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μ-Coordination Chemistry of NO Ligands: Adducts of *trans*-$Mo(dmpe)_2(Cl)(NO)$ with Lithium Salts

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Reaction of *trans*-$Mo(dmpe)_2(Cl)(NO)$ (**1**) [dmpe = bis(dimethylphosphanyl)ethane] with lithium triethylborohydride and lithium bis(trimethylsilyl)amide affords the adducts $[Mo(dmpe)_2(Cl)(NO)(LiHBEt_3)]_n$ (**2**) and $\{Mo(dmpe)_2(Cl)(NO)[LiN(SiMe_3)_2]_2\}_n$ (**3**), respectively, and the reaction of **1** with *n*-butyllithium and iodomethane generates the complex $[Mo(dmpe)_2(Cl)(NO)]_3(LiI)_2$ (**4**). Complexes **2**–**4** have been characterized by elemental analysis, IR spectroscopy, NMR spectroscopy, and single-crystal X-ray diffraction analysis. The structure of **2** shows an infinite one-dimensional "zigzag" chain constructed from an alternating arrangement of $Mo(dmpe)_2(Cl)(NO)$ and $LiHBEt_3$ moieties, whereas the structure of **3** exhibits an infinite linear chain generated by the alternating arrangement of the $Mo(dmpe)_2(Cl)(NO)$ moiety and the dimeric $[LiN(SiMe_3)_2]_2$ unit. In both compounds, the $Mo(dmpe)_2(Cl)(NO)$ moieties act as bridging ligands by coordination of the nitrosyl oxygen atom and the chlorine atom to the lithium ions. Complex **4** displays a discrete structure formed by two separate monomeric LiI units that are bridged by the nitrosyl oxygen atoms of three $Mo(dmpe)_2(Cl)(NO)$ moieties. The chlorine atoms of **4** are not involved in coordination.

Transition metal nitrosyl complexes have received considerable attention for many years due to their potential applications as catalysts in organic synthesis and small molecule activation.[1,2] Our interest in this field lies mainly in the chemistry of nitrosyl hydrido transition metal complexes. In this context a series of compounds of manganese,[3] rhenium,[4] chromium,[5] tungsten,[6] and molybdenum[7] have been synthesized and explored in particular with regard to hydride-transfer chemistry. It has been found that the nitrosyl group exhibits versatile functions in such compounds. It can stabilize the different oxidation states of the metal center,[1,8] and it can induce quite strong hydridic polarization by the "nitrosyl effect"; thus the nitrosyl group promotes the activation of the metal–hydrogen bond.[9] Additionally, the nitrosyl group can show a certain amount of Lewis base behavior by interacting with Lewis acids at the oxygen atom site.[8,10]

The nitrosyl ligand/Lewis acid interactions have been found to sometimes play a key role in organic (organometallic) syntheses and reactions. For example, the catalytic oxidation of alcohols by a cobalt nitro/nitrosyl couple with the use of molecular oxygen as an oxidant was found to be facilitated by Lewis acids such as $BF_3{\cdot}Et_2O$ or $LiPF_6$.[11] The effects of the Lewis acids in the reaction were attributed to their interactions with nitro and nitrosyl ligands. In dinitrosyl complexes $Re(H)(NO)_2(PR_3)_2$ (R = *i*Pr, Cy), one nitrosyl group was found to be capable of coordinating to one or two BF_3 molecules, and the interaction of a second BF_3 molecule caused the bending of the nitrosyl group; thus, a new coordination site in the metal sphere is provided.[12] The coordination of the nitrosyl group to the lithium ions in the compounds $[Cp^*Mo(NO)(CH_2SiMe_3)(=CHSiMe_3)]_2[Li_2(THF)_3]$, $[(\eta^5,\eta^1\text{-}C_5Me_4CH_2)Mo(NO)(CH_2SiMe_3)_2][Li(THF)_3]$, and $\{[Cp^*Mo(NO)(CH_2SiMe_3)_2][Li(THF)]\}_2$ was thought to further stabilize the corresponding anionic complexes thus facilitating the isolations of these species.[13] Despite the apparent significance of coordinated nitrosyl ligand/Lewis acid interactions, studies on such interactions are relatively rare[14] in contrast to the rich chemistry of the Lewis basicity of coordinated carbonyl ligands.[15] We describe here the isolation and structural characterization of the compounds formed by *trans*-$Mo(dmpe)_2(Cl)(NO)$ (**1**) [dmpe = bis(dimethylphosphanyl)ethane] with lithium reagents. To the best of our knowledge, fully structurally characterized adducts formed by neutral nitrosyl complexes with metal ions by the coordination of bound nitrosyl have not yet been reported.

Results

Preparation and Characterization of 2, 3, and 4

Complex 2

Treatment of **1** with 1 equiv. of lithium triethylborohydride in diethyl ether did not provide the product of a H/Cl

