Organomolybdenum(VI) and Lithium Organomolybdate(VI) and -(V) Complexes with *C,N*-Chelating Aminoaryl Ligands

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Received January 21, 1999

The synthesis and characterization of new, five-coordinate molybdenum bis(imidoaryl) complexes [Mo(NAr)$_2$(*C*−*N*)X] (Ar = C_6H_3*i*-Pr$_2$-2,6; *C*−*N* = [$C_6H_4(CH_2NMe_2)$-2]$^-$; X = Cl (**1**), Me (**2**), Et (**3**), Bu (**4**), CH_2SiMe_3 (**5**), (*p*-tolyl) (**6**), (*C*−*N*) (**7**)) is reported. The solid-state structure of **2** has been elucidated by single-crystal X-ray analysis. Compounds **2**, **3**, **4**, **5,** and **6** react with alkyl- or aryllithium compounds to form lithium molybdate(VI) derivatives, of which [Li(DME)Mo(NAr)$_2$(*C*−*N*)(Me)(*p*-tolyl)] (**10**), formed by the reaction of **2** with [Li(*p*-tolyl)], has been structurally (X-ray) characterized. Thermal activation of these lithium molybdates leads to the formation of paramagnetic lithium molybdate(V) compounds instead of the anticipated molybdenum(VI) alkylidenes. The actual temperature (between −10 and 80 °C) at which paramagnetic Mo(V) radical anions are formed is dependent on both the type of alkyl or aryl substituent (introduced via LiR′) and the solvent. The synthesis of [LiMo(NAr)$_2$(*C*−*N*)$_2$] (**11**) by reaction of **7** with *n*-BuLi is described. The initially formed lithium molybdate(VI) compound [Li(DME)$_n$Mo(NAr)$_2$(*C*−*N*)$_2$(*n*-Bu)] is not stable at room temperature and converts directly to the lithium molybdate(V) derivative **11**. The solid-state structure of **11** has been elucidated by single-crystal X-ray analysis. None of the lithium molybdate(VI) nor -(V) derivatives described herein are active catalysts for ROMP, as thermal activation does not lead to the formation of a molybdenum alkylidene complex but to electron transfer and formation of a lithium molybdate(V) instead. However, upon treatment of a solution of any of the molybdate(V) derivatives with dry air, catalytic ROMP is observed.

Introduction

Tungsten(VI)[1] and tantalum(V)[2,3] alkylidenes containing monoanionic *C,N*- (*C*−*N* = $C_6H_4(CH_2NMe_2)$-2) or *O,N*-chelating (*O,N* = η^2-OCPh$_2$(2-py), η^2-OCMe$_2$(2-py) or 8-quinolinolate) ligands reveal remarkable thermal stability and reactivity toward olefins and strained cyclic alkenes. Some of these tungsten(VI) alkylidenes also show temperature-dependent ring-opening metathesis polymerization (ROMP) activity toward norbornene.[2] For example, [W(=CHSiMe$_3$)(CH$_2$SiMe$_3$){η^2-OCPh$_2$(2-py)}(NPh)] is unreactive at room temperature but produces more than 2 × 10^4 turnovers per hour at 70 °C in benzene.[1a] These so-called “latent” catalysts allow the mixing of monomer and catalyst precursor in advance without polymerization taking place. Only when the reaction mixture is heated would initiation and polymerization occur.

We became interested in the synthesis of the analogous compounds based on molybdenum primarily because of their expected higher stability. From a synthetic point of view [Mo(NAr)$_2$Cl$_2$(DME)][4] (Ar = C_6H_3(*i*-Pr)$_2$-2,6, DME = 1,2-dimethoxyethane) is an attractive starting material to synthesize monoanionic, *C,N*-chelating aminoaryl ligands containing Mo(VI) complexes, from which molybdenum alkylidene complexes can be generated. At this point we have focused on the synthesis of Mo(VI) compounds with the general formula [Mo(NAr)$_2$(*C*−*N*)(R)] (*C*−*N* = $C_6H_4(CH_2NMe_2)$-2; R = Cl (**1**), Me (**2**), Et (**3**), *n*-Bu (**4**), CH$_2$SiMe$_3$ (**5**), *p*-tolyl (**6**), (*C*−*N*) (**7**)) and studied the possible C−H activation reactions that could lead to molybdenum alkylidene complexes (Scheme 1).

Examples of NMe$_2$-group-assisted intramolecular α-C−H activation reactions (route *i*) have been reported

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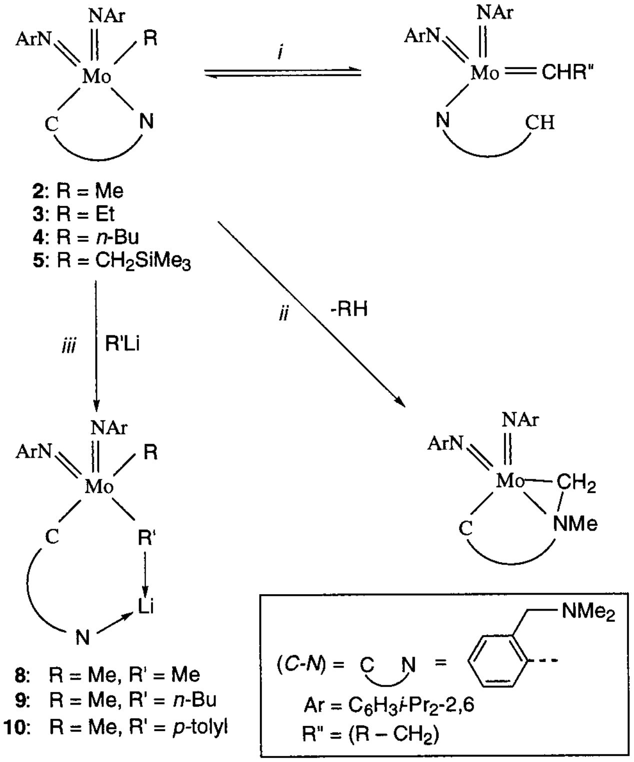
10.1021/om9900364 CCC: $18.00
Publication on Web 06/15/1999

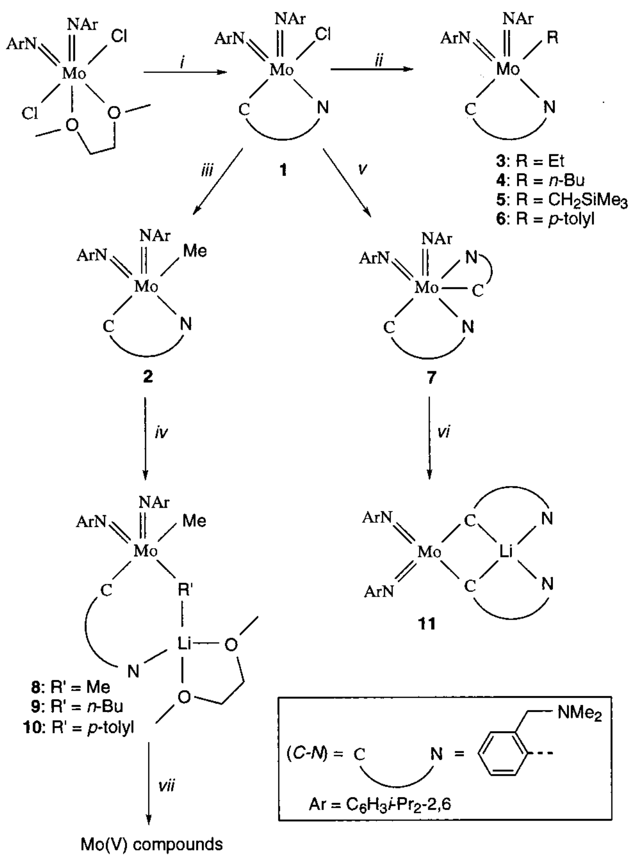
Scheme 1: Possible Alkylidene Formation via C−H Activation Reactions of [Mo(NAr)$_2$(*C-N*)R] Complexes Based on Examples from Ta,[2,6,7] W,[8] and Zr[5] Chemistry



for Ta alkylidene complexes.[3] Many examples of C−H activation reactions of a NMe$_2$ moiety (route *ii*) have been reported for Zr,[5] Ta,[6,7] and W[8] complexes. After a second α-C−H activation reaction the azamolybdenacyclopropane ring could be converted to a molybdenum alkylidene compound as shown for analogous tantalum[7] and tungsten[8] complexes. A new approach, explored in the present study, is the introduction of additional, α-H hydrogen-containing alkyl groups (or alkyl/aryl groups that can easily abstract an α-H) on the molybdenum center via formation of the corresponding lithium molybdates (route *iii*).

