Syntheses and Structures of Molybdenum(IV) Complexes with 3,5-Dimethyl- and 3,5-Di-*tert*-butylpyrazolato Ligands. Variable Coordination Modes and C−H Bond Activation

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Treatment of tetrakis(dimethylamido)molybdenum(IV) ($Mo(NMe_2)_4$) with 4 equiv of 3,5-dimethylpyrazole (Me_2pzH) in pentane yields $Mo(Me_2pzH)(Me_2pz)_3(\eta^2\text{-}CH_2NHCH_3)$ (**1**), whereby the reaction with 3,5-di-*tert*-butylpyrazole ($t\text{-}Bu_2pzH$) leads to $Mo(t\text{-}Bu_2pz)_3(NMe_2)$ (**2**), independent of the molar ratio. The homoleptic $Mo(t\text{-}Bu_2pz)_4$ (**3**) was synthesized from tetrachlorobis(tetrahydrofurano)molybdenum(IV) ($MoCl_4(thf)_2$) with 4 equiv of 3,5-di-*tert*-butylpyrazolatopotassium ($t\text{-}Bu_2pzK$). Magnetic measurements show the three complexes to be paramagnetic with two unpaired electrons (**1**, 3.0; **2**, 2.8; and **3**, 2.8 μ_B, respectively). The molecular structures of all compounds determined by X-ray diffraction analysis are reported. Complex **1** reveals a η^2-coordinate CH_2NHCH_3 ligand arranged in an azametallacyclic fashion, verified by a small Mo−C−N angle and a typical C−N single bond length. The bonding mode of the pyrazolato ligands in all three compounds **1**, **2**, and **3** is influenced by the steric bulk around the metal center leading to η^1-, “slipped” η^2-, and η^2-coordinate ligands.

Introduction

Pyrazolato ligands have an extensive coordination chemistry among transition metal complexes, where $\mu\text{-}\eta^1\text{:}\eta^1$ and η^1 bonding modes are prevalent.[1−4] Recent investigations with sterically demanding derivatives of the heterocycle have led to a variety of new coordination modes, such as η^2, η^3, η^5, $\mu\text{-}\eta^2\text{:}\eta^1$, or $\mu\text{-}\eta^2\text{:}\eta^2$. Whereas most of these are limited to a single or a few examples,[5−10] the η^2-bonding type is predominant in lanthanoide and actinoide as well as early transition metal complexes and has opened a new field of research.[11−22] The bidentate binding to one metal atom allows the synthesis of mononuclear complexes, which were not accessible with sterically less demanding ligands, rendering bulky pyrazolates as a new class of ancillary ligands in organometallic chemistry. Thus, we have reported the synthesis of molybdenum dioxo compounds containing η^2-di-*tert*-butylpyrazolato ligands that proved to be active reagents in oxygen-transfer reactions.[12] These two-electron redox transformations involve Mo(IV) intermediates.[23,24] Until recently, η^2-coordination was limited to transition metals with empty d-shells. After our initial discovery of η^2-pyrazolatotitanium(III) compounds further examples with d^2-, d^3-, and d^5-electron configuration were published.[11,13,15] Molecular orbital analyses on model compounds carried out by Winter and co-workers confirm the higher stability of the bidentate versus the monodentate binding in the d^2- and d^3-systems.[11,13]

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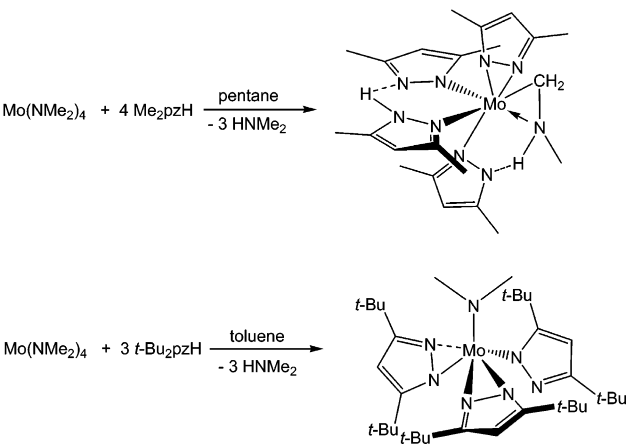
Scheme 1. Synthesis of Complexes 1 and 2



