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Article

Molybdenum Oxo and Imido Complexes of β-Diketiminate Ligands: Synthesis and Structural Aspects

Ganna Lyashenko,[†] Regine Herbst-Irmer,[‡] Vojtech Jancik,[‡,§] Aritra Pal,[‡] and Nadia C. Mösch-Zanetti*[,†]

Institut für Chemie, Karl-Franzens-Universität Graz, Schubertstrasse 1, A-8010 Graz, Austria, and
Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstrasse 4,
D-37077 Göttingen, Germany

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Treatment of [$MoO_2(\eta^2\text{-Pz})_2$] (Pz = 3,5-di-*tert*-butylpyrazolate) with the diketiminate ligand NacNacH (NacNac = $CH[C(Me)NAr]_2^-$, Ar = 2,6-$Me_2C_6H_3$) at 55 °C leads under reduction of the metal to the formation of the dimeric molybdenum(V) compound [{MoO_2(NacNac)}$_2$] (**1**). The compound was characterized by spectroscopic means and by X-ray crystal structure analysis. The dimer consists of a [Mo_2O_4]$^{2+}$ core with a short Mo–Mo bond (2.5591(5) Å) and one coordinated diketiminate ligand on each metal atom. The reaction of [$MoO_2(\eta^2\text{-Pz})_2$] with NacNacH in benzene at room temperature leads to a mixture of **1** and the monomeric molybdenum(VI) compound [MoO_2(NacNac)(η^2-Pz)] (**2**). From such solutions, yellow crystals of **2** suitable for X-ray structural analysis were obtained revealing the coordination of one bidentate NacNac and one η^2-coordinate Pz ligand. This renders the two oxo groups inequivalent. Further high oxidation state molybdenum compounds containing the NacNac ligand were obtained by the reaction of [$Mo(NAr)_2Cl_2$(dme)] (Ar = 2,6-$Me_2C_6H_3$) and [Mo(N-*t*-Bu)$_2Cl_2$(dme)] (dme = dimethoxyethane) with 1 equiv of the potassium salt NacNacK forming [$Mo(NAr)_2Cl$(NacNac)] (**3**) and [Mo(N-*t*-Bu)$_2$Cl(NacNac)] (**4**), respectively, in good yields. The X-ray structure analysis of **3** revealed a penta-coordinate compound where the geometry is best described as trigonal-bipyramidal.

Introduction

The β-diketiminate ligands are being widely used for syntheses of different kinds of metal compounds.[1] First examples were already reported in the 1960s for late-transition metals.[2] But the real development in this direction started in the 1990s, after β-diketiminato ligands were used as spectator ligands and metal complexes thereof were synthesized for various applications such as catalysis (Cr,[3] Ni,[4] and Ti [5]), bioinorganic chemistry (Cu,[6] Fe [7]), or coordination chemistry (Al,[8] Fe,[9] and Zn [10]). A reason for the success of the ligand system is the easy variation of the substitutents which allows for the adjustment of steric bulk and electronic effects leading to unusual complexes. In addition, the conjugated nature of the bidentate nitrogen-

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* To whom correspondence should be addressed. E-mail: nadia.moesch@uni-graz.at.

[†] Karl-Franzens-Universität Graz.

[‡] Georg-August-Universität Göttingen.

[§] Currently at Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510, México D.F., México.

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based ligand makes it an interesting candidate for the development of model complexes for metalloenzymes where the metal is coordinated by histidine of porphyrin ligands.

In recent years, our research has focused on model chemistry for a class of enzymes that catalyze oxygen atom transfer (OAT) from or to a substrate commonly referred as *oxotransferases*.[11,12] They consist of a mononuclear high oxidation state molybdenum atom that is coordinated by at least one oxygen atom and one or two molybdopterin ligands, the latter being a dithiolene system.[13,14] To influence steric and redox properties of the OAT reaction, model chemistry has focused on the $[MoO_2]^{2+}$ core and on the variation of co-ligands that are S,S-, N,S-, and N,O-based.[12,15,16] Far less investigated are N,N-based molybdenum dioxo compounds that are catalysts in OAT reactions.[11,17] Recently, we reported unusual complexes employing η^2-pyrazolate ligands that lead to trigonal prismatic molybdenum dioxo complexes capable of catalyzing the oxygen atom transfer from dimethyl sulfoxide to triphenylphosphine.[11] The hard nitrogen atoms contrast the soft ligation in the natural enzymes leading to systems with unique properties.

For this reason, we got attracted by the idea of coordinating the widely used nitrogen-based β-diketiminate ligands to the molybdenum dioxo core. To our surprise, a literature search did not reveal any molybdenum(VI) oxo complexes with the β-diketiminate ligands. A few related examples are known that contain 1,4,8,11-tetraaza(14)annulene type ligands consisting of a β-diketiminate unit.[18,19] In addition, the literature search revealed not only the absence of oxo compounds but also the scarcity of any high oxidation state molybdenum compound with these types of ligands. Only very recently, imido alkylidene complexes containing β-diketiminate ligands were reported by Schrock and co-workers.[20]

In this paper we describe the introduction of the NacNac ligand to the $[MoO_2]^{2+}$ core by using $[MoO_2(\eta^2\text{-Pz})_2]$ as a precursor where the η^2-Pz ligand serves as the leaving group. In comparison, the non-oxidizing cores $[Mo(NAr)_2]^{2+}$ (Ar = 2,6-$Me_2C_6H_3$) and $[Mo(N\text{-}t\text{-}Bu)_2]^{2+}$ allowed the coordination of the NacNac ligand by conventional metal−chloride metathesis. Syntheses, spectroscopic data, and the crystallographic characterization of new oxo and imido compounds are reported.