Herein we report the synthesis, reactivity, and structural aspects of the Mo(VI) bis(imidoaryl) compounds **1**−**7**, the organolithium molybdate(VI) compounds [Li(DME)Mo(NAr)$_2$(*C*−*N*)(Me)(R′)] (R′ = Me (**8**), *n*-Bu (**9**), *p*-tolyl (**10**)), and a study of the possible C−H activation reactions mentioned in Scheme 1. Unexpectedly odd-electron organolithium molybdate(V) anions were formed during the thermal activation of **8**−**10**. The structure in the solid state of one example, [LiMo(NAr)$_2$(*C*−*N*)$_2$] (**11**), has been characterized by X-ray diffraction techniques. Surprisingly, some of these odd-electron molybdate(V) compounds showed ROMP of norbornene after dry air activation.

Scheme 2[a]



[a] *i*: 1/2 [Zn(*C-N*)$_2$], Et$_2$O/benzene, −DME, −ZnCl$_2$, >95% yield. *ii*: LiR (R = *n*-Bu, CH$_2$SiMe$_3$, *p*-tolyl, Et$_2$O, −LiCl or RMgCl (R = Et), THF, −MgCl$_2$, >90% yield. *iii*: MeMgCl, THF, −MgCl$_2$, 96% yield. *iv*: R′Li (R′ = Me, *n*-Bu, *p*-tolyl), THF/DME, −78 °C, >70% yield. *v:* 1/2 [Li$_2$(*C-N*)$_2$], Et$_2$O, −LiCl, 91% yield. *vi: n*-BuLi, toluene. *vii:* Thermal activation reaction strongly depending on the solvent, temperature, and R′.

Results and Discussion

Synthesis of Aminoaryl Molybdenum(VI) Complexes. The novel molybdenum(VI) compound [Mo(NAr)$_2$(*C*−*N*)Cl] (**1**) was obtained as a yellow solid in almost quantitative yield by treatment of [Mo(NAr)$_2$Cl$_2$(DME)][4] (Ar = C$_6$H$_3$(*i*-Pr)$_2$-2,6), DME = 1,2-dimethoxyethane) with 0.5 equiv of [Zn(*C*−*N*)$_2$][9] (*C*−*N* = [C$_6$H$_4$-(CH$_2$NMe$_2$)-2]$^-$). The methyl-containing derivative [Mo(NAr)$_2$(*C*−*N*)(Me)] (**2**) was synthesized via transmetalation of compound **1** using MeMgCl. The molybdenum(VI) complexes [Mo(NAr)$_2$(*C*−*N*)(Et)] (**3**), [Mo(NAr)$_2$(*C*−*N*)(*n*-Bu)] (**4**), [Mo(NAr)$_2$(*C*−*N*)(CH$_2$SiMe$_3$)] (**5**), and [Mo(NAr)$_2$(*C*−*N*)(*p*-tolyl)] (**6**) were obtained using a similar synthetic route (Scheme 2).

Compounds **1**−**6** are yellow solids that melt or decompose above 125 °C in an inert atmosphere. In air **1** (Cl) decomposes within several hours (similar to that found for [Mo(NAr)$_2$(η^2-*C*,*N*-NCN)Cl][10a] with NCN = [C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6]$^-$), while **2**, **3**, **4,** and **6** are more stable and decompose within several days. Compound **5** is stable in air for weeks. These materials are soluble in the common polar and aromatic solvents, but **1** and **2** have limited solubility in pentane or hexanes.

The ^{1}H NMR spectra of **1**−**6** (C$_6$D$_6$) show for the *i*-Pr *ortho*-substituents of the NAr ligands one septet and two

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doublet resonances. In the $^{13}C\{^1H\}$ NMR spectra these *i*-Pr groups appear as three separate resonances, indicating that all four *i*-Pr groups are equivalent (isochronous) but that the CMe_2 groupings are diastereotopic. These results show that these molecules lack an apparent molecular symmetry plane containing the prochiral $(Me_2)C$ centers. It is therefore significant that both the benzylic and the dimethylamino groups of the *ortho*-CH_2NMe_2 substituent appear as singlets over the whole temperature range (220−330 K) studied. This can only be rationalized either by a structure with Mo−N coordination in which the prochiral benzylic C and $(Me_2)N$ centers are residing in an apparent molecular symmetry plane or when the *C,N*-ligand is η^1-*C*-coordinated and the NMe_2 substituent undergoes rapid pyramidal inversion at the N center as well as rotation around the C−N bond (extensive discussions of the detection by ^1H and ^{13}C NMR of the various bonding possibilities of *C,N*- and *N,C,N*-ligands have been reported).[11]

In the ^1H NMR spectra of **2**, **3**, **4,** and **5** the α-H protons all appear between 0.95 and 1.76 ppm (^1H NMR) and 22.6 and 30 ppm (^{13}C NMR), indicating that agostic α-H- - -Mo interactions in the Mo−CH_2R grouping are absent.[12] As compounds **1**−**6** have similar NMR features, it can be assumed that these compounds have the same structural characteristics.

To get further insight in the molecular geometry of **1**−**6**, a single-crystal X-ray structure determination of one of them was carried out. Crystals were obtained for **2**, and its molecular structure, with the adopted numbering scheme, is depicted in Figure 1, while selected bond distances and angles are given in Table 1.

Compound **2** has the ligands arrayed in a distorted square pyramidal geometry around the metal center (73.1% along the Berry-pseudorotation coordinate from trigonal bipyramid to square pyramid). One imido ligand occupies the apical position N(3), while the N atom N(2) of the second imido group resides in the basal plane. The metal lies slightly above the basal plane defined by C(101), N(1), N(2), and the methyl group C(4). The Mo−C(4) distance is rather large (this bond in other molybdenum alkyl complexes lies in the range 2.08−2.20 Å).[10] The (dimethylamino)methyl substituent is indeed coordinating to the molybdenum center. Although the solid-state structure of **2** shows η^2-*C,N*-coordination to the molybdenum center, the NMR data suggest fluxional behavior in solution.

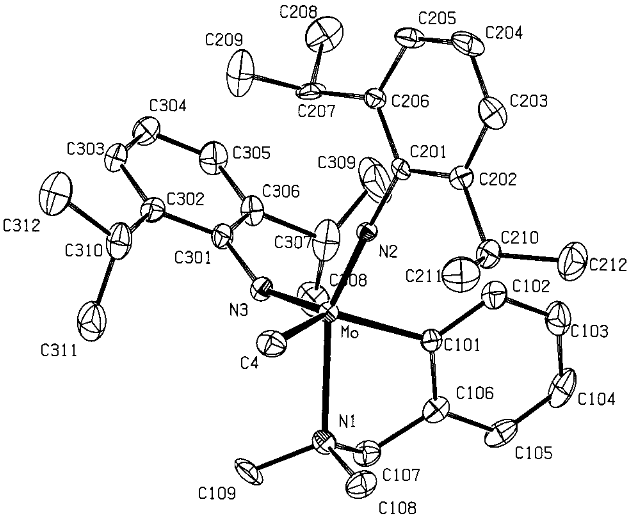

Figure 1. Thermal motion ellipsoid plot (ORTEP, at 50% probability level) of the molecular structure of **2**, together with the adopted numbering scheme. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Geometrical Details for $[Mo(NAr)_2(C\text{-}N)(Me)]$ (2)[a] and $[Li(DME)Mo(NAr)_2(C{-}N)(Me)(p\text{-tolyl})]$ (10)[a]

	2	**10**
	Bond Lengths (Å)	
Mo−C(101)	2.176(2)	2.239(4)
Mo−C(4)	2.177(2)	
Mo−C(401)		2.216(4)
Mo−C(5)		2.195(6)
Mo−N(1)	2.383(2)	
Mo−N(2)	1.7495(13)	1.770(4)
Mo−N(3)	1.773(2)	1.772(4)
C(201)−N(2)	1.386(3)	1.382(6)
C(301)−N(3)	1.401(4)	1.397(6)
Li(1)−O(1)		2.012(10)
Li(1)−O(2)		1.993(9)
Li(1)−N(1)		2.074(10)
	Bond Angles (deg)	
C(4)−Mo−C(101)	136.61(12)	
N(2)−Mo−N(3)	111.56(10)	
C(201)−N(2)−Mo	176.58(17)	156.7(4)
C(301)−N(3)−Mo	150.37(16)	174.1(3)
C(4)−Mo−N(1)	82.12(10)	
C(401)−Mo(1)−C(5)		148.47(16)
C(5)−Mo(1)−C(101)		79.07(15)

[a] The estimated standard deviations of the last significant digits are shown in parentheses.

According to their composition and structural features, it was unlikely that **1**−**6** as such can be active as ring-opening polymerization (ROMP) catalysts. At best they can be seen as latent catalysts that need thermal activation to create the active metal alkylidene moiety via one of the routes shown in Scheme 1. Indeed **1**−**6** were inactive at room temperature, but from the fact that also at higher temperatures no ROMP activity was observed it has to be concluded that compounds **1**−**6** have a surprising thermal stability.