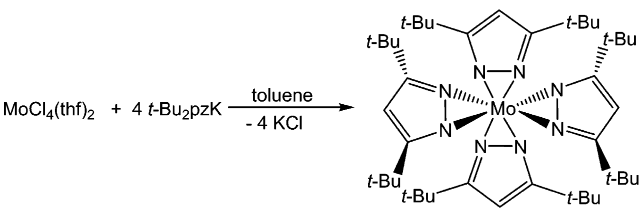
As part of our interest in molybdenum chemistry as well as in the influence of d-electrons on η^2 bonding we investigated the coordination properties of the pyrazolato ligand toward the Mo(IV) center. Herein, we report the syntheses of three molybdenum(IV) complexes, $Mo(Me_2pzH)(Me_2pz)_3(\eta^2\text{-}CH_2NHCH_3)$ (**1**), $Mo(t\text{-}Bu_2pz)_3(NMe_2)$ (**2**), and the homoleptic $Mo(t\text{-}Bu_2pz)_4$ (**3**). Our studies have yielded two different compounds depending on the steric demand of the pyrazolato ligand, allowing a statement on structural factors governing the different coordination modes. In addition, cyclometalation of a NMe_2 ligand forming a metal carbon bond was observed, which is potentially significant for the understanding of possible pathways for the incorporation of undesired carbon residues in metal nitride films in chemical vapor deposition (CVD) reactions.[14,25−27] Lanthanoide-based pyrazolato complexes have been developed as precursors for doped semiconductor films.[16]

Results and Discussion

Synthesis of Compounds 1−3. Treatment of tetrakis(dimethylamido)molybdenum(IV) ($Mo(NMe_2)_4$) with 4 equiv of 3,5-dimethylpyrazole (Me_2pzH) in pentane at room temperature afforded after crystallization at −25 °C dark green crystals of $Mo(Me_2pzH)(Me_2pz)_3(\eta^2\text{-}CH_2NHCH_3)$ (**1**) (Scheme 1). Reaction of $Mo(NMe_2)_4$ with 3 equiv of 3,5-di-*tert*-butylpyrazole ($t\text{-}Bu_2pzH$) in toluene at room temperature led after crystallization at −25 °C to brown crystals of dimethylamidotris(3,5-di-*tert*-butylpyrazolato)molybdenum(IV) ($Mo(t\text{-}Bu_2pz)_3(NMe_2)$, **2**) (Scheme 1). Treatment of $Mo(NMe_2)_4$ with ≥4 equiv of $t\text{-}Bu_2pzH$ did not allow the synthesis of $Mo(t\text{-}Bu_2pz)_4$ (**3**), but rather **2** was obtained. Attempts to prepare bis(dimethylamido)bis(3,5-di-*tert*-butylpyrazolato)molybdenum(IV) ($Mo(t\text{-}Bu_2pz)_2(NMe_2)_2$) by reacting $Mo(NMe_2)_4$ with 2 equiv of $t\text{-}Bu_2pzH$ also resulted in the isolation of complex **2**. Recrystallization from concentrated hexane and toluene solutions afforded crystals of **1** and **2**, respectively, suitable for single-crystal X-ray diffraction analyses.

Complexes **1** and **2** are readily soluble in aromatic and aliphatic hydrocarbons and ethers. The structures of **1** and **2** were assigned on the basis of spectral and analytical data and from X-ray crystallographic structure determination (vide infra). Electron impact (EI) mass spectrometry shows the $[M^+]$ species with correct isotopic distribution pattern for **2** at $m/z = 679$, whereas the spectrum for compound **1** shows the $[M^+ - CH_2NHCH_3]$ and the $[M^+ - Me_2pzH]$ species with correct isotopic distribution patterns at $m/z = 479$ and $m/z = 427$, respectively. Due to the paramagnetism of the two compounds and the complex structure, ^1H NMR spectra show several broad signals that do not allow a statement on structural properties. The two measurements of the magnetic moments for $Mo(Me_2pzH)(Me_2pz)_3(\eta^2\text{-}CH_2NHCH_3)$ and $Mo(t\text{-}Bu_2pz)_3(NMe_2)$ in a benzene solution at 22 °C by the Evans' method gave values of 3.0 and 2.8 μ_B, which are similar to the spin-only magnetic moment expected for two unpaired electrons (2.83 μ_B).[28,29] The triplet ground state in **1** and **2** is in contrast to the singlet ground state in $Mo(NMe_2)_4$.[30] The spin pairing in the latter compound is described to occur due to significant pπ−dπ interaction of the Mo−N bonds, substantiating the pyrazolato ligands to be weak π-donors.

Scheme 2. Synthesis of Complex 3



3

Treatment of tetrachlorobis(tetrahydrofurano)molybdenum(IV) ($MoCl_4(thf)_2$) with 4 equiv of 3,5-di-*tert*-butylpyrazolatopotassium ($t\text{-}Bu_2pzK$) in toluene at room temperature afforded the homoleptic tetrakis(3,5-di-*tert*-butylpyrazolato)molybdenum(IV) ($Mo(t\text{-}Bu_2pz)_4$, **3**) as a brown crystalline solid (Scheme 2). The analogous reaction employing Me_2pzK did not yield in any product, but rather decomposition occurred. Crystals of **3** suitable for X-ray diffraction analysis were grown from a concentrated toluene solution at −25 °C.