Experimental Section

General Methods. All manipulations were carried out under dry nitrogen or argon using standard Schlenk line or glovebox techniques. All solvents were purified by standard methods and distilled over sodium/benzophenone under argon atmosphere immediately prior to use. NacNacH,[1] NacNacK,[21] KPz,[22] $[MoO_2Cl_2]$,[23] $[MoO_2(\eta^2\text{-Pz})_2]$,[11b] $[Mo(NAr)_2Cl_2(dme)]$ (dme = dimethoxyethane),[24] and $[Mo(N\text{-}t\text{-}Bu)_2Cl_2(dme)]$[24] were prepared according to literature procedures. All other chemicals mentioned were used as purchased from commercial sources (Aldrich, Merck).

Samples for mass spectrometry were measured on a BIO-RAD Digilab FTS-7 mass spectrometer with a Finnigan MAT 95 and all NMR spectra on a Bruker Avance 200, 360, or 500 MHz. Spectra were obtained at 25 °C unless otherwise noted. Elemental analyses were performed by the Analytisches-Chemisches Laboratorium des Instituts für Anorganische Chemie der Technischen Universität Graz, Austria. IR spectra were recorded on a Perkin-Elmer FT-IR Spectrometer 1725X as Nujol mull between KBr plates.

$[\{MoO_2(NacNac)\}_2]$ (1). Freshly sublimed $[MoO_2(\eta^2\text{-Pz})_2]$ (0.50 g, 1.02 mmol) and NacNacH (0.61 g, 1.99 mmol) were dissolved in toluene (30 mL) and stirred for 12 h at 55 °C. After cooling to room temperature, a significant amount of black-green solid was filtered off. The brown-orange filtrate was evaporated in vacuo, and the resulting solid was thoroughly rinsed with pentane affording the dimer **1** as a brown powder. Yield: 0.22 g (25% based on Mo). Crystals suitable of X-ray diffraction analysis were obtained by cooling a toluene solution to +5 °C. ^1H NMR (360 MHz, C_6D_6): δ 1.37 (s, 6H, N−C(CH_3)), 1.47 (s, 6H, CH_3-Ar), 2.30 (s, 6H, CH_3-Ar), 5.29 (s, 1H, γ-*H*), 6.80−6.99 (m, 6H, *H*-Ar). $^{13}C\{^1H\}$ NMR (360 MHz, C_6D_6): δ 18.1, 18.5, 24.8, 103.3, 125.2, 129.2, 130.4, 133.1, 150.6, 167.4. MS (EI): *m/z* 867 (100%) ($[\{MoO_2(NacNac)\}_2^+]$). IR (KBr): 959 (vs), 762 (vs) cm^{-1}. Anal. Calcd for $C_{42}H_{50}N_4O_4Mo_2$: C, 58.20; H, 5.81; N, 6.46. Found: C, 57.91; H, 5.77; N, 6.45.

$[MoO_2(NacNac)(\eta^2\text{-Pz})]$ (2). Crystals suitable for X-ray diffraction analysis were obtained by the following procedure: a solution of NacNacH (0.016 g, 0.052 mmol) in C_6D_6 (2 mL) was added to a vigorously stirred solution of freshly sublimed $[MoO_2(\eta^2\text{-Pz})_2]$ (0.025 g, 0.051 mmol) in C_6D_6 (2 mL) giving a clear orange solution. A ^1H NMR spectrum which was recorded after 20 min of ligand addition shows resonances for compound **2** and $[MoO_2(\eta^2\text{-Pz})_2]$ in the ratio 1:1, together with those for approximately 5 equiv of PzH. Storing the solution at room temperature for a few days led to the formation of a dark-green precipitate together with several yellow crystals. These crystals were picked for the crystal structure determination. ^1H NMR of the aliquot taken after 20 min reaction time (200 MHz, C_6D_6) of **2**: δ 1.10 (br s, 18 H, 2C(CH_3)$_3$), 1.50 (s, 6H, 2CH_3), 2.20 (s, 12H, 4CH_3), 5.20 (s, 1H, γ-*H*), 6.14 (s, 1H, γ-*H*), 6.90−7.20 (m, 6H, *H*-Ar).

$[Mo(NAr)_2Cl(NacNac)]$ (3). To $[Mo(NAr)_2Cl_2(dme)]$ (0.49 g, 0.99 mmol) and NacNacK (0.34 g, 0.98 mmol) was added diethyl ether (30 mL). The mixture was stirred under reflux for 12 h affording a dark cherry-red suspension, which was cooled to room temperature and filtered over a pad of Celite. The filtrate was concentrated to half and left at −20 °C overnight. Orange crystals were collected on a frit, thoroughly rinsed with pentane and dried in vacuo, giving **3** as an orange powder. Yield: 0.51 g (75%).