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metathetical reaction, but the polymeric **1**/$LiHBEt_3$ adduct of $[Mo(dmpe)_2(Cl)(NO)LiHBEt_3]_n$ (**2**), [Equation (1)] which was isolated as yellow crystals in 88% yield after slow evaporation of the solvent at room temperature. Complex **2** is apparently stable enough to resist hydride formation and no further conversion was observed even under forced reaction conditions, for example, the application of up to 5 equiv. of lithium triethylborohydride and heating to 50 °C for two days. Complex **2** has been characterized by IR spectroscopy, NMR spectroscopy, elemental analysis, and a single-crystal X-ray diffraction study. The IR spectrum of **2** in a Nujol mull shows a nitrosyl stretching band at 1486 cm^{-1}, which is 52 cm^{-1} lower in energy than the corresponding nitrosyl band of **1** (ν_{NO} = 1538 cm^{-1} in Nujol). The lowering of the nitrosyl stretching frequency typically indicates the coordination of the O_{NO} atom to the lithium ion. The ^1H- and $^{13}C\{^1H\}$ NMR spectra of **2** in C_6D_6 display all of the resonances that correspond to the $Mo(dmpe)_2(Cl)(NO)$ and $LiHB(C_2H_5)_3$ moieties. The chemical shifts of the ^1H-, ^{13}C-, and ^{31}P NMR resonances for the $Mo(dmpe)_2(Cl)(NO)$ moiety in **2** are similar to those exhibited by **1**. The fact that the ^7Li NMR spectrum shows a singlet at 2.1 ppm and that the ^{11}B NMR spectrum displays a broad singlet at δ = –2.76 ppm further confirms the presence of the $LiHB(C_2H_5)_3$ moiety in the molecule. The elemental analysis is in good agreement with the composition of a 1:1 adduct of $Mo(dmpe)_2(Cl)(NO)$ and $LiHBEt_3$.

$$z{\cdot}x\ Mo(dmpe)_2(Cl)(NO) + z{\cdot}y LiX \rightarrow \{[Mo(dmpe)_2(Cl)(NO)]_x(LiX)_y\}_z$$

$$\mathbf{2}: x = y = 1;\ z = \infty;\ X = HBEt_3$$

$$\mathbf{3}: x = 1;\ y = 2;\ z = \infty;\ X = N(SiMe_3)_2$$

$$\mathbf{4}: x = 3;\ y = 2;\ z = 1;\ X = I \qquad (1)$$

Complex 3

The reaction of **1** with lithium bis(trimethylsilyl)amide in diethyl ether produced $\{Mo(dmpe)_2(Cl)(NO)[LiN(SiMe_3)_2]_2\}_n$ (**3**) with a 1:2 ratio of **1** and $LiN(SiMe_3)_2$ [Equation (1)]. It is found that this ratio is independent on the initially employed amounts of lithium bis(trimethylsilyl)amide. Treatment of **1** with an equimolar amount or with 2 equiv. of $LiN(SiMe_3)_2$ always resulted in **3**. In a typical reaction, **3** was isolated as yellow crystals in a yield of 84%. Once it has been isolated **3** is difficult to redissolve in diethyl ether, but is readily soluble in THF. Dissolution of the complex in chlorinated solvents such as CH_2Cl_2 and $HCCl_3$ resulted in immediate decomposition. In the IR spectrum of **3** (in Nujol) the nitrosyl stretching band appears at 1489 cm^{-1}. This value is 49 cm^{-1} lower than that of precursor **1** (ν_{NO} = 1538 cm^{-1}). The decrease in the nitrosyl stretching frequency is again indicative of the coordination of the O_{NO} atom. The ^1H NMR spectrum of **3** in $[D_8]$THF displays two multiplets at δ = 1.68 and 1.55 ppm and two singlets at 1.48 and 1.43 ppm, which correspond to the resonances of the methylene and methyl groups of the dmpe ligands, respectively. The signal for the $SiMe_3$ moieties is observed as a singlet at δ = –0.16 ppm. The ^{13}C- and ^{31}P NMR spectra for the $Mo(dmpe)_2(Cl)(NO)$ moiety are similar to those exhibited by **1**. The ^{13}C NMR resonance for the $SiMe_3$ group appears as a singlet at 6.2 ppm. In the ^7Li NMR spectrum, a singlet is found at δ = 4.26 ppm, which, together with its resemblance to the ^1H- and ^{13}C NMR spectra of **1**, may imply dissociation of **3** in THF.

Complex 4

To extend the scope of these investigations, the capability of **1** to form adducts with inorganic lithium salts has also been probed. According to literature reports, lithium halides form an extremely variable and structurally diverse family of complexes with simple nitrogen- or oxygen-containing ligands.[16] However, compounds of lithium halides with complexes as ligands have been reported only in rare instances.[17] An in situ generation of the lithium halide has been proven to be superior for the syntheses of its adducts.[16] Thus, the reactions of a **1**/*n*BuLi mixture with *n*BuCl, $SiMe_3Cl$, and *n*BuBr were investigated. They failed to produce any **1**/LiCl or **1**/LiBr adduct. However, a unique **1**/LiI adduct could be prepared from the reaction of **1**/*n*BuLi with MeI. In a typical batch, complex **1** (0.061 mmol) in toluene (2 mL) was mixed with equimolar amounts of *n*BuLi and iodomethane in that order. The final mixture was left undisturbed at room temperature. Overnight, well-defined crystals of a **1**/LiI adduct $[Mo(dmpe)_2(Cl)(NO)]_3(LiI)_2$ (**4**) precipitated from the solution [Equation (1)], which was isolated in 70% yield. Complex **4** has been characterized by elemental analysis, IR and NMR spectroscopy. The elemental analysis is consistent with the composition of a 3:2 **1**/LiI adduct stoichiometry. The IR spectrum of **4** in Nujol mull displays a nitrosyl band at 1449 cm^{-1}, which is 89 cm^{-1} lower than that of precursor **1**. It is worth noting that the decrease in the ν_{NO} vibration of **4** appears at significantly higher wavenumbers than those observed for **2** and **3**, which is presumably caused by the bridging mode of the nitrosyl oxygen (vide infra). The ^1H NMR spectrum of **4** in CD_2Cl_2 exhibits resonances for the methylene and methyl groups of the dmpe ligands as a multiplet at δ = 1.51 ppm and as a singlet at δ = 1.42 ppm. The ^{13}C NMR spectrum is similar to that exhibited by precursor **1**. The signals for the methylene and the methyl carbon atoms appear at δ = 29.8 ppm (quintet) and 15.3 and 14.6 ppm (two quintets), respectively. The ^{31}P NMR spectrum displays a singlet at δ = 34.6 ppm and in the ^7Li NMR spectrum a singlet is observed at δ = 3.28 ppm.