Complex **3** is soluble in common organic solvents and has been characterized by electron impact (EI) mass spectrometry and elemental analyses. The $[M^+]$ species with correct isotopic distribution patterns has been identified at $m/z = 814$. Compound **3** is also paramagnetic, and the measurement of the magnetic moment gave a value of 2.8 μ_B, similar to the expected spin-only magnetic moment.

Structure Discussion for Complexes 1−3. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with half a molecule of hexane in the asymmetric unit as shown in Figure 1; selected bond lengths and angles are listed in Table 1, and crystallographic data are listed in Table 4. The molybdenum atom is surrounded by six nitrogen atoms and one carbon atom, with N(3) and N(7) as well as N(2) and N(9) being in *trans* position to each

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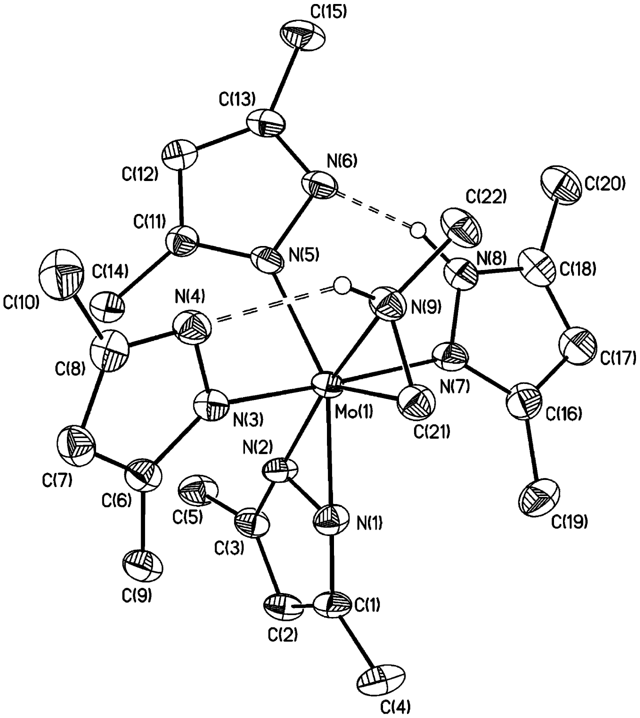

Figure 1. Molecular structure of **1**. Hydrogen atoms are omitted for clarity, except those involved in intramolecular hydrogen bonds (thermal ellipsoids at the 50% probability level).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1

	Bond Lengths		
Mo(1)−C(21)	2.123(4)	Mo(1)−N(7)	2.219(3)
Mo(1)−N(1)	2.096(3)	Mo(1)−N(9)	2.145(3)
Mo(1)−N(2)	2.128(3)	N(9)−C(21)	1.424(6)
Mo(1)−N(3)	2.143(3)	N(9)−C(22)	1.469(5)
Mo(1)−N(5)	2.152(3)		
	Angles		
N(1)−Mo(1)-N(2)	38.05(13)	C(1)−N(1)-Mo(1)	178.2(3)
N(9)−C(21)−Mo(1)	71.3(2)	C(3)−N(2)−Mo(1)	177.8(3)
N(3)−Mo(1)−(N(7)	171.59(12)	N(2)−Mo(1)−N(9)	173.76(14)
Mo(1)−N(9)−H(9)	107.6	C(22)−N(9)−H(9)	109.7
C(21)−N(9)−C(22)	120.1(2)	C(22)−N(9)−Mo(1)	128.8(3)
C(21)−N(9)−Mo(1)	69.7(2)		

	Hydrogen Bonds			N−H···N
	d(N−H)	*d*(H···N)	*d*(D···A)	Angles
N(8)−H(8A)···N(6)	0.96(5)	1.71(5)	2.635(5)	159(5)
N(9)−H(9)···N(4)	0.84(5)	2.13(5)	2.767(5)	133(5)

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2

	Bond Lengths		
Mo(1)−N(1)	2.092(3)	Mo(1)−N(5)	2.153(3)
Mo(1)−N(3)	2.066(3)	Mo(1)−N(6)	2.087(3)
Mo(1)−N(4)	2.196(3)	Mo(1)−N(7)	1.914(3)
	Angles		
N(3)−Mo(1)−N(4)	37.79(10)	C(14)−N(4)−Mo(1)	169.9(2)
N(5)−Mo(1)−N(6)	38.21(11)	C(23)−N(5)−Mo(1)	162.9(3)
C(12)−N(3)−Mo(1)	169.8(2)	C(25)−N(6)−Mo(1)	162.5(3)
C(34)−N(7)−C(35)	109.2(4)	C(34)−N(7)−Mo(1)	121.6(4)
C(35)−N(7)−Mo(1)	129.2(3)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3