Formation of Molybdenum(VI) Anions. The introduction of more α-H-containing (and bulkier) substituents on the molybdenum center might force α-H elimination to occur with formation of the corresponding molybdenum alkylidenes. To this end the various alkyl derivatives were reacted with different alkyl- or aryllithium reagents. For example, when **2** was treated with equimolar amounts of an alkyl- or aryllithium reagent in the presence of DME, bright yellow and very air-sensitive compounds could be isolated (Scheme 2).

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The ^{1}H and ^{13}C{^{1}H} NMR spectra and elemental analysis of the products pointed to the selective formation of new compounds that contained in all cases the organic groups originally present in the starting compounds, as well as the new alkyl or aryl group (introduced via LiR′). Moreover, DME quantities were included that varied between 1 and 4 equiv per (*C*−*N*) ligand.[13] From these data it was concluded that rather than molybdenum alkylidenes, new lithium molybdate(VI) compounds were synthesized and isolated as pure compounds.

The dimethylmolybdate(VI) **8**, its (methyl)(butyl) analogue **9**, and the (methyl)(*p*-tolyl) derivative **10** are very soluble in polar solvents such as Et_2O, THF, and DME. As solids they all slowly decompose at room temperature. Compound **8** is insoluble in benzene and toluene, whereas **9** is slightly soluble in these solvents, but decomposes in these solvents within 5 min. Although **10** is stable for several hours in a benzene solution at room temperature, it decomposes within half an hour at 50 °C. During the decomposition reaction of **10** in a benzene solution a mixture of products is formed.[14] However, no toluene or $C_6H_5CH_2NMe_2$ could be detected (NMR or GC−MS), which indicates that α- or NMe_2 C−H activation reactions (cf. routes *i* and *ii* in Scheme 1) are not taking place.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **8** in THF-d_8 show singlet resonances at 294 K for the benzylic, NMe_2, and Mo−Me resonances (200−294 K), and as in the case of the alkyl(*C*−*N*)Mo(VI) compounds, no conclusion about the actual binding mode of the *C*,*N*-ligand in the molybdate complexes could be drawn. At room temperature the same spectral characteristics are found for the (methyl)(butyl) derivative **9** in THF-d_8. However, on cooling the solution to 230 K, the benzylic protons start to decoalesce, whereas the other resonances remain unchanged. The ^{1}H and ^{13}C{^{1}H} NMR spectra of the *p*-tolyllithium adduct **10** in THF-d_8 show singlet resonances at 294 K for the benzylic, NMe_2, and Mo−Me resonances (200−294 K). No kinetic parameters for the dynamic solvent- and temperature-dependent NMR behavior of **10** were collected. However, the ^{1}H NMR spectra of **10** in toluene-d_8 show a clear AB pattern for the benzylic protons and a broad singlet resonance for the (dimethylamino)methyl substituent of the (*C*−*N*) ligand. This resonance further decoalesced, yielding two separate singlet resonances upon cooling the sample (−10 °C) in toluene-d_8; that is, as a result of solvent−solute interactions in toluene-d_8, the η^2-*C*,*N*-bonding of the *C*,*N*-ligand became detectable. The diastereotopicity of the protons of the CH_2 group indicated already that **10** lacks a molecular symmetry plane containing both the $(H_2)C$ and $(Me_2)N$ centers. The fact that also the NMe_2 grouping becomes diastereotopic at temperatures below −10 °C is proof for M−N coordination (M = Mo or Li). Moreover, the ^{1}H NMR shows two separate septet resonances, indicating the presence of inequivalent imidoaryl ligands. The ^{1}H NMR chemical shift values of compound **10** are also strongly dependent upon the amount of DME in the sample. From these NMR data we were unable to establish the site of attack of the R′$^-$ nucleophile, i.e. whether a new Mo−R′ bond had been formed. Neither was it possible to clarify the position of the lithium cation and the overall structure in general. Fortunately, X-ray quality single crystals could be obtained from the reaction mixture, and the molecular structure of the (methyl)(*p*-tolyl)molybdate(VI) derivative **10** (see Figure 2) in the solid state could be elucidated. Important bond distances and angles are given in Table 1.

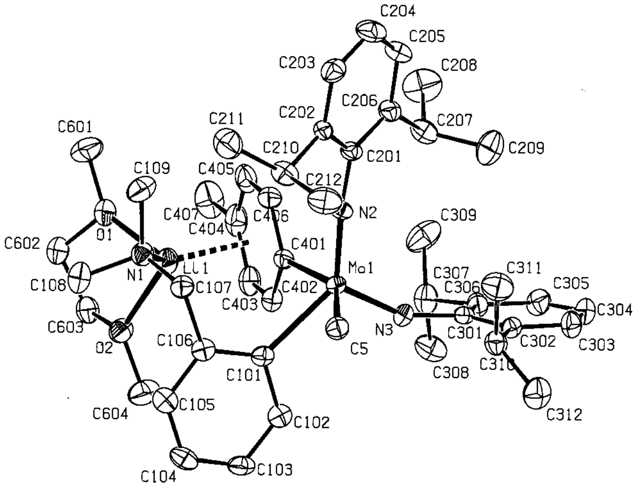

Figure 2. Thermal motion ellipsoid plot (ORTEP, at 50% probability level) of the molecular structure of **10**, together with the adopted numbering scheme. Hydrogen atoms and a C_6D_6 solvent molecule have been omitted for clarity.

The X-ray structure study shows that the (methyl)(*p*-tolyl)molybdenum(VI) compound **10** is a lithium molybdate(VI) complex in which all of the introduced organic and inorganic groups are bonded to the molybdenum(VI) center. The latter center is pentacoordinated (54.9% along the Berry-pseudorotation coordinate from trigonal bipyramid to square pyramid) and formally carries a negative charge with a lithium positive counterion. The lithium cation is bonded to the 2-(dimethylamino)methyl nitrogen atom N(1) and η^6 to the *p*-tolyl ligand, a phenomenon also observed for Lewis-base free, σ-bonded lithium aryls with very bulky *ortho*-substituents.[15] One chelate bonded DME molecule completes the tetrahedral coordination sphere of the lithium atom. The total amount of DME present in solid **10** is dependent on the synthetic procedure followed. In general DME amounts varying between 2 and 4 were observed (^{1}H NMR). Apparently, DME is incorporated differently in the crystal lattice and the powder. The *p*-tolyl ligand and methyl groups are virtually positioned *trans* with respect to each other. The molybdenum alkyl and aryl bond distances are slightly elongated compared to the distances in the neutral compound **2**, most likely because of the influence of the *trans* ligands. Although both molybdenum compounds **2** and **10** are formally 14-electron species (the (NAr) ligands are counted as 4 e donor ligands), the Mo(VI) center in **10** contains more

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[13] The amount of DME found in the lithium molybdates was strongly dependent upon the source of lithium reagent and workup procedure and could only partly be removed by evaporation.

[14] When the lithium molybdates **8**−**10** were thermally activated, NMR and ESR of the resulting reaction mixtures always showed the presence of Mo(V) complexes and a number of $[Mo(NAr)_2(C-N)R]$ compounds resulting from ligand exchange reactions. When **8** was heated, always small amounts of **2** were found. When **9** was heated, always small amounts of **2** and **4** were found and small amounts of 1-butene were detected as a result of β-H elimination reacions. When **10** was heated, always small amounts of **2** and **6** were found.

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Table 2. Thermal Activation of Lithium Molybdates Depending on Solvent and Temperature[a]

compound	R′	solvent	T (°C)[a]
8	Me	THF	50
		toluene	insol.
9	*n*-Bu	THF	80
		toluene	<25
10	*p*-tolyl	THF	80
		toluene	50

[a] Temperature required to decompose half of the amount of the lithium molybdate in 1 h.

anionic ligands. As a result, the Mo(VI) center in **10** is much less electrophilic than in **2**. Another rare example of an "ate" structure ([Li(DME)Mo(NAr)(=CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)(OTf)$_2$]) has recently been reported by Schrock and co-workers.[16] Finally it is noteworthy that compound **10** can also be made by reacting compound **6** with MeLi under similar conditions.

Formation of Paramagnetic Molybdenum(V) Anions. Lithium molybdate compounds **8**–**10** are stable as solids at temperatures below 0 °C and do not undergo α-H elimination reactions to give Mo(VI) alkylidene species upon heating the samples in different solvents. Instead, thermal activation of **8**–**10** generates paramagnetic molybdenum(V) species (see *vii*, Scheme 2) at different temperatures, while the onset of this conversion is strongly solvent dependent; see Table 2.