Structures of 2, 3, and 4

Structure of 2

The molecular structure of **2** has been established by X-ray diffraction analysis. Suitable crystals were obtained by the slow evaporation of a diethyl ether solution. An ORTEP representation of the molecule is shown in Figure 1 and reveals the NO group and chlorine atom disorder. Selected bond lengths and bond angles are listed in Table 1. The striking feature of the structure of **2** is its infinite one-di-

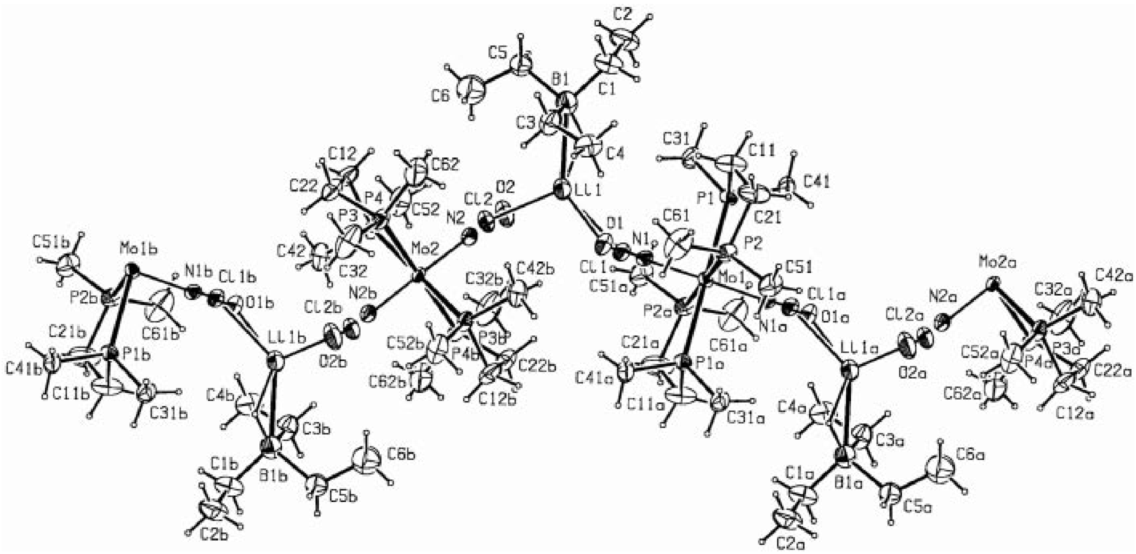

Figure 1. ORTEP plot of the structure of **2**. Displacement ellipsoids are drawn with 50% probability. The chloride and NO group display positional disorder.

mensional "zigzag" chain. The Mo(dmpe)$_2$(Cl)(NO) moiety acts as a bridging "complex ligand", and two adjacent LiHB(C_2H_5)$_3$ moieties are O_{NO} and Cl connected to the Li atoms by the Mo(dmpe)$_2$(Cl)(NO) moieties. The two LiHB(C_2H_5)$_3$ moieties on the two sides of a Mo(dmpe)$_2$(Cl)(NO) molecule create an inversion at the Mo atom center. Infinite repetition of these motifs build a polymeric chain of alternating Mo(dmpe)$_2$(Cl)(NO) and LiHB(C_2H_5)$_3$ units. The lithium ion of **2** is tricoordinated by oxygen and furthermore by one chlorine and a hydrogen atom. The coordination geometry at the Li center can be described as pseudopyramidal where the three bond angles at the Li center are O1–Li1–H1, Cl2–Li1–H1, and O1–Li1–Cl2 with the values 120.2(9)°, 125.5(9)°, and 103.9(3)°, respectively. The Li1–H1 distance of 1.76(3) Å is comparable to that in the (LiH)$_\infty$ lattice (av. 1.78 Å)[18], but shorter than those found for the complexes containing Li(μ_2-H)$_2$B or Li(μ_2-H)$_3$B bridges (ca. 1.90–2.20 Å).[19] The B1–Li1 distance of 2.420(5) Å is similar to that in LiBH$_4$·3(py) [2.401(7) Å].[20] The O1–Li1 distance of 1.944(6) Å and the Cl2–Li1 distance of 2.329(4) Å are in the normal ranges of O–Li and Cl–Li bond lengths in organolithium compounds.[17] The coordination geometry around Mo is close to that of parent complex **1**, which becomes particularly evident from a comparison of the Mo–P bond lengths and P–Mo–P angles. The Mo1–N1 bond length of 1.832(5) Å and the Mo2–N2 bond length of 1.826(5) Å are shorter than that found in **1** (1.851(4) Å[7b]), whereas the N1–O1 and N2–O2 bond lengths of 1.229(6) and 1.230(5) Å are longer than the N–O distance of 1.187(4) Å in **1**. The shortening of the Mo–N bond and the lengthening of the N–O bond can be explained by the lithium induced enhancement of the Mo→NO back-bonding. The average Mo–Cl bond length is close to that of **1**. The N1–O1–Li1 and Mo2–Cl2–Li1 linkages show a certain extent of bending [145.1(6)° and 156.76(13)°, respectively], which is presumably due to the steric interaction between neighboring Mo(dmpe)$_2$(Cl)(NO) and B(C_2H_5)$_3$ moieties.