	Bond Lengths		
Mo(1)−N(1)	2.214(2)	Mo(1)−N(4)	2.097(2)
Mo(1)−N(2)	2.078(3)	N(1)−N(2)	1.372(3)
Mo(1)−N(3)	2.183(2)	N(3)−N(4)	1.369(2)
	Angles		
N(1)−Mo(1)−N(2)	37.12(7)	C(3)−N(2)−Mo(1)	166.46(16)
N(3)−Mo(1)−N(4)	37.23(7)	C(12)−N(3)−Mo(1)	170.32(15)
C(1)−N(1)−Mo(1)	166.97(15)	C(14)−N(4)−Mo(1)	170.25(16)

Table 4. Crystallographic Data

	1	**2**	**3**
formula	$C_{25}H_{42}MoN_9$	$C_{35}H_{63}MoN_7$	$C_{44}H_{76}MoN_8$
fw	564.62	677.86	813.07
cryst syst	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a, Å	9.2550(19)	9.897(2)	24.771(5)
b, Å	12.931(3)	10.588(2)	11.442(2
c, Å	13.565(3)	19.985(4)	20.144(4)
α, deg	100.95(3)	91.11(3)	90
β, deg	108.62(3)	103.56(3)	125.65(3)
γ, deg	105.31(3)	108.67(3)	90
V, Å	1415.4(5)	1918.7(7)	4639.3(16)
Z	2	2	4
F(000)	594	728	1725
ρ_{calcd}, g cm^{-3}	1.325	1.173	1.164
T, K	133(2)	133(2)	133(2)
μ(Mo Kα), mm^{-1}	0.493	0.373	0.320
no. of measd rflns	13 551	31 446	14 192
no. of unique rflns	4817 (R_{int} = 0.0514)	5631 (R_{int} = 0.0717)	3959 (R_{int} = 0.0815)
no. of params	310	496	240
$R(I > 2\sigma(I))$	R1^a = 0.0457 wR2^b = 0.1075	R1 = 0.0420 wR2 = 0.1044	R1 = 0.0293 wR2 = 0.0650
R(all data)	R1 = 0.0576 wR2 = 0.1131	R1 = 0.0545 wR2 = 0.1096	R1 = 0.0407 wR2 = 0.0670
GOF on F^2	1.082	0.997	0.918

^{a} R1 = $\Sigma|F_o|^2 - |F_c|^2/\Sigma|F_o|^2$. ^{b} wR2 = $[\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$.

other (N(3)−Mo(1)−(N(7) 171.59(12)°, N(2)−Mo(1)−N(9) 173.76(14)°). Therefore, considering the centers of the N(1),N(2)- and C(21),N(9)-ligands as one coordination site, it is best described as a distorted trigonal bipyramid with N(3) and N(7) being in the apical positions. The arrangement of the Me_2pz ligands is interesting, as all four coordinate in a different binding mode, whereby one of them is protonated. The N(1),N(2)-pyrazolato ligand is coordinated in a η^2-fashion with Mo−N bond lengths of 2.096(3) and 2.128(3) Å. The pyrazolato bite angle is 38.05(13)°, comparable to those found in other η^2-pyrazolato complexes,[11−13] and the dihedral angle between the Mo−N−N plane and the N−C−C−C−N best plane is 2°. The N(3),N(4)- and N(5),N(6)-ligands are coordinated in a η^1-mode, with a Mo(1)−N(3) bond length of 2.143(3) Å and a Mo(1)−N(5) of 2.152(4) Å. The distances between Mo(1) and N(4) as well as N(6) are 3.004 and 3.097 Å, too long to assume bonding. However, these two nitrogen atoms are involved in intramolecular hydrogen bonds to N(8) (N(8)−H(8A) 0.96(5) Å, H(8A)···N(6) 1.71(5) Å) and N(9) (N(9)−H(9) 0.84(5) Å, H(9)···N(4) 2.13(5) Å), respectively. The hydrogen bond formation is a common feature in pyrazolato complexes containing both pyrazolato and pyrazole ligands.[1,31] In addition to the four pyrazole-based ligands a cyclometalated NMe_2 ligand is coordinated to the metal center. C−H bond activation in one of the two methyl groups leads to the formation of an azametallacycle including a metal−carbon bond. The overall reaction represents a β-H migration to the nitrogen atom. The hydrogen atom H(9) bound to N(9) and H(8A) bound to N(8) were located in the difference Fourier map