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Crystals suitable for X-ray diffraction were obtained by storing of a concentrated THF solution at −20 °C. ^{1}H NMR (360 MHz, toluene-d_8): δ 1.53 (s, 3H, N−C(CH_3)), 1.67 (s, 3H, N−C(CH_3)), 2.14 (s, 6H, CH_3-Ar), 2.32 (s, 6H, CH_3-Ar), 2.41 (s, 12H, CH_3-Ar), 5.43 (s, 1H, γ-*H*), 6.45−7.02 (m, 12H, *H*-Ar). ^{1}H NMR (360 MHz, toluene-d_8, −30 °C): δ 1.45 (s, 3H, N−C(CH_3)), 1.62 (s, 3H, N−C(CH_3)), 2.14 (s, 6H, CH_3-Ar), 2.24 (s, 3H, CH_3-Ar), 2.32 (s, 3H, CH_3-Ar), 2.43 (s, 6H, CH_3-Ar), 2.51 (s, 3H, CH_3-Ar), 2.67 (s, 3H, CH_3-Ar), 5.34 (s, 1H, γ-*H*), 6.47−7.06 (m, 12H, *H*-Ar). ^{13}C{^{1}H} NMR (500 MHz, C_6D_6): δ 19.9, 20.1, 20.2, 24.0, 26.1, 104.7, 125.6, 125.8, 131.6, 152.0, 157.0, 164.4, 167.7. IR (KBr): 1375 (vs), 1265 (vs), 1243 (s), 963 (m), 763 (s) cm^{-1}. MS (EI): *m*/*z* 676 (100%) ([Mo(NAr)$_2$ClNacNac]$^+$). Anal. Calcd for $C_{37}H_{43}ClN_4Mo\cdot 3Et_2O$: C, 65.57; H, 8.20; N, 6.24. Found: C, 65.68; H, 8.26; N, 6.36.

[Mo(N-*t*-Bu)$_2$(NacNac)$_2$] (4). A mixture of [Mo(N-*t*-Bu)$_2$Cl$_2$(dme)] (0.12 g, 0.30 mmol) and NacNacK (0.10 g, 0.30 mmol) was dissolved in 30 mL of diethyl ether and refluxed for 4 h. Cooling the mixture and filtration over a pad of Celite afforded a bright yellow filtrate, which was evaporated to dryness, giving **4** as a yellow solid. Recrystallization from pentane at −30 °C overnight yielded analytically pure yellow crystals of **4**. Yield: 0.096 g (55%). ^{1}H NMR (360 MHz, C_6D_6): δ 1.23 (s, 18H, N−C(CH_3)$_3$), 1.40 (s, 3H, N−C(CH_3)), 1.64 (s, 3H, N−C(CH_3)), 2.23 (s, 6H, CH_3-Ar), 2.32 (s, 6H, CH_3-Ar), 5.23 (s, 1H, γ-*H*), 6.87−7.08 (m, 6H, *H*-Ar). ^{13}C{^{1}H} NMR (360 MHz, C_6D_6): δ 19.8, 23.2, 25.6, 29.8, 71.6, 102.5, 124.8, 125.4, 131.7, 132.1, 152.1, 158.4, 163.2, 166.6. IR (KBr): 1262 (s), 1020 (s), 856 (m), 766 (vs) cm^{-1}. MS (EI): *m*/*z* 580 (100%) ([Mo(N-*t*-Bu)$_2$ClNacNac]$^+$). Anal. Calcd for $C_{29}H_{43}ClN_4Mo$: C, 60.15; H, 7.48; N, 9.68. Found: C, 60.03; H, 7.63; N, 9.78.

X-ray Crystallographic Determinations. Crystals of compounds **1**−**3** were taken from the solution, covered with oil, mounted on nylon loops, and placed immediately in a protective stream of cold nitrogen (100 K). Data were collected on a Bruker three-circle diffractometer equipped with Smart 6000 CCD area detector using mirror-monochromated Cu Kα radiation (α = 1.541 78 Å). The data for compounds **2** and **3** were collected on a non-merohedrally twinned and on a split crystal, respectively. The data were corrected with the program TWINABS.[25a] The fractional contributions of the minor domains were determined as 0.3842 and 0.014, respectively. The structures were solved by direct methods using SHELXS-97[25b] and refined against F^2 on all data by full-matrix least-squares method with SHELXL-97.[25c] All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model with U_{ij} tied to the parent atom, except the γ-proton from the NacNac ligand, whose localization from the electron density map led to a better model and better *R* values. In structure 3 the THF group was disordered about two positions. It was refined with distance restraints and restraints for the anisotropic displacement parameters. Selected bond lengths and angles as well as a summary of crystallographic and refinement details is found in Tables 1 and 2 as well as in the Supporting Information in CIF format.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes [{MoO$_2$(NacNac)}$_2$] (**1**), [MoO$_2$(NacNac)(η^2-Pz)] (**2**), and [Mo(NAr)$_2$Cl(NacNac)] (**3**)[a]