Table 1. Selected bond lengths [Å] and bond angles [°] of **2**.

Bond lengths		Bond angles	
Mo1–N1	1.832(5)	N1–Mo1–P1	87.44(13)
Mo1–Cl1	2.5088(19)	N1–Mo1–P2	92.47(16)
Mo1–P1	2.4598(5)	Cl1–Mo1–P1	91.37(4)
Mo1–P2	2.4601(5)	Cl1–Mo1–P2	86.92(5)
N1–O1	1.229(6)	Mo1–N1–O1	178.4(7)
O1-Li1	1.944(6)	N1–O1–Li1	145.1(6)
Li1–H1	1.76(3)	O1–Li1–H1	120.2(9)
Li1–B1	2.420(5)	O1–Li1–Cl2	103.9(3)
B1–H1	1.23(2)	Cl2–Li1–H1	125.5(9)
Mo2–N2	1.826(5)	P1–Mo1–P2	80.223(18)
Mo2–Cl2	2.4759(18)	N2–Mo2–P3	90.77(15)
Mo2–P3	2.4573(5)	N2–Mo2–P4	85.32(15)
Mo2–P4	2.4550(5)	P3–Mo2–P4	80.90(2)
N2–O2	1.230(5)	Cl2–Mo2–P3	88.37(5)
Cl1–Li1	2.443(4)	Cl2–Mo2–P4	93.48(5)
Cl2–Li1	2.329(4)	Mo2–Cl2–Li1	156.76(13)
B1–C1	1.624(4)	Mo2–N2–O2	174.1(5)
B1–C3	1.659(3)	C1–B1–C3	110.3(2)
B1–C5	1.735(8)[a]	C1–B1–C5	98.1(3)
B1–C7	1.618(5)[a]	C3–B1–C5	105.9(3)

[a] C(5) and C(7) represent split positions of a disordered ethyl group.

Structure of 3

The molecular structure of **3**, established by single-crystal X-ray crystallographic analysis, is arranged as an infinite linear chain as shown in Figure 2. The molecular chain can be viewed as being composed of alternating Mo(dmpe)$_2$(Cl)(NO) moieties and dimeric [LiN(SiMe$_3$)$_2$]$_2$ units. Two neighboring units of the dimeric [LiN(SiMe$_3$)$_2$]$_2$ part are thus linked by the "complex ligand" of Mo(dmpe)$_2$(Cl)(NO) acting as a bridging unit. The complex LiN(SiMe$_3$)$_2$ has previously been reported to be trimeric.[21] The

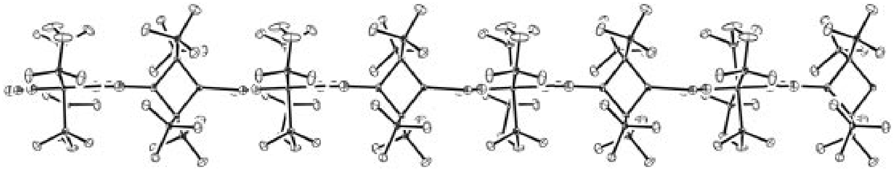

Figure 2. One-dimensional chain structure of **3**. The hydrogen atoms have been omitted for clarity.

solvated species $[Li(Et_2O)N(SiMe_3)_2]_2$[22] and $[Li(THF)N(SiMe_3)_2]_2$[23] were found to be dimeric. Figure 3 displays the asymmetric unit of the structure of **3**. In the dimeric $[LiN(SiMe_3)_2]_2$ unit, each lithium ion possesses a triangular-coordination geometry built up from two nitrogen atoms of the amides and one O_{NO} or a chlorine atom of the $Mo(dmpe)_2(Cl)(NO)$ moiety. The average Li–N distances are 2.034(4) Å for Li1 and 2.053(4) Å for Li2 (Table 2). They are comparable to those distances found in some symmetric dimeric lithium amides such as $[Li\{HN(iPr)_2\}N\text{-}1\text{-}c\text{-}C_6H_9Ph]_2$ (Li–N = 2.05 Å),[24] $[Li(THF)HMCTS]_2$ (Li–N = 2.04 Å),[25] $[Li(THF)NSiMe_3HMCTS]_2$ (Li–N = 2.04 Å)[26] etc. and are in the same range as for $[Li(THF)N(SiMe_3)_2]_2$[23] [2.025(9) Å] and for $[Li(Et_2O)N(SiMe_3)_2]_2$[22] [2.055(5) Å]. However, both bond lengths are longer than those observed in trimeric $[LiN(SiMe_3)_2]_3$ [Li–N = 2.00(2) Å],[21] which is presumably due to the higher coordination number of the Li ion and the bridging mode of the $[N(SiMe_3)_2]^-$ ligand in **3**. The average Li–N–Li angle of 75.76(16)° and N–Li–N angle of 104.24(17)° are similar to related bond angles observed in $[Li(Et_2O)N(SiMe_3)_2]_2$[22] and $[Li(THF)N(SiMe_3)_2]_2$.[23] Because of enhanced Mo→NO back-bonding in the $Mo(dmpe)_2(Cl)(NO)$ moiety of **3**, the average Mo–N bond length of 1.753(6) Å is 0.098 Å shorter and the average N–O bond length of 1.253(7) Å is 0.066 Å longer than the corresponding ones in **1**. The coordination of the chloride ligand to the lithium center does not induce a significant change in the Mo–Cl bond length [2.4937(15) Å in **3** versus 2.4881(14) Å in **1**], which may indicate only a weak interaction of the chlorine atom with the lithium center. In contrast to **2**, the N–O–Li and Mo–Cl–Li linkages are almost straight with average bond angles of 171.8(4)° and 172.94(12)°, which provokes the chain structure of **3**, composed of an MoCl–Li–Li–O–N–Mo backbone, to be linear overall as shown in Figure 2.