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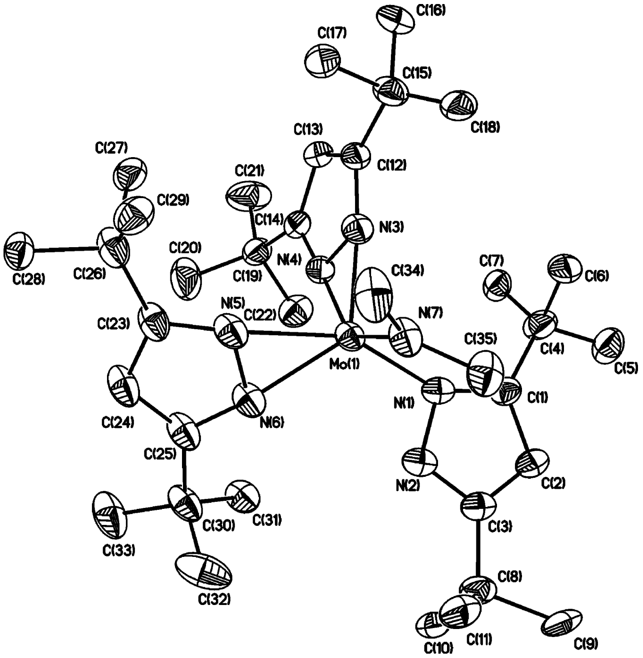

Figure 2. Molecular structure of **2**; hydrogen atoms are omitted for clarity (thermal ellipsoids at the 30% probability level).

and refined without restraints. The bonding of the η^2-CH_2NHCH_3 group may be considered as a π-bonded iminium cation $[CH_2{=}NHCH_3]^+$ or as an azametallacycle involving a Mo(1)−C(21) σ-bond and a bond between the electron lone pair at N(9) and Mo(1). Typical N−C single bonds are approximately 1.48 Å, whereas N=C double bonds are approximately 1.32 Å. In an iminium ligand the angles at nitrogen should be close to 120° and in the sp^3-hybridized nitrogen of the metallacycle close to 109°. The N(9)−C(21) bond length is 1.424(6) Å in the η^2-CH_2NMHCH_3 ligand, very short in comparison to other systems employing this kind of metallacycle,[25,32,33] but still too long for the assignment of a double bond. The angles within the metallacycle (Mo(1)−N(9)−H(9) 107.6°, C(22)−N(9)−H(9) 109.7°, C(21)−N(9)−C(22) 120.1(2)°, C(22)−N(9)−Mo(1) 128.8(3)° and C(21)−N(9)−Mo(1) 69.7(2)°) are found in a wide range, so that a definite assignment due to angles is not possible. Altogether, the data are more consistent with the formulation of a metallacycle rather than a cationic iminium ligand $[CH_2{=}NHCH_3]^+$.

Figure 2 shows the ORTEP drawing of the structure of **2** obtained by X-ray structure determination with the adopted numbering scheme. Selected structural parameters are listed in Table 2, crystallographic data in Table 4. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit. The molybdenum atom is surrounded by six nitrogen atoms. The geometry about the metal center is best described as an elongated tetrahedron, considering N(1), N(7), and the centers of the N,N-bonds of the two other pyrazolato ligands as one coordination site. The coordination modes of the pyrazolato ligands are interesting, as they differ significantly from each other. The N(4),N(5)-ligand has molybdenum−nitrogen bond lengths of Mo(1)−N(5) 2.153(3) Å and Mo(1)−N(6) 2.087(3) Å η^2-coordinate, whereas the N(3),N(4)-ligand, with a bond length difference of 0.13 Å (Mo(1)−N(3) 2.066(3) Å, Mo(1)−N(4) 2.196(3) Å), can be described as “slipped” η^2-coordinate, a denotation previously referred to this kind of asymmetric binding.[21] The N(1),N(2)-ligand is clearly η^1-coordinate with a Mo(1)−N(1) bond length of 2.092(3) Å and a Mo(1)−N(2) distance of 2.598 Å, so that no bond to N(2) can be assumed. Despite the different bonding modes to the metal atom, the bond lengths and angles within the ligands are in the same range. The bond length of Mo(1)−N(7) is 1.914(3) Å, significantly shorter than the Mo−N(pyrazolato) distances, but comparable with other Mo−N(amido) bond lengths.[30,34] The pyrazolato bite angles range from 37.79(10)° to 38.21(11)° and are comparable to those found in **1**. The dihedral angle between the Mo−N−N plane and the N−C−C−C−N best plane is in contrast to compound **1** (10.15° for the N(3),N(4)-ligand and 17.3° for the N(5),N(6)-ligand) but comparable to our recently reported molybdenum(VI) complex $MoO_2Cl(t\text{-}Bu_2pz)$,[12] which suggests π-interaction properties. This deviation from coplanarity with the metal atom as well as the “slipped” η^2- and η^1-coordination demonstrates the coordinational freedom of the pyrazolato ligands.