	Compound **1**		
Mo1−O1	1.966(1)	Mo1−N2	2.094(2)
Mo1−O2	1.686(1)	Mo1−Mo1a	2.5591(5)
Mo1−N1	2.151(2)	Mo1−O1a	1.907(1)
O2−Mo1−N1	94.77(6)	O2−Mo1−O1	104.99(6)
O1a−Mo1−N1	82.96(6)	O1a−Mo1−O1	89.90(6)
N2−Mo1−N1	86.45(6)	O2−Mo1−N2	110.65(6)
O1−Mo1−N1	159.95(6)	O1a−Mo1−N2	128.63(6)
O2−Mo1−O1a	120.22(6)	O1−Mo1−N2	83.43(6)
	Compound **2**		
Mo1−O1	1.706(2)	Mo1−N2	2.094(2)
Mo1−O2	1.725(2)	Mo1−N3	2.290(2)
Mo1−N1	2.327(2)	Mo1−N4	2.052(2)
O2−Mo1−N4	95.32(9)	N4−Mo1−N3	36.50(7)
O1−Mo1−N4	107.98(8)	N2−Mo1−N3	99.12(8)
O2−Mo1−O1	102.99(9)	N1−Mo1−O1	86.09(8)
O1−Mo1−N2	113.21(8)	O2−Mo1−N1	169.89(8)
N2−Mo1−O2	91.60(8)	N4−Mo1−N1	85.92(8)
N4−Mo1−N2	135.38(8)	N2−Mo1−N1	80.59(8)
O1−Mo1−N3	142.58(8)	N3−Mo1−N1	80.95(7)
O2−Mo1−N3	94.06(8)		
	Compound **3**		
Mo1−N1	2.086(2)	Mo1−N4	1.761(2)
Mo1−N2	2.271(2)	Mo1−Cl1	2.3918(8)
Mo1−N3	1.759(2)		
N2−Mo1−Cl1	81.88(6)		
Mo1−N4−C30	165.41(16)	N4−Mo1−N2	159.28(8)
N3−Mo1−N1	106.57(8)	N2−Mo1−N1	84.25(7)
N4−Mo1−N1	94.73(8)	N3−Mo1−Cl1	108.90(7)
N2−Mo1−N3	92.45(8)	Mo1−N3−C22	157.89(16)

[a] Symmetry transformations used to generate equivalent atoms: (a) $-x, y, -z + {}^{1}/_{2}$.

Results and Discussion

Syntheses of the Compounds. The reaction of [MoO$_2$(η^2-Pz)$_2$] with 1 equiv of NacNacH in toluene was investigated in order to obtain compound [MoO$_2$(NacNac)(η^2-Pz)] by substitution of one pyrazolate with a NacNac ligand. The unusual starting material containing η^2-coordinate pyrazolate ligands is conveniently prepared by the reaction of [MoO$_2$Cl$_2$] and KPz as we have previously reported.[11b] The reduced stability of the three-membered metallacycle in [MoO$_2$(η^2-Pz)$_2$] in comparison to a six-membered cycle formed by a coordinated NacNac ligand seemed to us the appropriate driving force for product formation.

For this reason a 1:1 mixture of [MoO$_2$(η^2-Pz)$_2$] and NacNacH in C_6D_6 was heated to 55 °C and monitored by ^{1}H NMR spectroscopy by taking aliquots every hour. Figure 1 depicts the ^{1}H NMR spectrum of the aliquot taken after 1 h (olefinic region between 6.2 and 5.2 ppm). Next to the resonance at 5.98 and 6.20 ppm belonging to the γ-H of the Pz ligand in PzH and [MoO$_2$(η^2-Pz)$_2$], respectively, new resonances appeared that are assignable to compound [MoO$_2$(NacNac)(η^2-Pz)] (**2**) (see Scheme 1): two singlets of equal intensity at 5.20 and 6.14 ppm for the γ-H of coordinated NacNac and η^2-Pz units. However, another singlet at 5.29 ppm for an additional compound is apparent. With progressive reaction time (12 h), in the ^{1}H NMR spectrum only resonances for this additional compound were detectable. The chemical shifts point to a compound containing a coordinated NacNac ligand. The absence of an additional resonance for a η^2-Pz ligand and the unlikeliness of two coordinated NacNac ligands to one molybdenum atom led to the

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Table 2. Summary of Crystallographic Data for Compounds **1**, **2,** and **3**·THF

	1	**2**	**3**·THF
M	866.74	604.60	747.25
formula	$C_{42}H_{50}Mo_2N_4O_4$	$C_{32}H_{44}MoN_4O_2$	$C_{37}H_{43}ClMoN_4$·THF
cryst syst	monoclinic	orthorhombic	triclinic
space group	*C*2/*c*	*Pbca*	$P\bar{1}$
a (Å)	19.982(3)	15.823(3)	8.747(2)
b (Å)	8.848(2)	14.668(3)	10.923(2)
c (Å)	23.761(2)	26.703(5)	19.725(4)
α (deg)	90	90	84.18(3)
β (deg)	109.81(2)	90	79.16(3)
γ (deg)	90	90	83.00(3)
V ($Å^3$)	3952(1)	6198(2)	1831(1)
cryst size (mm^3)	0.15 × 0.10 × 0.10	0.10 × 0.05 × 0.05	0.30 × 0.20 × 0.10
ρ_{calc} ($g \cdot cm^{-3}$)	1.457	1.313	1.355
Z	4	8	2
μ (mm^{-1})	5.558	3.718	3.883
Θ range (deg)	3.95−58.95	3.31−59.05	2.29−58.99
reflns collected	18 849	85 569	32 292
R_{int}	0.0286	0.0550	0.0382
data/restraints/params	2806/0/242	4391/0/367	5099/196/494
GOF on F^2	1.073	1.065	1.055
R1 indices [$I > 2\sigma(I)$][a]	0.0191	0.0300	0.0250
wR2 (all data)[a]	0.0523	0.0798	0.0649
largest peak and hole ($e \cdot Å^{-3}$)	0.371 and −0.309	0.468 and −0.626	0.444 and −0.361

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

conclusion that the dimeric compound $[\{MoO_2(NacNac)\}_2]$ (**1**) formed under reduction of the metal center.