At the onset temperature the solution of the complexes changes in color from yellow/orange to dark brown. Spectroscopic characterization of these clear brown solutions by NMR showed only very broad peaks, pointing to the presence in solution of DME, diamagnetic molybdenum(VI) compounds,[14] and paramagnetic species. This conclusion was corroborated by the EPR measurements of solutions of these compounds, which revealed the presence of paramagnetic molybdenum species with splitting patterns and *g*-values characteristic for molybdenum(V) compounds.[17]

All the products obtained from the thermal activation reactions (Table 2) are brown, air-sensitive oils. Therefore, we have investigated the synthesis of molybdenum bis(imidoaryl) compounds that contain additional donor ligands in an attempt to structurally stabilize the paramagnetic product. The synthesis of [Mo(NAr)$_2$(C–N)$_2$] (**7**) can be performed by treatment of **1** with 0.5 equiv of [(Li$_2$(C–N)$_2$] or by reacting [Mo(NAr)$_2$Cl$_2$(DME)] with 1 equiv of [(Li$_2$(C–N)$_2$] (see Scheme 2). The resulting red crystalline solid (**7**) is thermally (>200 °C) and air stable and can be obtained in almost quantitative yield from both reactions. When this bis(aryl)molybdenum(VI) compound **7** is reacted with 1 equiv of *n*-BuLi in toluene at room temperature, crystals suitable for single-crystal X-ray analysis of a reaction product (**11**) can be obtained (32% yield). The crystal structure contains two independent molecules in the unit cell (Z = 4). Both molecules have the ligands arrayed very similarly. Although the bond distances and angles are different (listed in Table 3), only one (molecule 1) is depicted in Figure 3.

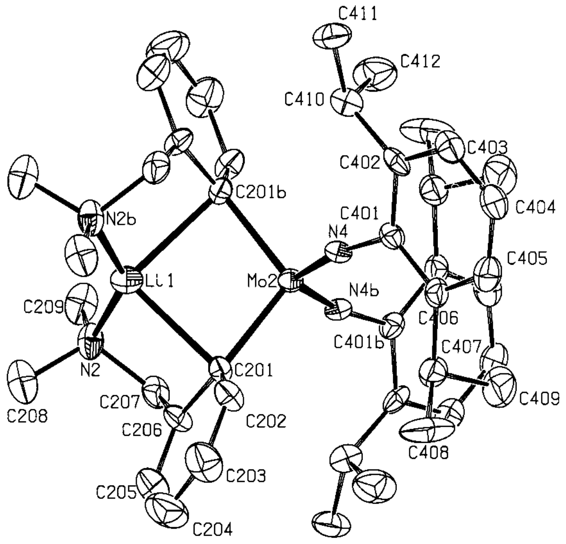

Figure 3. Thermal motion ellipsoid plot (ORTEP, at 50% probability level) of one of the two independent molecular structures of **11**, together with the adopted numbering scheme. Hydrogen atoms have been omitted for clarity.

The solid-state structure of the lithium diarylmolybdate(V) (**11**) compounds comprises two (C–N) ligands, which each bridge via C$_{ipso}$ of the C–N ligand between the molybdenum and the lithium center. Both Mo and Li have a distorted tetrahedral coordination. The Li–N coordination of the two nitrogen atoms of the (C–N) ligands renders the lithium four-coordinate and thereby probably helps to stabilize the complex. Possibly crystal-packing forces can explain the formation of two independent molecules. A similar type of bridging mode of a (C–N) ligand has been observed in related lithium–zincates[18a] and tantalum(V)–zinc[18b] complexes. Compound **11**, being an 13-electron molybdate(V) species, can be considered as a persistent organometallic radical. It is very reactive toward electrophiles, e.g., O$_2$, but is unreactive with linear alkenes.

During the reaction of **7** with *n*-BuLi the formation of amounts of 1-butene, which must result from β-H elimination reactions, was detected. This indicates that at least some of the *n*-butyl nucleophiles were bonded to the Mo center. Because the amounts of 1-butene found were not quantitative, it cannot be ruled out that this β-H elimination, which will give Mo–H[19] complexes, is the only pathway leading to the formation of **11**. Alternative routes involve direct butyl radical formation[20] after Mo–C bond cleavage or innersphere single electron transfer between **7** and *n*-BuLi clusters.[21]

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(16) Schrock, R. R.; Luo, S.; Lee, J. C.; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3883.

(17) (a) Balagopalakrishna, C.; Kimbrough, J. T.; Westmoreland, T. D. *Inorg. Chem.* **1996**, *35*, 7758. (b) Legzdins, P.; Sayers, S. F. *Organometallics* **1996**, *15*, 3907. (c) Barnard, K. R.; Bruck, M.; Huber, S.; Grittini, Enemark, J. H.; Gable, R. W.; Wedd, A. G. *Inorg. Chem.* **1997**, *36*, 637.

(18) (a) Rijnberg, E.; Jastrzebski, J. T. B. H.; Boersma, J.; Kooijman, H.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 2239. (b) Rietveld, M. H. P.; Lohner, P.; Nijkamp, M. G.; Grove, D. M.; Veldman, N.; Spek, A. L.; Pfeffer, M.; van Koten, G. *Chem. Eur. J.* **1997**, *3*, 817.

(19) We were unable to detect traces of "Mo–H" species during the process of β-H elimination (monitored by NMR), probably due to the instability of the Mo–H bond.

(20) After the reaction all volatiles were collected in a cold trap, and the mixture was analyzed by NMR and GC–MS. We were unable to detect any products arising from butyl radicals, even when the reaction was carried out in the presence of a radical trap like TEMPO.

(21) (a) Tamura, M.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1487. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed., 1988; pp 1306–1315.

Table 3. Selected Geometrical Details for [LiMo(NAr)$_2$(*C*−*N*)$_2$] (11)[a]

molecule 1		molecule 2	
	Bond Lengths (Å)		
Mo(1)−C(101)	2.159(5)	Mo(2)−C(201)	2.129(6)
Li(2)−C(101)	2.361(11)	Li(1)−C(201)	2.401(12)
Li(2)−N(1)	2.002(7)	Li(1)−N(2)	1.996(7)
Mo(1)−N(3)	1.770(5)	Mo(2)−N(4)	1.772(4)
N(3)−C(301)	1.375(7)	N(4)−C(401)	1.396(6)
	Bond Angles (deg)		
Mo(1)−C(101)−Li(2)	79.3(3)	Mo(2)−C(201)−Li(1)	80.9(3)
N(1)−Li(2)−N(1a)	143.4(8)	N(2)−Li(1)−N(2b)	142.2(9)
C(101)−Li(2)−C(101a)	94.5(5)	C(201)−Li(1)−C(201b)	91.1(6)
C(101)−Mo(1)−C(101a)	106.84(19)	C(201)−Mo(2)−C(201b)	107.2(2)
Mo(1)−N(3)−C(301)	162.3(4)	Mo(2)−N(4)−C(401)	165.1(4)

[a] Comparable bonds lengths and angles in molecules 1 and 2 are combined on one line. The estimated standard deviations of the last significant digits are shown in parentheses.

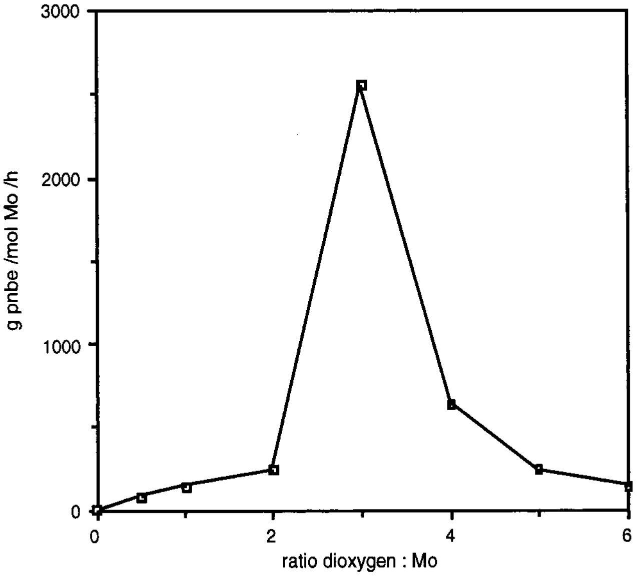

Figure 4. ROMP activity measured on varying [O$_2$].

Attempts to isolate the precursor of **11**, i.e., the lithium molybdate(VI) complex [Li(DME)$_n$Mo(NAr)$_2$(*C*−*N*)$_2$(*n*-Bu)] by reaction of **7** with *n*-BuLi in THF/DME or DME solutions, failed because *n*-BuLi reacts with these solvents before the target product is formed. Likewise, the use of other strongly coordinating molecules such as tetramethylethylenediamine was unsuccessful.

Dry Air Activation. As no evidence was found for direct alkylidene formation, i.e., α-H elimination does not take place (cf. route *iii* in Scheme 1), it was surprising to find ROMP activity when the in situ prepared Mo(V) compounds were activated by bubbling dry air (air passed over a NaOH(s) column) through the solution in the presence of norbornene or norbornene derivatives. No ROMP activity was found when norbornene was mixed with **2**, the lithium molybdate(VI) compounds derived from it, or the corresponding lithium molybdate(V) derivatives without dry air activation. The addition of 3 equiv of O$_2$ (~21% v/v of the dry air used is O$_2$)[22] resulted in the highest ROMP activity (see Figure 4). The polymerization of norbornene was followed in time employing the in situ prepared catalyst system (**2** with 1 equiv of *n*-BuLi in toluene) by GC (see Figure 5), and the resulting polynorbornene was characterized by gel permeation chromatography (GPC) and ^{1}H NMR.

