl oxygen atom. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **2** in Et<sub>2</sub>O-*d*<sub>10</sub> display the expected resonances corresponding to the Mo(dmpe)<sub>2</sub>H(NO) and LiHBEt<sub>3</sub> moieties. The signal for the Mo–H proton is observed at –4.75 ppm. This resonance is a little upfield from the related resonance of **1**. However, this effect is believed to be more due to a solvent effect rather than a consequence of the interaction with the lithium ion. The <sup>31</sup>P resonance is found at 44.2 ppm, which is the same as the spectrum of the precursor **1**. The <sup>11</sup>B NMR spectrum shows a singlet at –13.6 ppm, which is quite different from that observed in the adduct of [Mo(dmpe)<sub>2</sub>(Cl)(NO)LiHBEt<sub>3</sub>]<sub>*n*</sub> [10]. Despite this observation, the <sup>7</sup>Li spectra of both compounds are comparable, a singlet at 2.3 ppm is observed for **2**



**Complex 3:** Reaction of **1** with 1 equiv of lithium bis(trimethylsilyl)amide in diethyl ether at room temperature and recrystallization from diethyl ether afforded yellow crystals

of [Mo(dmpe)<sub>2</sub>(H)(NO)LiN(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (**3**) in 81% yield (Eq. (1)). **3** has been characterized by elemental analysis, IR and NMR. The analysis data are in good agreement with the 1:1 stoichiometry of **1**/LiN(SiMe<sub>3</sub>)<sub>2</sub>. The IR spectrum as a Nujol mull shows the nitrosyl stretching mode at 1528 cm<sup>-1</sup>, which is 15 cm<sup>-1</sup> lower than that found for precursor **1**. The extent of the decrease of ν<sub>NO</sub> is for **3** apparently smaller than that of **2**, which is the consequence of the non-bridging coordination mode of the nitrosyl oxygen in **3** (*vide infra*). The <sup>1</sup>H and <sup>13</sup>C NMR spectra in Et<sub>2</sub>O-*d*<sub>10</sub> display the expected resonances corresponding to the Mo(dmpe)<sub>2</sub>H(NO) and LiN(SiMe<sub>3</sub>)<sub>2</sub> moieties. The chemical shifts of –4.75 ppm for the Mo–H proton resonance (<sup>1</sup>H NMR) and 44.7 ppm for the <sup>31</sup>P resonance (<sup>31</sup>P NMR) are comparable to those exhibited by **2**. In the <sup>7</sup>Li NMR spectrum the <sup>7</sup>Li resonance appears at 4.0 ppm.

**Complex 4:** Treatment of **1** with LiBH<sub>4</sub> at room temperature in diethyl ether afforded the adduct [Mo(dmpe)<sub>2</sub>(H)(NO)]<sub>3</sub>(LiBH<sub>4</sub>)<sub>2</sub> (**4**) with a 1/LiBH<sub>4</sub> ratio of 3:2 (Eq. (1)). It was found that this stoichiometry is independent on the 1/LiBH<sub>4</sub> ratio employed in the reaction. Reactions of **1** with 1 equiv or with 6 equiv of LiBH<sub>4</sub> produced the same compound of **4**. In a typical reaction, **4** was isolated as yellow crystals in 67% yield. The IR spectrum of **4** as Nujol mull shows the nitrosyl stretching mode at 1497 cm<sup>-1</sup>. This value is 44 cm<sup>-1</sup> lower than that of the precursor **1**. It is noteworthy that the extent of this ν<sub>NO</sub> shift is significantly greater than those exhibited by **2** and **3**, which suggests an even stronger NO–Li interaction in **4**. Surprisingly the <sup>1</sup>H NMR spectrum of **4** displays in Et<sub>2</sub>O-*d*<sub>10</sub> among others characteristic resonances at –0.22 to –0.70 ppm for the BH<sub>4</sub><sup>-</sup> group and a quintet at –4.78 ppm for the Mo–H resonance. A broad quartet at –2.95 ppm with a coupling constant of 80.4 Hz is assigned to the previously reported borohydride *trans*-Mo(η<sup>1</sup>-BH<sub>4</sub>)(dmpe)<sub>2</sub>(NO) [11]. Accordingly, the <sup>31</sup>P{<sup>1</sup>H} and <sup>11</sup>B{<sup>1</sup>H} NMR spectra of **4** show also additional resonances corresponding to the borohydride species (36.5 ppm and –43.0 ppm, respectively). This indicates the appearance of *trans*-Mo(η<sup>1</sup>-BH<sub>4</sub>)(dmpe)<sub>2</sub>(NO) in the diethyl ether solution of **4**. We assume that **4** dissociates in Et<sub>2</sub>O into the corresponding components of the hydride **1** and LiBH<sub>4</sub>. And then hydride **1** is assumed to react with LiBH<sub>4</sub> in an equilibrium to form slowly the borohydride and LiH (Eq. (2)). This assumption could be confirmed by NMR. The <sup>1</sup>H and <sup>31</sup>P NMR spectra recorded from the mixture of **1** and LiBH<sub>4</sub> in Et<sub>2</sub>O-*d*<sub>10</sub> show indeed the occurrence of the borohydride *trans*-Mo(η<sup>1</sup>-BH<sub>4</sub>)(dmpe)<sub>2</sub>(NO). The <sup>7</sup>Li{<sup>1</sup>H} NMR spectrum of **4** in Et<sub>2</sub>O-*d*<sub>10</sub> displays only a singlet at 3.2 ppm for LiBH<sub>4</sub> (3.3 ppm, recorded in Et<sub>2</sub>O-*d*<sub>10</sub>). The other product LiH could not be traced due to its insolubility in ether.



**Complex 5:** Reaction of the chloride *trans*-Mo(dmpe)<sub>2</sub>(Cl)(NO) with 5 equiv of LiBH<sub>4</sub> and 8 equiv of quinuclidine in Et<sub>2</sub>O at room temperature for four days and subsequent treatment produced unexpectedly a poly-

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