The NMR experiment provided us with a protocol for the isolation of **1** in bulk quantity. Thus, $[MoO_2(\eta^2\text{-Pz})_2]$ and 2 equiv of NacNacH were dissolved in 30 mL of toluene and heated to 55 °C for 12 h. After workup compound **1** was isolated in low yield. ^1H and ^{13}C NMR spectra show resonances for one set of a symmetrically coordinated NacNac ligand. Thus, the ^1H NMR spectrum shows three singulets of equal intensity at 1.37, 1.47, and 2.30 ppm for the six methyl groups in each ligand consistent with a symmetric coordination and a barrier to rotation along the nitrogen aryl bond rendering the two *o*-methyl groups at Ar inequivalent. The resonance for the *γ*-proton appears at 5.29 ppm identical to the value detected with the NMR experiment discussed above. The ^{13}C NMR spectrum also confirms the coordination of a NacNac ligand: three signals for the six methyl groups at 18.1, 18.5, and 24.8 ppm and one resonance at 103.3 ppm for the *γ*-proton. The line width and the shift of the resonances point to a diamagnetic compound consistent with a dimeric species in which the two d electrons of the two Mo(V) centers couple with each other. Mass spectrometry (EI) revealing a peak for $[\{MoO_2(NacNac)\}_2]^+$ at *m*/*z* 867 with the correct isotopic distribution, whereas a peak for $[MoO_2(NacNac)_2]^+$ was consistently absent, also provided evidence for a dimeric compound. The $[Mo_2O_4]^{2+}$ core in general is pervasive in molybdenum chemistry, but low coordination numbers at the metal center as in **1** are rarer.[26−30] The large steric influence of the NacNac ligand is presumably responsible, so that the usual octahedral geometry is not obtained. A search in the Cambridge Structural Database showed examples with anionic nitrogen ligands to be almost absent. A vaguely related compound represents the octamolybdenum oxo-pyrazolate cluster containing $[Mo_2O_2]^{2+}$ cores bridged by anionic pyrazolates.[31] The IR spectrum of **1** revealed a vibration typical for terminal Mo═O groups at 959 cm^{-1} and one due to the Mo−O−Mo stretching vibration at 762 cm^{-1}, which is in a good agreement with literature compounds.[17,32]

The X-ray diffraction analysis unambiguously confirmed the dimeric structure (Figure 2, crystallographic data in Tables 1 and 2). Suitable single crystals of $[\{MoO_2(NacNac)\}_2]$ (**1**) were obtained by cooling a concentrated toluene solution to +5 °C. A symmetry axis running between the two Mo═O bonds converts the crystallographically independent unit into a dimer. Thus, in the compound each

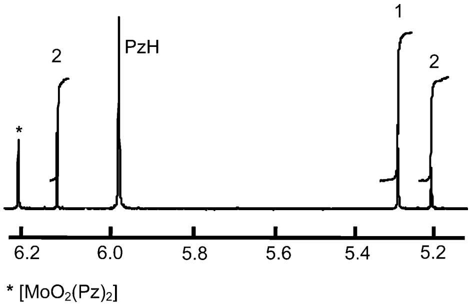

Figure 1. ^1H NMR spectrum of the reaction between $[MoO_2(\eta^2\text{-Pz})_2]$ and NacNacH taken after 1 h reaction time showing resonances for the *γ*-H of $[\{MoO_2(NacNac)\}_2]$ (**1**) and $[MoO_2(NacNac)(\eta^2\text{-Pz})]$ (**2**) next to those of unreacted $[MoO_2(\eta^2\text{-Pz})_2]$ and formed PzH.

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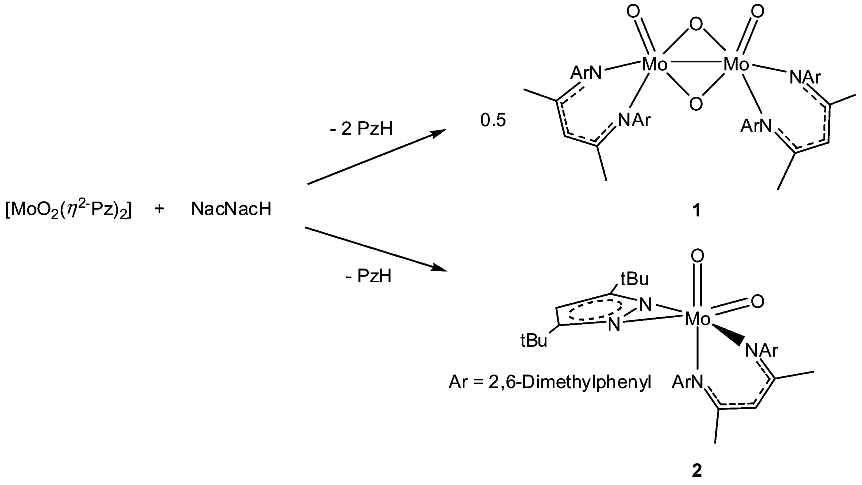
Scheme 1