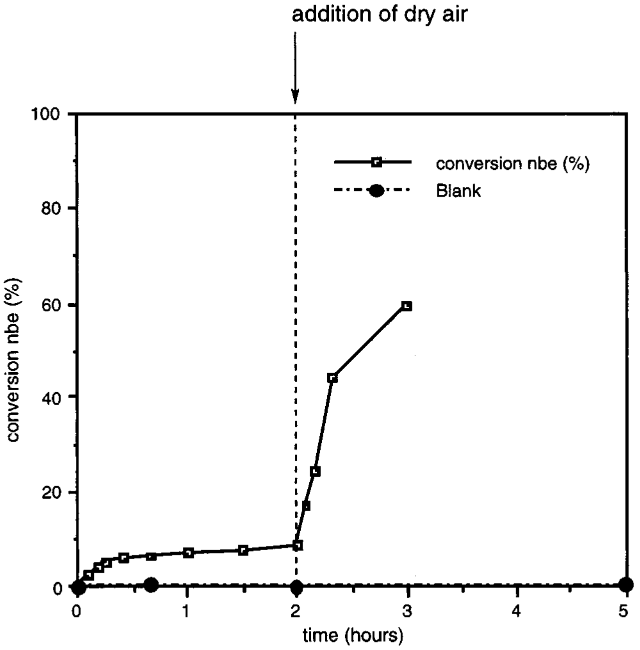

Figure 5. Concentration of free norbornene as measured over time by GC.

After the addition of the catalyst solution was complete, slow polymerization was observed initially, but this activity ceased after approximately 10 min. However, most noteworthy is the dramatic effect of the addition of dry air to the reaction mixture. The addition of 3 equiv of O$_2$ (from dry air) caused rapid polymerization, and within 20 min stirring problems occurred because of the greatly increased viscosity of the solution. The polymerization reaction was stopped by the addition of methanol, and the polymer was subsequently isolated. Analysis showed high molecular weight polynorbornene with a high polydispersity (MW = 953 000 g/mol, PDI = 2.63, and 91% *cis*-double bonds in polynorbornene).

Although O$_2$ activation has been reported earlier in the literature for tungsten and molybdenum complexes[23] (often in combination with aluminum compounds), its role in the catalytic system employed here is still unclear. As indicated by the high molecular weight of the polynorbornene thus produced, only a small percentage of the catalyst actually participates in the polymerization. We believe that the very high propaga-

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(22) *CRC Handbook of Chemistry and Physics*, 76th ed.; Lide, D. R., Ed.; CRC Press, Inc.: Boca Raton, FL, 1995; pp 14−14.

tion rate with respect to initiation rate using norbornene derivatives is a contributing factor to the small number of catalytic particles that are active in the polymerization reaction.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of dry and deoxygenated dinitrogen using standard Schlenk techniques unless otherwise stated. All solvents were carefully dried and distilled from sodium under nitrogen, prior to use, except CH_2Cl_2, which was distilled from CaH_2. The ^1H (300 MHz) and $^{13}C\{^1H\}$ (75 MHz) NMR spectra were recorded in benzene-d_6 at room temperature unless otherwise indicated. Chemical shifts (in ppm) are referenced to Me_4Si. GC measurements were performed on a Philips PU 4600 gas chromatograph with a J. & W. Scientific 30 m × 0.320 mm, 0.25 μm film thickness and liquid-phase DB-5 column. GPC measurements were taken on a Jordi-Gel DVB mixed bed, 300 mm and i.d. 7.8 mm column, using a Thermo Separation Products P200 pump and UV2000 and Shodex RI-71 detectors. EPR spectra were recorded in toluene at room temperature on a Varian E-9 EPR spectrometer. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Commercially available reagents were distilled prior to use. $[Mo(NAr)_2Cl_2(DME)]$,[4] $[Zn(C{-}N)_2]$,[9] [Li(*p*-tolyl)],[24] $[LiCH_2SiMe_3]$,[25] and $[Li_2(C{-}N)_2]$[26] were synthesized according to literature procedures. Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany.

$[Mo(NAr)_2(C{-}N)Cl]$ (1). To an Et_2O/benzene (70 mL/30 mL) solution of $[Mo(NAr)_2Cl_2(DME)]$ (1.92 g, 3.16 mmol) was added a solution of $[Zn(C{-}N)_2]$ (0.53 g, 1.60 mmol) in Et_2O (20 mL) at ambient temperature. After the addition was complete, the mixture was stirred overnight. After 17 h, all volatiles were removed in vacuo (3 h; 60 °C). The residual orange solids were extracted with benzene (2 × 80 mL), and after centrifugation the benzene layers were collected. All volatiles were removed in vacuo, leaving behind 1.85 g (95%) of a yellow product (compound **1**) which was pure by NMR and elemental analysis. The complex can be recrystallized by cooling an Et_2O solution of **1** to −30 °C. ^1H NMR (δ): 7.83 (d, 1, *o*-aryl−H), 7.03 (m, 8, NAr−H + ArH), 6.80 (t, 1, *p*-aryl−H), 3.85 (s, 2, CH_2), 3.78 (sept, 4, C*H*Me_2), 2.61 (s, 6, NMe_2), 1.12 (d, 12, CH*Me*$_2$), 1.10 (d, 12, CH*Me*$_2$). ^{13}C NMR (δ): 176.9 (C_{ipso}), 152.5 (C_{ipso} NAr), 147.2, 145.2, 143.1, 142.5, 129.3, 127.0, 123.5, 122.9 (aryl−C), 72.1 (CH_2), 48.7 (NMe2), 28.7 (*C*HMe_2), 24.2 (CH*Me*$_2$), 23.5 (CH*Me*$_2$). T_{melt} > 200 °C. Elemental Anal. (Calcd) for $C_{33}H_{46}ClMoN_3$: C, 64.41 (64.33); H, 7.50 (7.53); N, 6.75 (6.82).

$[Mo(NAr)_2(C{-}N)(Me)]$ (2). To a solution of **1** (0.85 g, 1.38 mmol) in THF was carefully added 0.48 mL (1.44 mmol) of a 3 M solution of MeMgCl (THF) at −30 °C. After the addition was complete, the reaction mixture was warmed to room temperature. After 4 h, all volatiles were removed in vacuo (3 h; 60 °C). The residual orange solids were extracted with Et_2O (2 × 80 mL), and the Et_2O layers were collected following centrifugation. The Et_2O was evaporated, yielding 1.86 g (96%) of a yellow product (pure by NMR and elemental analysis). The complex can be recrystallized by cooling a Et_2O solution of **2** to −30 °C. ^1H NMR (δ): 7.98 (d, 1, *o*-aryl−H), 7.06 (m, 8, NAr−H + ArH), 6.88 (t, 1, *p*-aryl−H), 3.84 (s, 2, CH_2), 3.79 (sept, 4, C*H*Me_2), 2.30 (s, 6, NMe_2), 1.13 (d, 12, CH*Me*$_2$), 1.12 (d, 12, CH*Me*$_2$), 1.12 (s, 3, Mo−Me). ^{13}C NMR (δ): 179.8 (C_{ipso}), 152.5 (C_{ipso} NAr), 147.3, 144.5, 143.1, 143.4, 126.5, 125.9, 123.0, 122.8 (aryl−C), 74.0 (CH_2), 48.9 (NMe2), 28.4 (*C*HMe_2), 24.2 (CH*Me*$_2$), 23.4 (CH*Me*$_2$), 23.4 (Mo−Me).[27] T_{melt} >188 °C. Elemental Anal. (Calcd) for $C_{34}H_{49}MoN_3$: C, 68.57 (68.55); H, 8.21 (8.29); N, 6.79 (7.05).

$[Mo(NAr)_2(C{-}N)(Et)]$ (3). To a clear yellow solution of **1** (0.71 g, 1,15 mmol) in 60 mL of THF was added 0.39 mL of a freshly prepared THF solution of EtMgBr (0.39 mL, 1.5 M, 0.58 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. After 17 h the reaction was complete. All volatiles were removed in vacuo. The residual yellow solids was extracted with pentane (3 × 50 mL). The collected pentane fraction were concentrated to 20 mL. After several days at −30 °C, 0.31 g (0.51 mmol) of yellow crystals of compound **3** could be isolated from the solution (2 crops). Yield: 88%. ^1H NMR (330 K) (δ): 7.98 (d, 1, *o*-aryl−H), 7.10−6.98 (m, 8, NAr−H + ArH), 6.92 (t, 1, *p*-aryl−H), 3.87 (sept, 4, C*H*Me_2), 3.82 (s, 2, CH_2), 2.32 (s, 6, NMe_2), 1.97 (t, 3, CH_2CH_3), 1.76 (q, 2, CH_2-CH_3), 1.14 (d, 12, CH*Me*$_2$), 1.10 (d, 12, CH*Me*$_2$). ^{13}C NMR (300 K) (δ): 180.3 (C_{ipso}), 152.1 (C_{ipso} NAr), 147.3, 144.7 (broad), 144.0, 126.3, 125.8, 123.0, 122.8 (aryl−C), 74.0 (CH_2N), 49.0 (NMe2), 45.7 (Mo−CH_2CH_3), 28.3 (*C*HMe_2), 24.0 (CH*Me*$_2$), 20.7 (Mo−CH_2CH_3). T_{decomp} = 162 °C. Elemental Anal. (Calcd) for $C_{35}H_{51}MoN_3$. Found: C, 68.86 (68.94); H, 8.48 (8.43); N, 6.77 (6.89).