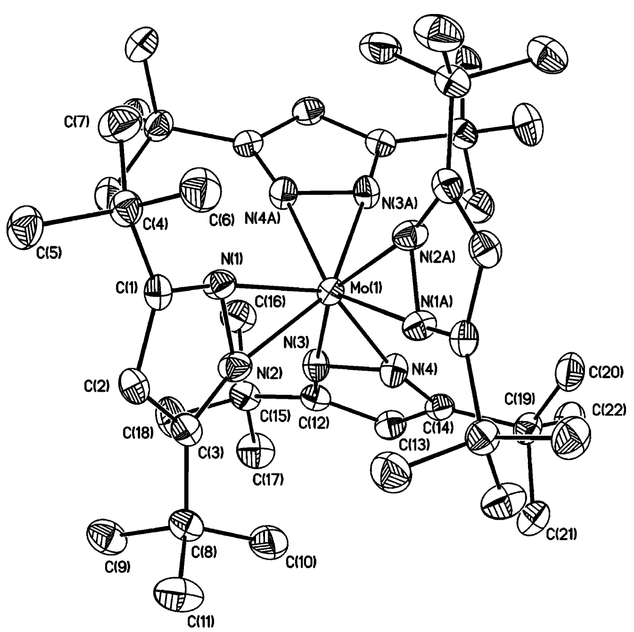

Figure 3. Molecular structure of **3**. Hydrogen atoms are omitted for clarity (thermal ellipsoids at the 50% probability level).

The solid state structure of compound **3** is shown in Figure 3; selected bond lengths and angles are shown in Table 3, and crystallographic data in Table 4. The molecule crystallizes in the monoclinic space group *C*2/*c* with four molecules in the unit cell. The *C*2 axis runs through the molybdenum center. The geometry around the metal atom is best described as an elongated tetrahedron, with the three angles being 92.0(2)°, 115.7(3)°, and 121.7(3)°, with the 3,5-di-*tert*-butylpyrazolato ligand occupying one coordination site. The metal center is surrounded by eight nitrogen atoms. The metal−nitrogen bond distances are 2.214(2) and 2.078(3) Å for

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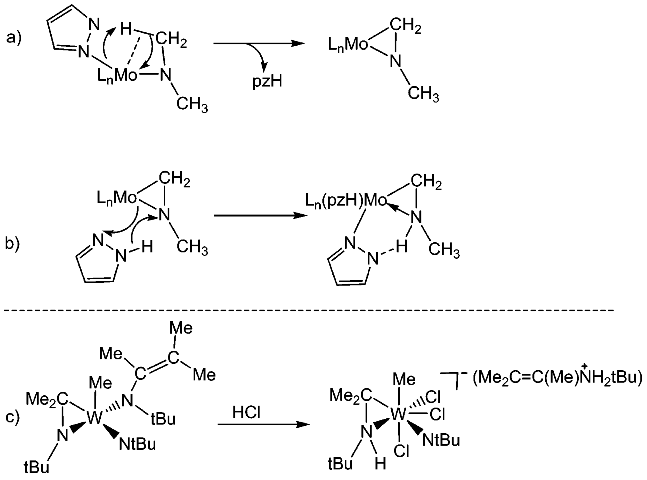
the N(1),N(2)-ligand and 2.183(2) and 2.097(2) Å for the N(3),N(4)-ligand. Whereas the latter pyrazolato can be considered as η^2-coordinate, the former one with a Mo−N bond length difference of 0.136 Å is consistent with a "slipped" η^2-ligand and comparable to compound **2**. Again, the bonding situation within each pyrazolato ligand in **3** is independent of the coordination mode to the metal atom. Comparison of the structure of **3** to that of other homoleptic complexes with four η^2-azolato ligands, like Ti(η^2-$Me_2pz)_4$ or Ti(η^2-i-$Pr_2tz)_4$ (i-Pr_2tz = 3,5-diisopropyl-1,2,4-triazolato), reveals different geometries and binding modes.[20,35] In both titanium compounds two azolato ligands are coplanar to each other and with a perpendicular plane containing the two other ligands. This is in contrast to complex **3**, where the N(1),N(2)- and N(3),N(4)-ligand planes include an angle of approximately 130° and the N(1),N(2)- and N(1A),N(2A)-ligand planes one of approximately 90°. In addition, in the titanium complexes the Ti−N bond lengths are with one exception in Ti(η^2-$Me_2pz)_4$ (in one ligand the Ti−N bond length is 0.095 Å longer than the other) identical within experimental error. The pyrazolato bite angles range from 37.12(7)° to 37.23(7)° and are in the same range as those found in **1** and **2**. The dihedral angle between the Mo−N−N plane and the N−C−C−C−N best plane is 13.3° for the N(1),N(2)-ligand and 9.7° for the N(3),N(4)-ligand, respectively, just like those found in **2**.