Mo center is pentacoordinate and the two terminal oxo ligands are in the cis position to each other. The geometry about the metal is between a trigonal bipyramid and a square pyramid with a τ value of 0.52,[33] where 1 would represent the former and 0 the latter geometry. The τ value is large in comparison to other structures of this type pointing to a high degree of distortion.[27−30] Other features, such as the metal−metal distance (Mo1−Mo1a, 2.5591(5) Å) or the metal oxygen single bonds (Mo1−O1, 1.966(1) Å) and double bonds (Mo1−O2, 1.686(1) Å) are similar to those in the literature.[29] The Mo−N distances, Mo1−N1 = 2.151(2) and Mo1−N2 = 2.094(2) Å, are in a good agreement with those in the octamolybdenum oxo pyrazolate cluster mentioned above.[31]

The isolation and characterization of compound **2** was more challenging as all attempts to obtain it in pure form led to material that was contaminated by **1** or by [MoO$_2$(η^2-Pz)$_2$]. This is consistent with the data obtained by monitoring the reaction by NMR spectroscopy showing always additional resonances for [MoO$_2$(η^2-Pz)$_2$] and/or **1**. The crystallizing behavior of these compounds seems to be similar as no separation could be achieved. However, from such mixtures, crystals of **2** could be selected that were suitable for X-ray diffraction analysis confirming the coordination of a NacNac and a η^2-Pz ligand (Figure 3 and crystallographic data in Tables 1 and 2). The molecular structure of [MoO$_2$(NacNac)(η^2-Pz)] (**2**) shows several interesting features. The coordination of a η^2-Pz ligand evidenced by the two bond lengths Mo1−N3 = 2.290(2) Å and Mo1−N4 = 2.052(2) Å can still be considered unusual although we[11] and others[34] have published several examples in recent years. The small bite angle of the coordinated η^2-Pz unit (N3−Mo1−N4 = 36.50(7)°) in comparison to that of the NacNac ligand (N1−Mo1−N2 = 80.59(8)°) renders the geometry about the metal into a highly distorted octahedron. This leads to two unsymmetric metal oxo groups O1 and O2. In compound **2**, the largest O1−Mo−N angle is 142.52(8)°, whereas the angle O2−Mo−N is 169.89(8)°, pointing to heavy distortion from an octahedral structure as well as to the unsymmetrical coordination of the two oxygen atoms. Interest in such unsymmetrical dioxo compounds is large in view of the discussion that in dioxo complexes one of the two oxo groups serves as *a spectator oxo ligand* while the other is actually transferred.[35,36] In addition, trigonal prismatic transition states seem to play a role in biological OAT reactions,[37] but model compounds showing this geometry are limited.[11] In compound **2**, the pyrazolate ligand lies approximately coplanar with the metal atom, one of the two oxygen atoms (O1) and one of the two nitrogen atoms of NacNac (N2). We have previously observed the preferred coordination of the metal oxo group coplanar to the Pz-plane in the molecular structure of the molybdenum(IV) compound [MoO(η^2-Pz)$_2$(PEt)$_2$].[11] The Mo═O bond lengths in **2,** Mo1−O1 = 1.706(2) Å and Mo1−O2 = 1.725(2) Å, are in the expected range for compounds containing the [MoO$_2$]$^{2+}$ core.[11,12,38,39]

A common way to introduce a ligand to the [MoO$_2$]$^{2+}$ core is the use of [MoO$_2$Cl$_2$] or [MoO$_2$Cl$_2$(dme)] as starting materials and the addition of either a mixture of LH and triethylamine or by employing deprotonated ligands such as KL or LiL. However, all these methods were unsuccessful

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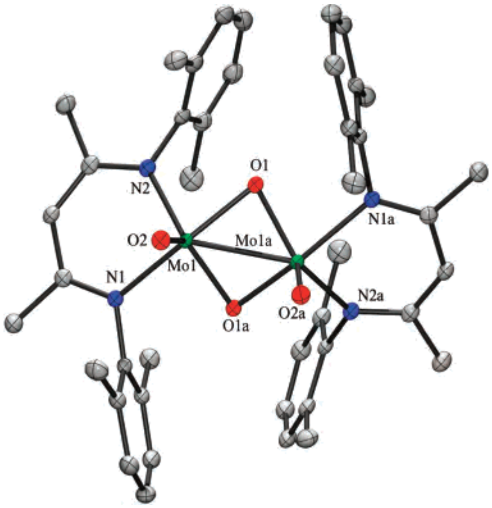

Figure 2. Molecular structure of [{MoO_2(NacNac)}$_2$] (**1**). Thermal ellipsoid plot (50% probability surface). Hydrogen atoms have been omitted for clarity.