$[Mo(NAr)_2(C{-}N)(n\text{-}Bu)]$ (4). A synthetic procedure similar to that described for **3** was used. Only *n*-BuLi was used and was added to **1** at −78 °C in Et_2O. Yield: 57% yield. ^1H NMR (320 K) (δ): 7.99 (d, 1, *o*-aryl−H), 7.10−6.99 (m, 8, NAr−H + ArH), 6.90 (t, 1, *p*-aryl−H), 3.87 (sept, 4, C*H*Me_2), 3.82 (s, 2, CH_2), 2.33 (s, 6, NMe_2), 2.22 (m, 2, $CH_2CH_2CH_2CH_3$), 1.74 (m, 2, $CH_2CH_2CH_2CH_3$), 1.47 (sextet, 2, $CH_2CH_2CH_2CH_3$), 1.15 (d, 12, CH*Me*$_2$), 1.11 (d, 12, CH*Me*$_2$), 0.96 (t, 3, $CH_2CH_2CH_2CH_3$). ^{13}C NMR (320 K) (δ): 180.3 (C_{ipso}), 152.2 (C_{ipso} NAr), 147.2, 144.7 (broad), 143.8, 126.3, 125.9, 123.0, 122.8 (aryl−C), 74.1 (CH_2N), 52.6 ($CH_2CH_2CH_2CH_3$), 49.1 (NMe2), 38.3 (CH_2CH_2-CH_2CH_3), 29.9 ($CH_2CH_2CH_2CH_3$), 28.2 (*C*HMe_2), 23.9 (CH*Me*$_2$), 13.7 ($CH_2CH_2CH_2CH_3$). T_{decomp} = 125 °C. Elemental Anal. (Calcd) for $C_{37}H_{55}MoN_3$: C, 69.68 (69.76); H, 8.69 (8.61); N, 6.59 (6.51).

$[Mo(NAr)_2(C{-}N)(CH_2Si(CH_3)_3)]$ (5). A synthetic procedure similar to that described for **3** was used. Only $LiCH_2Si(CH_3)_3$ (0.11 g, 1.15 mmol) was used and was added to **1** at −78 °C in Et_2O. Yield: 80%. ^1H NMR (δ): 8.04 (d, 1, *o*-aryl−H), 7.04 (m, 8, NAr−H + ArH), 6.92 (t, 1, *p*-aryl−H), 3.82 (sept, 4, C*H*Me_2), 3.75 (s, 2, CH_2), 2.34 (s, 6, NMe_2), 1.15 (d, 12, CH*Me*$_2$), 1.07 (d, 12, CH*Me*$_2$), 0.95 (s, 2, Mo−CH_2), 0.24 (s, 9, $Si(CH_3)_3$). ^{13}C NMR (δ): 179.7 (C_{ipso}), 152.5 (C_{ipso} NAr), 147.6, 144.7, 143.7, 126.3, 126.2, 123.4, 123.0 (aryl−C), 73.2 (CH_2), 49.5 (NMe2), 39.0 (*C*HMe_2), 28.0 (CH*Me*$_2$), 24.3 (CH*Me*$_2$), 22.6 ($MoCH_2$), 3.4 ($Si(CH_3)_3$). T_{melt} > 200 °C. Elemental Anal. (Calcd) for $C_{37}H_{57}MoN_3Si$: C, 66.65 (66.54); H, 8.67(8.60); N, 6.21 (6.29).

$[Mo(NAr)_2(C{-}N)(p\text{-tolyl})]$ (6). To a solution of **1** (2.21 g, 3.59 mmol) in 50 mL of Et_2O and 50 mL of benzene was added dropwise 0.35 g (3.59 mmol) of [Li(*p*-tolyl)] in Et_2O at −78 °C. After the addition was complete, the mixture was warmed to room temperature. After 4 h the precipitate was separated from the clear solution by centrifugation. The residual precipitate was washed with Et_2O (20 mL), and the Et_2O/benzene layers were combined. The volatiles were removed in vacuo,

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[23] (a) Bilhou, J. L.; Mutin, R.; Leconte, M.; Basset, J. M. *Recl. Trav. Chim. Pays-Bas* **1977**, *96*, M5. (b) Bilhou, J. L.; Basset, J. M.Mutin, R.; Graydon, W. F. *J. Am. Chem. Soc.* **1977**, *99*, 4083. (c) Vanderyse, L. M., Verdonck, L.; Bossuyt, A. R.; Van Wijnsberghe, F. M. G.; van der Kelen, G. P. *Bull. Soc. Chim. Belg.* **1988**, *97*, 317. (d) Vanderyse, L. M.; Haemers, T.; Bossuyt, A. R.; Verdonck, L.; van der Kelen, G. P. *Ibid.* **1988**, *97*, 723. (e) van Ruyskensvelde, S.; Bossuyt, A. R.; Haemers, T.; Verdonck, L. *Ibid.* **1988**, *104*, 401.

[24] [Li(*p*-tolyl)] was synthesized from $[C_6H_4I\text{-}4]$ and *n*-BuLi in toluene.

[25] Sommer, L. H.; Mitch, F. A.; Goldberg, G. M. *J. Am. Chem. Soc.* **1949**, *71*, 2746.

[26] Jastrzebski, J. T. B. H.; van Koten, G. *Inorg. Synth.* **1989**, *26*, 152.

[27] The $^{13}C\{^1H\}$ NMR Mo−Me resonance in compound **2** (C_6D_6) is exactly situated under a *C*HMe_2 peak (23.4 ppm), which was proven by $^1H-^{13}C$ 2D heteronuclear NMR measurements.

leaving a yellow crystalline material that was washed with 40 mL of pentane. The pentane solution was removed, and the residual yellow precipitate was dried in vacuo. This afforded 1.74 g (2.59 mmol, 72% yield) of a yellow microcrystalline material, which was pure by NMR and elemental analysis. The pentane layer afforded another 0.22 g of crystalline compound **6**. Total yield: 81%. ^{1}H NMR (δ): 8.24 (d, 1, *o*-aryl−H), 7.96 (d, 2, *o*-tolyl−H), 7.05 (m, 11, NAr−H + ArH + *m*-tolyl−H),), 4.03 (sept, 4, C*H*Me$_2$), 3.83 (s, 2, CH$_2$), 2.19 (s, 3, tolyl−Me), 2.10 (s, 6, NMe$_2$), 1.14 (d, 12, CH*Me*$_2$), 1.06 (d, 12, CH*Me*$_2$). ^{13}C NMR (δ): 180.1 (C$_{ipso}$), 176.9 (C$_{ipso}$−tolyl), 153.1 (C$_{ipso}$ NAr), 148.5, 144.7, 144.6, 143.4, 135.6, 135.5, 128.4, 128.1, 126.4, 126.2, 123.6, 123.1 (aryl−C), 72.9 (CH$_2$), 49.6 (NMe$_2$), 28.2 (*C*HMe$_2$), 24.6 (CH*Me*$_2$), 24.2 (CH*Me*$_2$), 21.4 (tolyl−CH$_3$). T_{decomp} = 192 °C. Elemental Anal. (Calcd) for $C_{40}H_{53}MoN_3$: C, 71.62 (71.51); H, 7.99 (7.95); N, 6.18 (6.25).