C−H Bond Activation. Cyclometalation involving coordinated neutral RR′NMe groups is a common feature in high-valent early transition metals.[32,36−42] In most of these cases the hydrogen atom of the C−H activation process is transferred to a neighboring carbon atom. In contrast, β-H elimination in complexes containing anionic NMe groups is a rarely documented phenomenon.[25,43−47] The formation of **1** represents one of the rare examples where C−H bond activation in a coordinated anionic NMe_2 group takes place in an all-amido complex.

The pathway for the formation of **1** is not clear. It involves the breaking of a C−H and Mo−N bond and the making of a N−H and M−C bond by a hydrogen atom transfer reaction. A likely pathway involves the direct abstraction of a β-H atom in one of the NMe_2 ligands by a neighboring pyrazolato ligand (Scheme 3a).

Scheme 3. Possible Mechanism of the C−H Bond Activation



Subsequent protonation of the imino nitrogen atom in the β-H abstracted intermediate by a pyrazolato ligand leads to the formation of **1** (Scheme 3b). The protonation of the N atom in an azametallacyclopropane unit has a precedent as shown in Scheme 3c.[48] Less likely seems the formation of an alkyl hydrido intermediate and subsequent reductive elimination of pzH due to the high valency of the metal atom.

Conclusion. Compounds **1**−**3** represent rare examples of d-block metal complexes with d^2-electron configuration that contain η^2-coordinate pyrazolato ligands. The here reported results demonstrate the unique electronic features of the pyrazolato in contrast to other amido ligands. The paramagnetic character of the compounds points to weak π-donor properties of the pyrazolato ligands. Structural comparison of Mo(t-Bu_2-$pz)_4$ to Mo(Me_2pzH)($Me_2pz)_3$(η^2-CH_2NHCH_3) allows the conclusion that steric demand in the 3,5-position of the ligands is essential for the formation of homoleptic species. However, it is interesting to compare these structures to that of Ti(η^2-$Me_2pz)_4$, which has been synthesized and crystallographically analyzed some years ago.[20] The ionic radii of Ti^{4+} and Mo^{4+} are comparable, and bond lengths in the molybdenum compound are only slightly longer, presumably due to the higher steric demand of the bis-*tert*-butyl-substituted ligands. Therefore, it is likely that the putative Mo($Me_2pz)_4$ is also stable but on the way to its formation C−H bond activation of the NMe_2 ligand is preferred, forming a strong metal−carbon bond.[49] The C−H bond activation presumably occurs due to hydrogen bond formation from a coordinated pyrazole ligand to the amido nitrogen, forcing one of the methyl groups into an agostic interaction with the metal, which eventually leads to the β-H elimination process. In the sterically more demanding system there is less space for an additional coordination of t-Bu_2pzH, so that the reaction stops at the trisubstituted level Mo(t-$Bu_2pz)_3(NMe_2)$ (**2**).

The coordination number of the three compounds **1**, **2**, and **3** is noteworthy, being 7, 6, and 8, respectively.

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(49) As mentioned, using salt metathesis is also not a feasible method to synthesize the putative Mo($Me_2pz)_4$, which is presumably due to the reducing conditions.

With each ligand donating two electrons together with two electrons of the d^2 metal center, the total electron count adds up to 16, 14, and 18, respectively. To the very low electron count of compound **2** two additional electrons should be considered due to a π-bond of the lone pair at N(7) to Mo(1) leading to a 16-electron system. π-Bonding of the amido ligand is evidenced by the planarity of the Mo−NC_2 unit (sum of the bond angles about the nitrogen atom is 360°) as well as the short Mo(1)−N(7) bond length of 1.914 Å and represents the usually found coordination mode for the dimethylamido ligand.[50] It is surprising that the 16-electron systems of **1** and **2** do not coordinate a further ligand, which eventually would lead to formation of $Mo(pz)_4$ compounds. Apparently, the steric bulk at the metal center prevents further coordination. Therefore, for the preparation of compound **3** another method proved to be more successful. The smaller chloro in comparison to the dimethylamido ligand allows salt metathesis of the Mo−Cl bond with t-Bu_2pzK in the $Mo(t\text{-}Bu_2pz)_3Cl$ intermediate.

The presented results demonstrate that the bonding is not of mere ionic nature and that the d-electron configuration of the metal seems to play a role. The occurrence of different coordination modes at the same metal center suggests that with higher d-electron count the energy differences between η^1- and η^2-coordination become smaller and that steric effects influence the found bonding in contrast to metal centers with low d-electron count. In the d^0-systems $Ti(\eta^2\text{-}Me_2pz)_4$ and $Ti(\eta^2\text{-}i\text{-}Pr_2tz)_4$ the π-donor capability of the ligands is possibly higher, which leads to the found coplanarity of the pyrazolato planes with the metal center. Theoretical aspects are currently being investigated.