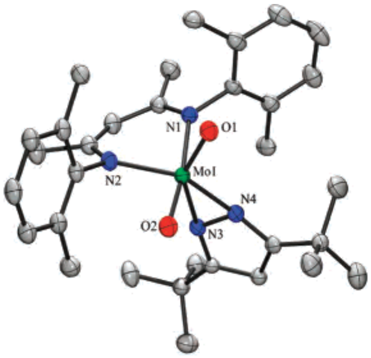

Figure 3. Molecular structure of [MoO_2(NacNac)(η^2-Pz)] (**2**). Thermal ellipsoid plot (50% probability surface). Hydrogen atoms have been omitted for clarity.

and led to mixtures from which we were not able to isolate any pure compounds, although mass spectrometry on samples obtained from such reactions gave evidence for the formation of **1** (a peak at *m*/*z* 867 for [{MoO_2(NacNac)}$_2$]$^+$). Thus, reduction of the metal center is encountered in all reactions employing the [MoO_2]$^{2+}$ core and the β-diketiminate ligand. The site of oxidation is as yet unclear, but oxidative degradation of the NacNac backbone seems likely. Such a degradation has recently been reported in NacNac copper and zinc complexes where aerobic conditions result in the formation of a ketone.[40] In addition, recently reported molybdenum imido alkylidene complexes containing a NacNac ligand feature activation at the γ-carbon in the backbone by the alkylidene.[20] In the system reported here, the nature of the decomposition product is unclear as the ^{1}H NMR spectra of the reaction solutions did not show any resonances for organic products other than the ones described above, suggesting insoluble oxidized products may have been produced.

In contrast, no reduction or any other kind of decomposition occurs by treatment of high oxidation state molybdenum(VI) compounds containing two imido instead of oxo groups. The reaction of the bisimido complexes [Mo(NAr)$_2$Cl$_2$(dme)][24] and [Mo(N-*t*-Bu)$_2$Cl$_2$(dme)][24] with the potassium salt NacNacK[21] in diethyl ether forms monosubstituted compounds [Mo(NAr)$_2$Cl(NacNac)] (**3**) and [Mo(N-*t*-Bu)$_2$Cl(NacNac)] (**4**), respectively, in good yields (eq 1).

$$[\mathrm{Mo(NR)_2Cl_2(dme)}] + \mathrm{KNacNac} \xrightarrow{-\mathrm{KCl}} \begin{array}{l} [\mathrm{Mo(NR)_2Cl(NacNac)}] \\ \mathbf{3},\ \mathrm{R} = 2,6\text{-}\mathrm{Me_2C_6H_3} \\ \mathbf{4},\ \mathrm{R} = t\text{-}\mathrm{Bu} \end{array} \qquad (1)$$

It is worth noting that treatment of [Mo(NAr)$_2$Cl$_2$(dme)] and [Mo(N-*t*-Bu)$_2$Cl$_2$(dme)] with 2 or more equiv of NacNacK does not afford disubstituted complexes, but rather compounds **3** and **4** are isolated in all attempts consistent with the large steric impact of the NacNac ligand.

The ^{1}H NMR spectra of **3** and **4** confirm the formation of monosubstituted compounds as the integration of the resonances attributable to the γ-protons of NacNac vs the aromatic region in **3** amounts to 1:12 and vs the aliphatic region in **4** to 1:36. In both compounds the NacNac ligand is coordinated in an unsymmetrical fashion as the two methyl groups in the backbone give rise to two singlets of equal intensity, whereas the two aromatic substituents can freely rotate along the N−C(Ar) bond evidenced by the occurrence of only two singlets with the intensity of 6 each. ^{13}C NMR data confirm the structure of the two compounds. However, the ^{13}C NMR spectrum of compound **4** shows only one resonance at 19.8 ppm for the two sets of two inequivalent methyl groups attached to the aromat of the NacNac unit which was confirmed by a HSQC spectrum (see Supporting Information). Interestingly, only one set of resonance appears in the spectra of both compounds for the two imido groups. Thus, the broad signal at 2.41 ppm in the ^{1}H NMR spectrum of **3** can be assigned to the four methyl groups of the imido aromats and in the spectrum of **4** the singlet at 1.23 ppm to the two imido *t*-Bu groups. This points to a dymanic process in solution which was investigated by low-temperature ^{1}H NMR spectroscopy by taking compound **3** as an example. Thus, cooling a sample of **3** in toluene-d_8 to −30 °C shows splitting of the broad resonance at 2.41 ppm into four singlets of equal intensity at 2.24, 2.32, 2.51, and 2.67 ppm. However, the rotation along the N−C(Ar) bond of the NacNac ligand is still not restricted at this temperature as the corresponding resonances broaden slightly but remain at 2.14 and 2.43 ppm. Similar behavior has been found in bisimido complexes with bidentate phenolate ligands [Mo(NAr)$_2$(L)X] (L = OC_6H_4-CH_2NMe_2), where the four ortho-substituents on the imido aryl groups are found to be equivalent at room temperature.[41]

The IR spectra shows characteristic Mo═N stretching vibrations at 1265 and 1262 cm^{-1} for **3** and **4**, respectively, which is in good agreement with the literature.[42] Electron impact mass spectrometry revealed the molecular ion for both compounds with the correct isotopic patterns.

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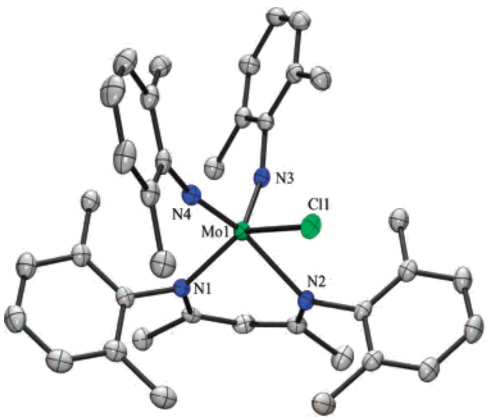
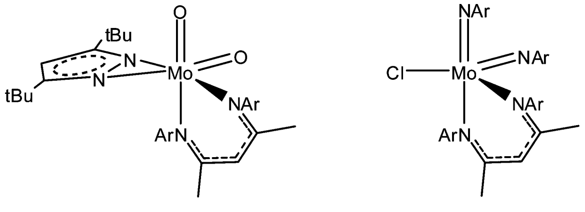


Figure 4. Molecular structure of [Mo(NAr)$_2$Cl(NacNac)] (**3**). Thermal ellipsoid plot (50% probability surface). Hydrogen atoms have been omitted for clarity.