[Mo(NAr)$_2$(*C*−*N*)$_2$] (7). To a clear red solution of [Mo(NAr)$_2$Cl$_2$(DME)] (1.70 g, 2.80 mmol) in 80 mL of Et$_2$O was added [Li$_2$(*C*−*N*)$_2$] (0.79 g, 2.80 mmol) as a solid at room temperture. After 18 h the reaction was complete. All volatiles were removed in vacuo (3 h, 50 °C). The residual precipitate was extracted with Et$_2$O (30 mL) and separated from the solids by centrifugation. The residual solids were extracted with CH$_2$Cl$_2$ (80 mL), and the CH$_2$Cl$_2$ layer was collected after centrifugation. All volatiles were removed in vacuo, leaving a red crystalline solid (1.83 g, compound **7**: 91% yield) which was pure by NMR and elemental analysis. ^{1}H NMR (δ): 8.39 (d, 2, *o*-aryl−H), 7.04 (m, 12, NAr−H + ArH), 4.27 (sept, 4, C*H*Me$_2$), 3.62 (d, 2, $^2J_{H_a\mathrm{H_b}}$ =13.8 Hz, CH$_a$H$_b$N), 3.34 (d, 2, $^2J_{\mathrm{H_a}H_b}$ =13.8 Hz, CH$_a$H$_b$N), 2.11 (s, 12, NMe$_2$), 1.14 (d, 12, CH*Me*$_2$), 1.04 (d, 12, CH*Me*$_2$). ^{13}C NMR (δ): 181.3 (C$_{ipso}$), 153.4 (C$_{ipso}$ NAr), 147.9, 143.1, 142.9, 126.6, 125.4, 125.2, 124.8, 123.7 (aryl−C), 70.2 (CH$_2$), 50.7 (NMe$_2$), 27.5 (*C*HMe$_2$), 26.6 (CH*Me*$_2$), 24.1 (CH*Me*$_2$). T_{melt} > 200 °C. Elemental Anal. (Calcd) for $C_{42}H_{58}MoN_4$: C, 70.64 (70.56); H, 8.21 (8.18); N, 7.80 (7.84).

[Li(DME)$_2$Mo(NAr)$_2$(*C*−*N*)(Me)$_2$] (8). Never let the temperature exceed 0 °C during the synthesis of **8**! To a DME/THF (30 mL/50 mL) solution of **2** (0.83 g, 1.39 mmol) was added 0.97 mL (1.55 mmol) of a 1.6 M solution of MeLi (Et$_2$O) at −78 °C. The mixture was allowed to warm to 0 °C. After 2 h, the reaction was complete, and the clear yellow solution was concentrated to a volume of 10 mL. To the reddish oil was added 50 mL of cold pentane, the mixture was stirred vigorously, and a yellow, sticky precipitate appeared. The yellow solution was decanted from the yellow precipitate, and the residual precipitate was washed with cold pentane (3 × 50 mL). The precipitate was dried in vacuo, and the residue was extracted with cold Et$_2$O (2 × 30 mL). The Et$_2$O layers were collected and concentrated to a volume of 15 mL. A yellow/brown oil precipitated from the solution and was isolated by decantation of the upper layer. All volatiles were removed in vacuo, leaving an air-sensitive, yellow powder (0.88 g, 1.10 mmol, 79% yield) that was pure by NMR and elemental analysis. ^{1}H NMR (δ in THF-d_8, 294 K): 7.49 (dd, 1, o-aryl−H), 7.23 (dd, 1, *m*-aryl−H), 6.81 (m, 4, NAr−H + ArH), 6.59 (m, 4, NAr−H + ArH), 4.04 (sept, 4, C*H*(CH$_3$)$_2$), 3.48 (s, 2, CH$_2$), 3.41 (s, 8, CH$_2$O), 3.24 (s, 12, OCH$_3$), 2.16 (s, 6, N(CH$_3$)$_2$), 1.10 (d, 12, (CH(C*H*$_3$)$_2$), 1.08 (d, 12, CH(C*H*$_3$)$_2$), 0.79 (s, 6, Mo−CH$_3$). ^{13}C NMR (δ in THF-d_8, 294 K): 203.3 (C$_{ipso}$ C−N), 154.1 (C$_{ipso}$ NAr), 153.7 (C$_{ipso}$ NAr), 141.0, 139.8, 136.4, 132.6, 124.0, 122.3, 120.1, 120.0, 118.7, 117.8, 117.7 (C−Ar), 70.8 (OCH$_3$), 67.5 (CH$_2$), 57.1 (CH$_2$O), 44.5 (N(CH$_3$)$_2$), 26.4, 26.3 (*C*H(CH$_3$)$_2$), 23.0, 22.6, 22.4, 20.1 (CH(*C*H$_3$)$_2$), 13.9 (Mo−CH$_3$). T_{decomp} < 20 °C. Elemental Anal. (Calcd) for $C_{43}H_{72}LiMoN_3O_4$: C, 64.54 (64.73); H, 9.18 (9.10); N, 5.09 (5.27).

[Li(DME)$_2$Mo(NAr)$_2$(*C*−*N*)(*n*-Bu)] (9). Never let the temperature exceed 0 °C during the synthesis of **9**! To a DME/THF (30 mL/50 mL) solution of **2** (0.74 g, 1.24 mmol) was added 1.02 mL of a 1.21 M solution of *n*-BuLi (1.26 mmol) in pentane at −78 °C. The mixture was allowed to warm to 0 °C. After 2 h the reaction was complete, and the clear orange solution was concentrated to a volume of 10 mL. To the reddish oil, 50 mL of cold pentane was added, the mixture was stirred vigorously, and a yellow precipitate appeared. The yellow solution was decanted from the yellow precipitate, and the precipitate was washed with cold pentane (3 × 50 mL). The precipitate was dried in vacuo, and the residue was extracted with cold Et$_2$O (2 × 30 mL). The Et$_2$O layers were collected and concentrated to a volume of 50 mL. After 3 days yellow air-sensitive crystals (0.74 g, 0.88 mmol, 71% yield) could be isolated at −30 °C. ^{1}H NMR (δ in THF-d_8, 294 K): 7.52 (dd, 1, *o*-aryl−H), 7.22 (dd, 1, *m*-aryl−H), 6.79 (m, 4, NAr−H + ArH), 6.60 (m, 4, NAr−H + ArH), 4.07 (sept, 2, C*H*(CH$_3$)$_2$), 4.06 (sept, 2, C*H*(CH$_3$)$_2$), 3.57 (s, 2, CH$_2$), 3.41 (s, 8, CH$_2$O), 3.25 (s, 12, OCH$_3$), 2.17 (s, 6, N(CH$_3$)$_2$), 1.94 (m, 2, MoCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.71 (m, 2, MoC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.46 (m, 2, MoCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.07 (4 × d, 4 × 6, CH(C*H*$_3$)$_2$), 0.71 (s, 3, Mo−CH$_3$) 0.63 (t, 3, MoCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (δ in THF-d_8, 294 K): 202.8 (C$_{ipso}$ C−N), 154.1 (C$_{ipso}$ NAr), 153.3 (C$_{ipso}$ NAr), 141.6, 140.0, 137.0, 133.0, 123.5, 121.8, 120.2, 120.1, 120.0, 118.8, 117.7 (C−Ar), 70.9 (OCH$_3$), 67.3 (CH$_2$), 57.0 (CH$_2$O), 44.5 (N(CH$_3$)$_2$), 41.5 (MoCH$_2$*C*H$_2$CH$_2$CH$_3$), 35.9 (Mo*C*H$_2$CH$_2$CH$_2$CH$_3$), 28.4 (MoCH$_2$CH$_2$*C*H$_2$CH$_3$), 26.2, 26.0 (*C*H(CH$_3$)$_2$), 23.2, 23.0, 22.7, 22.7, (CH(*C*H$_3$)$_2$), 20.7 (Mo−CH$_3$), 12.6 (MoCH$_2$CH$_2$CH$_2$*C*H$_3$). T_{decomp} < 20 °C. Elemental Anal. (Calcd) for $C_{46}H_{78}LiMoN_3O_4$: C, 65.65 (65.77); H, 9.42 (9.36); N, 4.87 (5.00).

[Li(DME)$_n$Mo(NAr)$_2$(*C*−*N*)(*p*-tolyl)] (10). To a DME/THF (30 mL/50 mL) solution of **2** (0.88 g, 1.48 mmol) was added a THF solution (20 mL) of 0.15 g of [Li(*p*-tolyl)] (1.53 mmol) at −78 °C. The mixture was allowed to warm to room temperature. After 12 h the reaction was complete, and the clear yellow solution was concentrated to a volume of 10 mL. To the reddish oil, 50 mL of pentane was added, the mixture was stirred vigorously, and a yellow precipitate appeared. The yellow solution was decanted from the yellow precipitate, and the residual precipitate was washed with cold pentane (3 × 50 mL). The precipitate was dried in vacuo, leaving an air-sensitive, yellow powder (1.00 g, 1.27 mmol, 86% yield) that was pure by NMR and elemental analysis. Crystals suitable for X-ray analysis were grown in a saturated C$_6$D$_6$ solution at 15 °C within 24 h. ^{1}H NMR (δ in toluene-d_8): 8.52 (d, 1, *o*-aryl−H), 8.05 (d, 2, *o*-tolyl−H), 7.04 (m, 9, NAr−H + ArH), 6.67 (d, 2, *m*-tolyl−H), 4.31 (sept, 2, C*H*Me$_2$), 4.21 (d, 1, $^2J_{H_a\mathrm{H_b}}$=12.0 Hz, CH$_a$H$_b$N) 3.88 (sept, 2, C*H*Me$_2$),3.08 (d, 1, $^2J_{\mathrm{H_a}H_b}$ = 12.0 Hz, CH$_a$H$_b$N), 2.59 (s, 14, CH$_2$O), 2.45 (s, 21, CH$_3$O), 1.92 (s, 3, *p*-tolyl−CH$_3$), 1.76 (s, 6, NMe$_2$), 1.36 (d, 6, CH*Me*$_2$), 1.31 (d, 6, CH*Me*$_2$), 1.30 (s, 3, Mo−CH3), 1.16 (d, 6, CH*Me*$_2$), 1.12 (d, 6, CH*Me*$_2$). ^{1}H NMR (δ in THF-d_8, 294 K): 7.94 (dd, 1, *o*-aryl−H), 7.23 (d, 2, *o*-(*p*-tolyl)−H), 7.05 (dd, 1, *m*-aryl−H), 6.80 (m, 4, NAr−H + ArH), 6.61 (m, 2, NAr−H + ArH), 6.51 (m, 4, NAr−H + ArH),4.00 (sept, 4, C*H*(CH$_3$)$_2$), 3.56 (s, 2, CH$_2$), 3.40 (s, 14, CH$_2$O), 3.24 (s, 21, OCH$_3$), 1.82 (s, 6, N(CH$_3$)$_2$), 1.04 (d, 12, (CH(C*H*$_3$)$_2$), 0.91 (s, 3, Mo−CH$_3$), 0.89 (d, 12, CH(C*H*$_3$)$_2$).