Experimental Section

All manipulations were carried out under dry nitrogen using standard Schlenk line or glovebox techniques. Toluene and hexane were dried by distillation from sodium, tetrahydrofuran (thf) from sodium/potassium alloy, and pentane from calcium hydride under a nitrogen atmosphere immediately prior to use. The starting materials $MoCl_4(thf)_2$, $Mo(NMe_2)_4$, t-Bu_2pzH, and t-Bu_2pzK were prepared according to literature procedures.[51−54] All other chemicals mentioned were used as purchased from Fluka.

Samples for mass spectra were measured with a Finnigan MAT 95. Elemental analyses were performed by the Analytisches Chemisches Laboratorium des Institutes für Anorganische Chemie, Göttingen. ^1H NMR spectra were recorded at 200.13 MHz on a Bruker Avance 500.

Preparation of $Mo(Me_2pzH)(Me_2pz)_3(CH_2NHCH_3)$ (1). To a solution of Me_2pzH (0.42 g, 4.38 mmol) in 10 mL of pentane was added a solution of $Mo(NMe_2)_4$ (0.29 g, 1.09 mmol) in 12 mL of pentane, and the mixture was stirred for 4 h at room temperature until gas evolution ceased. The solvent was reduced to a volume of approximately 10 mL. Crystallization at −25 °C afforded 0.36 g (64%) of green crystalline **1**. MS (EI): m/z (%) = 479 (20) [$M^+ - CH_3NHCH_2$], 427 (22) [$M^+ -$ Me_2pzH], 384 (60) [$M^+ - CH_3NHCH_2 - Me_2pz$], 96 (100) [$Me_2pzH$], 44 (55) [$CH_2NHCH_3$]. Anal. Calcd for $C_{22}H_{35}MoN_9$ (521.51): C 50.67, H 6.76, N 24.17. Found: C 49.5, H 7.1, N 23.3. Measurement of μ_{eff} by the Evans' method gave 3.0 μ_B.

Preparation of $Mo(t\text{-}Bu_2pz)_3(NMe_2)$ (2). A solution of t-Bu_2pzH (0.83 g, 4.19 mmol) in 10 mL of toluene was added to a solution of $Mo(NMe_2)_4$ (0.42 g, 1.54 mmol) in 12 mL of toluene, and the mixture was stirred for 15 h at room temperature. The solvent was reduced to a volume of approximately 5 mL. Crystallization at −25 °C afforded 0.93 g (89%) of brown crystalline **2**. MS (EI): m/z (%) = 679 (20) [M^+], 636 (100) [$M^+ - NMe_2$], 579 (10) [$M^+ - NMe_2, - t\text{-}Bu$], 499 (30) [$M^+ - t\text{-}Bu_2pz$]. Anal. Calcd for $C_{35}H_{63}MoN_7$ (677.86): C 62.01, H 9.37, N 14.46. Found: C 62.4, H 9.5, N 14.6. Measurement of μ_{eff} by the Evans' method gave 2.8 μ_B.

Preparation of $Mo(t\text{-}Bu_2pz)_4$ (3). A mixture of $MoCl_4(thf)_2$ (0.40 g, 1.05 mmol) and t-Bu_2pzK (0.91 g, 4.19 mmol) in 30 mL of toluene was stirred at room temperature for 15 h. After filtration through a 2.5 cm pad of Celite, the brown filtrate was concentrated to 5 mL and stored at −25 °C to afford **3** (0.36 g, 42%) as a brown crystalline solid. MS (EI): m/z (%) = 814 (100) [M^+], 757 (10) [$M^+ - t\text{-}Bu$], 635 (60) [$M^+ - t\text{-}Bu_2pz$]. Anal. Calcd for $C_{44}H_{76}MoN_8$ (813.07): C 65.00, H 9.42, N 13.78. Found: C 64.9, H 9.5, N 13.7. Measurement of μ_{eff} by the Evans' method gave 2.8 μ_B.

X-ray Crystallography Analyses. Single crystals of compound **1** suitable for X-ray diffraction were obtained by recrystallization from concentrated hexane solutions at −25 °C; those for **2** and **3** by recrystallization from concentrated toluene solutions at −25 °C. All the crystals were mounted on glass fibers in mineral oil. Diffraction data were collected at −140 °C on a STOE IPDS II diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97[55] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[56] The hydrogen atoms on N(8) and N(9) in complex **1** were located in the difference Fourier map and refined without restraints. All other hydrogen atoms were included in the model at geometrically calculated positions and refined isotropically according to the riding model. The crystal data are summarized in Table 4.

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Supporting Information Available: Complete data of X-ray diffraction analyses for structures of the complexes **1**−**3**, including tables of atomic coordinates, thermal parameters, bond lengths and angles, and hydrogen parameters. This material is available free of charge via the Internet at http://pups.acs.org.

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