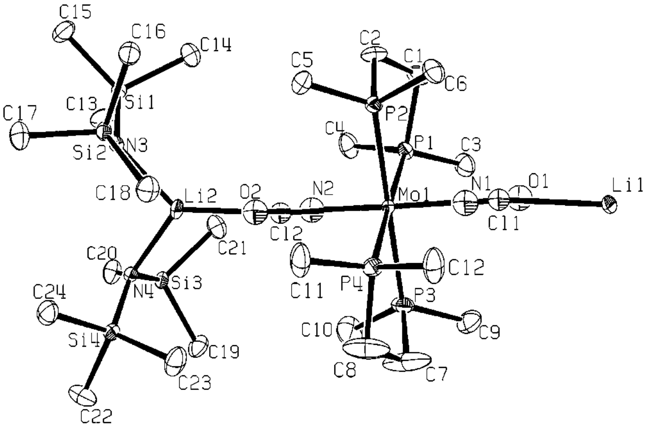

Figure 3. The asymmetrical unit of **3**. Displacement ellipsoids are drawn with 50% probability. The chloride ion and nitrosyl group show disorder.

Table 2. Selected bond lengths [Å] and bond angles [°] of **3**.

Bond lengths		Bond angles	
Mo1–N1	1.747(5)	N1–Mo1–P1	86.89(17)
Mo1–N2	1.758(6)	N1–Mo1–P2	91.30(17)
Mo1–Cl1	2.4966(14)	N1–Mo1–P3	88.23(17)
Mo1–Cl2	2.4907(16)	N1–Mo1–P4	91.34(17)
Mo1–P1	2.4749(6)	Cl2–Mo1–P1	93.75(3)
Mo1–P2	2.4628(6)	Cl2–Mo1–P2	89.06(3)
Mo1–P3	2.4572(7)	Cl2–Mo1–P3	91.41(4)
Mo1–P4	2.4707(7)	Cl2–Mo1–P4	88.03(3)
N1–O1	1.204(7)	Mo1–N1–O1	176.0(5)
N2–O2	1.301(7)	Mo1–N2–O2	175.8(4)
O1–Li1	1.975(6)	P1–Mo1–P2	80.56(2)
O2–Li2	1.866(6)	P3–Mo1–P4	80.74(2)
Cl1–Li1	2.426(4)	N1–O1–Li1	170.0(4)
Cl2–Li1	2.435(4)	N2–O2–Li2	173.5(4)
Li1–N3	2.040(4)	Mo1–Cl1–Li1	171.43(11)
Li1–N4	2.027(4)	Mo1–Cl2–Li2	174.45(12)
Li2–N3	2.051(4)	O1–Li1–N3	121.2(2)
Li2–N4	2.054(4)	O1–Li1–N4	133.8(2)
Li1–Li2	2.509(5)	N3–Li1–N4	104.92(17)
N3–Si1	1.702(2)	Cl2–Li2–N3	130.9(2)
N3–Si2	1.700(2)	Cl2–Li2–N4	125.53(19)
N4–Si3	1.702(2)	N3–Li2–N4	103.56(17)
N4–Si4	1.701(2)	Li1–N3–Li2	75.65(16)
		Li1–N4–Li2	75.87(16)

Structure of 4

An ORTEP plot of **4** is shown in Figure 4. Selected bond lengths and bond angles are listed in Table 3. As shown in Figure 4, complex **4** can be formulated as $\{[Mo(dmpe)_2(Cl)(NO)]_3(LiI)_2\}$ with a 2:3 Li/Mo stoichiometry. Its structure can be described as two unique LiI units that are bridged by the nitrosyl oxygen atoms of three "$Mo(dmpe)_2(Cl)(NO)$ ligands". For LiI-containing adducts 1:1 (Li:ligand), 1:2, and 1:3 monomers,[27] 1:1 and 1:2 dimers,[28] a 1:1 tetramer,[29] and ion-pair coordinated species[30] have been reported. A 2:3 adduct of LiI with 2,4,6-trimethylpyridine (tmpy) was found in fact to be a tetramer with the formulation $[(LiI)_4(tmpy)_6]$.[31] In dimers and higher agglomerates the iodine anion usually acts as a bridging ligand. The observation of the 2:3 stoichiometry and the structural feature of the donor-connected LiI monomers in **4** is quite unusual. To the best of our knowledge, only the case of a $[(LiBr)_2(HMPA)_3(toluene)_{0.5}]$ molecule (HMPA = hexamethylphosphoramide)[32] provides further analogy.

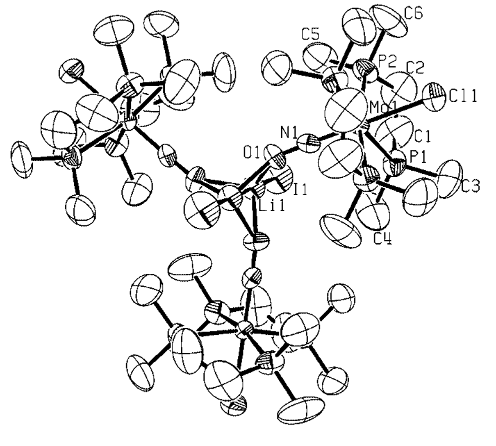

Figure 4. ORTEP plot of the structure of **4**. Displacement ellipsoids are drawn with 50% probability. Labeling of symmetry-related atoms is not shown (symmetry operations: $i_1 = x, y; -z+1/2$, $i_2 = -y+1, x-y, z$; $i_3 = -x+y+1, -x+1, z$).