^{13}C NMR (δ in THF-d_8, 294 K): 190.4 (C$_{ipso}$ C−N), 185.2 (C$_{ipso}$ *p*-tolyl), 153.3 (C$_{ipso}$ NAr), 144.2, 142.2, 141.2, 141.0, 135.1, 125.4, 124.1, 123.5, 121.9 120.2, 119.2 (C−Ar), 70.8 (OCH$_3$), 66.0 (CH$_2$), 57.1 (CH$_2$O), 44.2 (N(CH$_3$)$_2$), 44.1 (*p*-tolyl−CH$_3$), 26.4 (*C*H(CH$_3$)$_2$), 26.3, 23.2 (CH(*C*H$_3$)$_2$), 19.7 (Mo−CH$_3$). T_{decomp} < 20 °C. Elemental Anal. (Calcd) for $C_{41}H_{56}LiMoN_3(DME)_{3.5}$: C, 65.26 (65.46); H, 8.89 (9.09); N, 4.40 (4.16). ^{1}H NMR confirmed the presence of 3.5 equiv of DME.

[LiMo(NAr)$_2$(*C*−*N*)$_2$] (11). To a clear red solution of **6** (0.86 g, 1.21 mmol) in 50 mL of toluene was added 0.76 mL of *n*-BuLi (1.6 M solution in pentane) at −78 °C. The reaction mixture was allowed to warm to room temperature, and after 18 h all volatiles were removed in vacuo. The sticky brown residue was suspended in benzene (30 mL) and was filtered over Celite. The clear benzene solution was concentrated to a volume of 10 mL. After 2 weeks dark crystals were growing in two crops (0.28 g, 32%). The crystals showed no clear NMR spectrum and are extremely sensitive toward air. EPR: concentration = 8 mM, g_{iso} = 1.974, A_{iso} = 35 G (3420 G, 9.449 MHz, 1 G =

Table 4. Experimental Data for the X-ray Diffraction Studies of 2, 10, and 11

	2	**10**	**11**
formula	$C_{34}H_{49}MoN_3$	$C_{45}H_{66}LiMoN_3O_2$ (C_6D_6)	$C_{42}H_{58}LiMoN_4$
fw	595.70	868.07	721.80
temp, K	150	150	150
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	Cc	$P2/c$
a (Å)	10.9411(6)	18.856(2)	19.594(3)
b (Å)	29.098(2)	13.751(3)	10.996(2)
c (Å)	11.700(2)	19.4151(14)	23.335(7)
β (deg)	122.243(4)	100.064(6)	126.37(2)
volume (Å^3)	3150.5(6)	4956.7(13)	3517.9(5)
Z	4	4	4
d_{calcd} (g cm^{-3})	1.256	1.155	1.184
F(000) (electrons)	1264	1840	1532
μ(Mo Kα) (cm^{-1})	0.4	3.0	0.4
crystal size (mm)	0.33 × 0.35 × 0.35	0.5 × 0.20 × 0.20	0.05 × 0.50 × 0.50
radiation (Å)	Mo Kα (0.71073)^a	Mo Kα (0.71073)^a	Mo Kα (0.71073)^a
$\theta_{min},\theta_{max}$(deg)	1.4, 27.5	1.8, 27.5	1.3, 23.0
scan (ω-mode) (deg)	$0.65 + 0.35 \tan(\theta)$	$0.79 + 0.35 \tan(\theta)$	$1.00 + 0.35 \tan(\theta)$
h; k; l (min, max)	−9,14; −37,37; −15,12	−15,24; −14,17; −25,24	−20,21; −12,12; −20,25
total/unique reflns	17516, 7235	12075, 8350	11224, 5637
obsd reflns	5644 ($I > 2.0\sigma(I)$)	6588 ($I > 2.0\sigma(I)$)	3638 ($I > 2.0\sigma(I)$)
N_{ref}, N_{par}	7235, 354	8350, 537	5637, 444
R; wR; S^b	0.0352; 0.0788; 1.04	0.0520; 0.0997; 1.02	0.0522; 0.1019; 1.01
weight (w^{-1}) ^{c}	$\sigma^2(F_o^2) + (0.0308P)^2 + 1.4579P$	$\sigma^2(F_o^2) + (0.0349P)^2$	$\sigma^2(F_o^2) + (0.0257P)^2$
min, max resd dens (e/Å^3)	−0.50, 0.57	−0.71, 0.47	−0.41, 0.31

^{a} Graphite monochromated. ^{b} $R = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. ^{c} $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

10^{-4} T). No nitrogen or lithium couplings were detected. No satisfactory elemental analysis was obtained probably due to partial oxidation caused by air leakage.

General Polymerization Procedure. The catalyst system was prepared in situ by dissolving 0.30 g of **2** (0.5 mmol) in toluene (20 mL), to which 0.8 mL of a 1.6 M solution of *n*-BuLi (0.5 mmol) was added at −30 °C. The reaction mixture was allowed to warm to room temperature, was stirred overnight, and was used as such. In a Schlenk vessel 13.4 mL of a 3.72 M norbornene solution in toluene (50 mmol) was brought together with 3.61 g of mesitylene (30 mmol) and 63 mL of toluene. The catalyst solution was added to this mixture quickly, and the polymerization reaction was followed from this point on. Samples of 1 mL were taken from the reaction mixture and were mixed with 10 mL of methanol. The white precipitate was removed by filtration, and the clear solution was measured by GC. When the reaction was complete, the solution was quenched with methanol, and the polymer was precipitated from methanol, dried in vacuo, and analyzed by NMR and GPC.

Structure Determination and Refinement of 2, 10, and 11. X-ray data were collected on an Enraf-Nonius CAD4-T rotating anode diffractometer for a transparent, yellowish (**2** and **10**) or dark brown (**11**) crystal glued on top of a glass fiber. Accurate unit-cell parameters and an orientation matrix were determined by least-squares refinement of the setting angles of a set of 25 well-centered reflections (SET4).[28] The unit-cell parameters were checked for the presence of higher lattice symmetry. Data were corrected for Lorentz polarization effects. An empirical absorption correction was applied (PLATON/DELABS).[29] The structures were solved by Direct methods and subsequent difference Fourier techniques (SHELXS86).[30] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL93)[31] using no observance criterion. Hydrogen atoms were included on calculated positions, riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. All hydrogen atoms were refined with a fixed isotropic atomic displacement parameter related to the value of the equivalent isotropic atomic displacement parameter of their carrier atom. Weights were optimized in the final refinement cycles. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography.[32] Geometrical calculations and illustrations were performed with PLATON.[29] All calculations were performed on a DECstation 5000 cluster. Crystal data and numerical details of the structure determinations and refinements are collected in Table 4. Selected geometrical details of the structures of **2** and **10** are listed in Table 1 and for **11** in Table 3.

Acknowledgment. J.A.M.B., J.B., and G.v.K. gratefully thank Dr. G. J. M. Gruter (DSM Research), Dr. J. A. M. van Beek, Dr. F. H. van der Steen (Shell, Amsterdam), and Dr. A. A. van der Huizen (Shell) for the fruitful discussions. Financial support was granted by the Dutch Technology Foundation (STW) with financial aid from the Council for Chemical Science of The Netherlands/Organization for Scientific Research (NWO/CW).

Supporting Information Available: Tables of the structure determination, atomic coordinates, bond lengths and angles, and thermal parameters for **2**, **10**, and **11.** This material is available free of charge via the Internet at http://pubs.acs.org.

OM9900364

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