X-ray diffraction analysis of a suitable single crystal of **3** obtained by recrystallization from a cold THF solution (−20 °C) overnight allowed the determination of its molecular structure (Figure 4 and crystallographic data in Tables 1 and 2). The molybdenum atom is pentacoordinate and the geometry is best described as trigonal-bipyramidal[33] (largest angle, N2−Mo1−N4 = 159.28(8)°; second largest angle, N1−Mo1−Cl1 = 142.29(5)°) with N4(imido) and N2(NacNac) in the apical positions. The two Mo−N(imido)−C angles are 165.41(16) and 157.89(16)° consistent with the expected sp hybridized nitrogen atom and a M≡N triple bond.[43] Another imido ligand shows a much less obtuse Mo1−N3−C22 angle of 157.89(16)°, which is at the low end of the linear coordination. Thus, in the solid state, all methyl groups are inequivalent, contrasting the solution data at room temperature but being in good agreement with low-temperature NMR spectroscopy described above. Both imido units are cis to each other, as expected, and the Mo═N bond lengths are Mo1−N3 = 1.759(2) and Mo1−N4 = 1.761(2) Å, comparable to those in literature.[38,41,44] The molybdenum−chloride bond length is 2.3918(8) Å, similar to those in literature.[38,45] The bond Mo1−N1 = 2.086(2) Å is in the same range as the few other bisimido amido complexes reported before.[38,44−46]

A comparison of the geometry of compound [MoO$_2$(NacNac)(η^2-Pz)] (**2**) to that of [Mo(NAr)$_2$Cl(NacNac)] (**3**) reveals interesting similarities (Figure 5). Considering the middle of the N−N bond in the η^2-Pz ligand as the coordination site, both compounds adopt similar trigonal-bipyramidal geometries with one of the NacNac N atoms in a trans position to oxo or imido group, respectively. In compounds **2** and **3** bond lengths of coordinated NacNac ligands are comparable: Mo1−N1 = 2.327(2) Å, Mo1−N2 = 2.094(2) Å in **2** and Mo1−N1 = 2.086(2) Å, Mo1−N2 = 2.271(2) Å in **3** with the longer bond being the one which is trans to the oxo or imido substituent. The larger steric impact of the pyrazolate vs the chloride ligand apparently causes the bite angle of the NacNac ligand to be smaller in comparison (N1−Mo1−N2 = 80.59(8)° in **2** and N1−Mo1−N2 = 84.25(7)° in **3**) even though the NAr is larger than an oxo group.



2 **3**

Figure 5.

Other examples of molybdenum(VI) imido compounds that contain a NacNac ligand are the previously mentioned imido alkylidene complexes reported by Schrock and coworkers.[20] Their method of synthesis corresponds to the one described in this work as the imido alkylidene starting material[47] was treated with the lithium salt of a related NacNac ligand giving [Mo(NAr)(CH-*t*-Bu)(NacNac)(OTf)] (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$), which was crystallographically characterized. The relevant bond lengths and angles of the diketiminate ligands are similar in the two compounds (e.g. the N−Mo−N angles are 83.91(6)° in the imido alkylidene complex vs 84.25(7)° in **3** and the bond lengths are 2.1266(16) and 2.147(16) Å in Schrock's[20] and Mo1−N1 = 2.086(2), Mo1−N2 = 2.271(2) Å in **3**). This leads to similar overall geometries being trigonal-bipyramidal in both complexes with one of the NacNac nitrogen atoms and the triflate or the imido group in the apical positions, respectively.

Conclusion

We demonstrate that molybdenum oxo complexes that contain the β-diketiminate ligand NacNac can be prepared starting from the molybdenum dioxo pyrazolate complex [MoO$_2$(η^2-Pz)$_2$]. This represents a novel approach to use η^2-pyrazolate ligands as leaving groups. Monitoring of its reaction with NacNacH by NMR spectroscopy shows the formation of a mixture of dimeric [{MoO$_2$(NacNac)}$_2$] (**1**) and monomeric [MoO$_2$(NacNac)(η^2-Pz)] (**2**). The formation of the dimeric compound **1** is clearly predominant, and it is presumably formed by oxidative degradation of the ligand explaining the lack of NacNac complexes in oxidizing systems. The structures of both compounds were crystallographically determined. In contrast, the complexes [Mo(NAr)$_2$Cl(NacNac)] (**3**) and [Mo(N-*t*-Bu)$_2$Cl(NacNac)] (**4**) were prepared in good yields as the bisimido cores are not prone to reduction. We are currently working on the development of a protocol for the formation of compounds of the type [MoO$_2$(NacNac)X] by employing other molybdenum precursors allowing the introduction of the NacNac

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ligand under milder conditions in order to investigate the oxygen atom transfer activity of these unusual compounds.

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Supporting Information Available: Crystallographic data in CIF format and gHSQC spectrum of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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