Table 3. Selected bond lengths [Å] and bond angles [°] of **4**.[a]

Bond lengths		Bond angles	
Mo1–N1	1.780(7)	N1–Mo1–P1	93.85(14)
Mo1–P1	2.4466(17)	N1–Mo1–P2	96.98(13)
Mo1–P2	2.4551(17)	P1–Mo1–P2	80.06(6)
Mo1–Cl1	2.574(3)	Cl1–Mo1–P1	86.36(6)
N1–O1	1.234(8)	Cl1–Mo1–P2	82.80(6)
O1–Li1	2.040(10)	N1–O1–Li1	137.7(4)
I1–Li1	2.622(16)	Li1–O1–Li(i_1)	71.4(8)
Li1-Li(i_1)	2.38(3)	O1–Li1–O(i_2)	89.4(5)
		O1–Li1–I1	125.7(4)

[a] Symmetry transformations used to generate equivalent atoms: $i_1 = x, y, -z+1/2$; $i_2 = -y+1, x-y, z$; $i_3 = -x+y+1, -x+1, z$).

Unlike the three-coordinate Li ion in **2** and **3**, the lithium cation of **4** is tetra-coordinated in a pseudotetrahedral geometry and has one iodine atom and three oxygen atoms of the three "Mo(dmpe)$_2$(Cl)(NO) ligands" attached. In agreement with the higher coordination number of the Li ion in **4**, the O–Li distance of 2.040(10) Å is significantly longer than those observed in **2** and **3** [1.944(6) Å and 1.921(6) Å, respectively]. The I–Li bond length of 2.622(16) Å is particularly short compared with other tetracoordinated LiI complexes (usually in the range of 2.70 to 2.95 Å[27–31]). The transannular Li–Li "contact" is 2.38(3) Å, which is also particularly short [the shortest Li–Li distance reported in LiI complexes is 3.575(6) Å[29] and in **3** it is 2.509(5) Å]. The observation of unusually short Li–halide and Li–Li distances in **4** is similar to that of the structurally analogous complex [(LiBr)$_2$(HMPA)$_3$-(toluene)$_{0.5}$].[32] In this context, it is noteworthy that the Li–Li distances in both complexes are very close [2.36(3) Å in the LiBr complex]. The Mo–P bond lengths of **4** do not differ significantly from the bond of precursor **1**. However, related Cl–Mo–P bond angles are smaller than those exhibited by **1**, which indicating further bending of the dmpe ligands towards the chlorine side. This bending is apparently due to the mutual repulsion of the three "Mo(dmpe)$_2$(Cl)(NO) ligands". As a consequence of this bending, the Mo–Cl bond lengths increase distinctly from 2.4881(14) Å in **1** to 2.574(3) Å in **4**.

Discussion

The reactions of halide-containing transition metal complexes with organic lithium reagents normally afford metathetical products.[7] However, the reaction of **1** with the reagents LiHBEt$_3$, LiN(SiMe$_3$)$_2$, and *n*BuLi led to lithium reagent/**1** adduct formation. This result can be attributed to a relatively strong donicity of the O$_{NO}$ atom in **1** induced by strongly σ-donating dmpe ligands, which cause charge accumulation on the molybdenum center and concomitantly strong electron transfer to the NO group.

Compounds **2**, **3**, and **4** show different **1**/Li ratios and various structural features. Compound **2** exhibits an infinite one-dimensional "zigzag" chain with a 1:1 ratio of **1**/LiHBEt$_3$, whereas compound **3** displays an infinite linear chain with a 1:2 ratio of **1** and LiN(SiMe$_3$)$_2$. The strong bridging ability of the N(SiMe$_3$)$_2^-$ anion eases formation of a polymeric structure for the LiN(SiMe$_3$)$_2$ part. In addition, this is the main reason for **3** to adopt a higher **1**/Li ratio as compared to **1**. In **2** and **3**, complex **1** acts as a bridging ligand by coordinating the O$_{NO}$ and Cl atoms. The capability of the Cl atom to participate in the coordination can be ascribed to the strong Lewis acidic property and high reactivity of the Li$^+$ ion in LiHBEt$_3$ and LiN(SiMe$_3$)$_2$. In contrast to **2** and **3**, complex **4** forms a structure of distinct molecules with a 3:2 **1**/Li ratio. The chlorine atom of **4** is not involved in coordination. The fact that **4** prefers a small unit structure may be ascribed to the relatively small size of the iodine counterion in comparison with the bulky organic anions of **2** and **3** and the competition between the oxygen and iodine bridges. As a result, the O$_{NO}$ atom of **4** adopts a μ$_2$-bridging coordination mode rather than a terminal mode as in **2** and **3**, which allows for the formation of distinct molecular units in **4**.

The adducts formed from LiHBEt$_3$ and donor ligands have rarely been reported, and although the compounds formed from LiN(SiMe$_3$)$_2$ and LiI with ligands containing O- or N-donor atoms have been well documented, those with a metal complex as a ligand are not. The three compounds described here represent the first examples of lithium adducts with a complex as a ligand. The work documents not only excellent Lewis basicity of the NO ligand, but also shows the great structural diversity that such μ-NO complexation may lead to.

Conclusions

In summary, the reactions of the chloride complex Mo(dmpe)$_2$(Cl)(NO) (**1**) with the lithium reagents LiHB(C$_2$H$_5$)$_3$, LiN(SiMe$_3$)$_2$, and the mixture of *n*BuLi/MeI did not provide the usual products of a H/Cl metathetical reaction, but rather afforded the adducts of **1** with lithium salts because of the coordination of the nitrosyl group to the lithium ion. A relatively strong donicity of the bound nitrosyl group in **1** is indicated, which may be attributed, for the most part, to the effect of the strongly σ-donating dmpe ligands. The two dmpe ligands cause charge accumulation on the molybdenum center and thus enhance the electron density on the nitrosyl oxygen atom. The resulting propensity to act as a σ donor for the nitrosyl oxygen atom may also have implications on the reactivity of **1**, as for instance in the conversion of **1** to the corresponding borohydride $Mo(dmpe)_2(HBH_3)(NO)$, where the isolation of the borohydride proved to be troublesome presumably because of the adduct formation with the alkaline element borohydride starting material.[7b]

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry nitrogen with the use of conventional Schlenk techniques or a glove box. Solvents were dried by standard methods and freshly distilled under an atmosphere of nitrogen before use. *trans*-$Mo(dmpe)_2(Cl)(NO)$ (**1**) was prepared as described previously.[7b] Other reagents were purchased from Fluka or Aldrich. NMR spectra were recorded with the following spectrometers: Varian Gemini-300 instrument for ^1H-, ^{13}C-, ^{31}P-, and ^{11}B NMR; Bruker DRX-500 instrument for ^7Li NMR. $\delta(^1H)$ and $\delta(^{13}C)$ are relative to $SiMe_4$, $\delta(^{31}P)$ is relative to 85% H_3PO_4, $\delta(^{11}B)$ is relative to $BF_3{\cdot}OEt_2$, and $\delta(^7Li)$ is relative to $LiClO_4$ in H_2O. IR spectra were recorded with a Biorad FTS-45 instrument. Elemental analyses were performed with a Leco CHN(S)-932 instrument.

$[Mo(dmpe)_2(Cl)(NO)LiHB(C_2H_5)_3]_n$ (2): A lithium triethylborohydride solution (0.13 mL, 1.0 M solution in THF) was added to a solution of **1** (0.055 g, 0.12 mmol) in diethyl ether (15 mL). The mixture was stirred for 3 h and then left undisturbed at room temperature to allow the solvent to evaporate. Slow evaporation of the diethyl ether for 3 d provided **2** as yellow crystals that were suitable for an X-ray diffraction study. Yield: 0.060 g (88%). IR (Nujol): $\tilde{\nu}$ = 1486 (NO) cm^{-1}. ^1H NMR (300.1 MHz, C_6D_6): δ = 1.43 (m, 4 H, PCH_2), 1.24 (m, 4 H, PCH_2'), 1.32 (s, 12 H, PMe), 1.28 (s, 12 H, PMe′), 1.21 [t, $^3J_{H,H}$ = 7.2 Hz, 9 H, Me of $B(C_2H_5)_3$], 0.85 [m, 6 H, CH_2 of $B(C_2H_5)_3$] ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, C_6D_6): δ = 29.5 (quint, $^1J_{C,P}$ = 9.7 Hz, PCH_2), 15.0 (quint, $^1J_{C,P}$ = 5.0 Hz, PMe), 14.5 (quint, $^1J_{C,P}$ = 5.0 Hz, PMe′), 15.5 [br., CH_2 of $B(C_2H_5)_3$], 11.2 [br., Me of $B(C_2H_5)_3$] ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 34.6 (s) ppm. ^{11}B NMR (96.2 MHz, C_6D_6): δ = –2.76 (s, br) ppm. ^7Li NMR (194.4 MHz, C_6D_6): δ = 2.10 (s) ppm. $C_{18}H_{48}BClLiMoNOP_4$ (567.63): calcd. C 38.08, H 8.54, N 2.47; found C 38.33, H 8.17, N 2.44.

$\{Mo(dmpe)_2(Cl)(NO)[LiN(SiMe_3)_2]_2\}_n$ (3): A mixture of **1** (0.022 g, 0.048 mmol) and lithium bis(trimethylsilyl)amide (0.017 g, 0.102 mmol) was dissolved in diethyl ether (15 mL) and the resulting solution was stirred for 3 h. The solvent was then evaporated slowly at room temperature for 4 d to afford **3** as yellow crystals. Yield: 0.032 g (84%). IR (Nujol): $\tilde{\nu}$ = 1489 (NO) cm^{-1}. ^1H NMR (300.1 MHz, $[D_8]THF$): δ = 1.68 (m, 4 H, PCH_2), 1.55 (m, 4 H, PCH_2'), 1.48 (s, 12 H, PMe), 1.43 (s, 12 H, PMe′), –0.16 (s, 36 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $[D_8]THF$): δ = 30.6 (quint, $^1J_{C,P}$ = 10 Hz, PCH_2), 15.0 (quint, $^1J_{C,P}$ = 5.0 Hz, PMe), 14.8 (quint, $^1J_{C,P}$ = 5.0 Hz, PMe′), 6.2 (s, $SiMe_3$) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $[D_8]THF$): δ = 36.3 (s) ppm. ^7Li NMR (194.4 MHz, $[D_8]THF$): δ = 4.26 (s) ppm. $C_{24}H_{68}ClLi_2MoN_3OP_4Si_4$ (796.34): calcd. C 36.19, H 8.62, N 5.28; found C 36.52, H 8.40, N 5.31.

$[Mo(dmpe)_2(Cl)(NO)]_3(LiI)_2$ (4): A butyllithium solution (0.038 mL, 0.061 mmol, 1.6 M solution in hexane) and iodomethane (3.8 µL, 0.061 mmol) were added to a solution of **1** (0.028 g

Table 4. Crystallographic data and structure refinement parameters for **2**, **3**, and **4**.

	2	**3**	**4**
Formula	$C_{18}H_{48}BClLiMoNOP_4$	$C_{24}H_{68}ClLi_2MoN_3OP_4Si_4$	$C_{36}H_{96}Cl_3I_2Li_2Mo_3N_3O_3P_{12}$
Fw	567.59	796.32	1652.65
Color	yellow	yellow	orange
Crystal dimensions [mm]	0.37 × 0.28 × 0.16	0.35 × 0.22 × 0.18	0.32 × 0.25 × 0.22
Temperature [K]	173(2)	123(2)	183(2)
Crystal system	monoclinic	monoclinic	hexagonal
Space group (No.)	$P2_1/n$ (14)	$P2_1/n$ (14)	$P6_3/m$ (176)
a [Å]	9.0226(4)	12.3360(7)	14.8449(8)
b [Å]	21.0532(13)	18.9211(10)	14.8449(8)
c [Å]	15.9680(7)	19.4073(10)	18.3676(9)
α [°]	90	90	90
β [°]	105.029(5)	106.848(6)	90
γ [°]	90	90	120
V [Å^3]	2929.4(3)	4335.4(4)	3505.4(3)
Z	4	4	2
$D_{calcd.}$ [$g\,cm^{-3}$]	1.287	1.220	1.566
Abs. coeff. [mm^{-1}]	0.767	0.643	1.829
F(000)	1192	1688	1652
2θ Scan range [°]	$5.62 < 2\theta < 60.58$	$5.08 < 2\theta < 60.58$	$5.46 < 2\theta < 55.98$
No. of unique data	8134	12831	2899
No. of data obsd [$I > 2\sigma(I)$]	4922	9053	1418
Abs. corr.	numerical	numerical	numerical
Solution method	Patterson	Patterson	Patterson
No. of parameters refined	292	375	107
R, wR_2 [%] all data	5.74, 4.52	6.00, 8.65	9.51, 11.22
R_1, wR_2 (obsd.) [%][a]	2.85, 4.35	3.78, 8.32	5.13, 10.63
Goodness of fit	1.028	1.019	1.028

[a] $R_1 = \Sigma(F_o - F_c) / \Sigma F_o$; $I > 2\sigma(I)$; $wR_2 = \{\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2\}^{1/2}$.

(0.061 mmol) in toluene (ca. 2 mL). The mixture was stirred to obtain a homogeneous solution and then stood undisturbed at room temperature overnight. Large orange crystals of **4** were obtained. Yield: 0.023 g (70%). IR (Nujol): $\tilde{\nu}$ = 1449 (NO) cm^{-1}. ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 1.51 (m, 8 H, PCH_2), 1.42 (s, 24 H, PMe) ppm. $^{13}C\{^{1}H\}$ NMR (75.4 MHz, CD_2Cl_2): δ = 29.8 (quint, $^{1}J_{C,P}$ = 9.6 Hz, PCH_2), 15.3 (quint, $^{1}J_{C,P}$ = 4.7 Hz, PMe), 14.6 (quint, $^{1}J_{C,P}$ = 4.7 Hz, PMe′) ppm. $^{31}P\{^{1}H\}$ NMR (121.5 MHz, CD_2Cl_2): δ = 34.6 (s) ppm. ^{7}Li NMR (194.4 MHz, CD_2Cl_2): δ = 3.28 (s) ppm. $C_{36}H_{96}Cl_3I_2Li_2Mo_3N_3O_3P_{12}$ (1652.73): calcd. C 26.16, H 5.87, N 2.54; found C 26.29, H 6.11, N 2.71.

X-ray Crystal Structure Analyses: The X-ray diffraction data were collected at 173(2) K (**2**), 123(2) K (**3**), and 183(2) K (**4**) with the use of an imaging plate detector system (Stoe IPDS) with graphite monochromated Mo-K_α radiation. A total of 180, 167, and 167 images were exposed at constant times of 4.00, 3.00, and 2.80 min/image for compounds **2**, **3**, and **4**, respectively. The crystal-to-image distances were set to 50, 50, and 60 mm, respectively. The corresponding θ_{max} values were 30.29°, 30.29°, and 27.99°, respectively. ϕ-oscillation (**2**, **3**) or rotation scan modes (**4**) were selected for the ϕ increments of 1.0°,1.2°, and 1.2° per exposure in each case. Total exposure times for the three compounds were 25, 20, and 19 hours, respectively. After integrations and corrections for Lorentz and polarization effects, a total of 8000 reflections were selected out of the whole limiting sphere for the cell-parameter refinements. A total of 30218, 49957, and 33867 reflections were collected, of which 8134, 12831, and 2899 reflections were unique (R_{int} = 4.74%, 4.93%, and 4.90%); data reduction and numerical absorption corrections used 15, 18, and 17 indexed crystal faces.[33] The structures were solved by the Patterson method with the use of the program SHELXS-97,[34] and they were refined with SHELXL-97.[35] The X-ray data collections and the processing parameters are given in Table 4.

CCDC-606806 -606808 (for **2**, **3**, and **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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