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Unusual Nonoctahedral Geometry with Molybdenum Oxoimido Complexes Containing η^2-Pyrazolate Ligands

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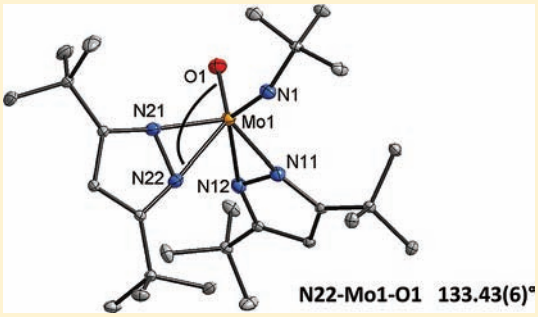
Supporting Information

ABSTRACT: The preparation and oxygen-atom-transfer (OAT) reactivity of oxoimido complexes [MoO(N-*t*-Bu)(*t*-Bu_2-4-Rpz)$_2$] [where R = H (**1**), Br (**2**), and Me (**3**); *t*-Bu_2pz = 3,5-di-*tert*-butylpyrazolate] are reported. The reaction of the potassium salt of the respective pyrazolate ligands and the molybdenum oxoimido precursor, [MoO(N-*t*-Bu)-Cl_2(dme)] (dme = dimethoxyethane), in toluene afforded complexes **1**−**3** in good yields. The complexes were fully characterized by ^{1}H and ^{13}C NMR and IR spectroscopy, mass spectrometry, elemental analysis, and single-crystal X-ray crystallography. The solid-state structures reveal that, in each case, the molybdenum center is coordinated by one oxo, one N-*t*-Bu group, and two sterically demanding pyrazolate ligands via their two adjacent nitrogen atoms in an η^2 fashion. Coordination around the metal center is severely distorted from octahedral and might be seen as closely approaching a distorted trigonal-prismatic geometry, which is relevant to the active site of dimethyl sulfoxide reductase in its oxidized form. The potential utility of all of the complexes **1**−**3** for OAT reactivity toward PMe_3 at room temperature is examined, and plausible mechanistic pathways are explored by density functional theory calculations. Furthermore, the complexes reported here open a new and convenient entry into mixed oxoimidomolybdenum complexes.



INTRODUCTION

The oxygen-atom-transfer (OAT) reaction is a fundamental process both in industrial applications and in natural systems. Its technological importance arises principally from the possibility of converting olefins (internal or terminal ones) to their corresponding epoxides, valuable starting materials for added-value synthetic products.[1] In biology, OAT is important in various degradation pathways of metabolites. A large group of enzymes is commonly referred to as oxotransferases or hydroxylases depending on whether the substrate is transformed by a primary OAT or whether a water molecule is involved in the substrate transformation. The common feature of such enzymes is the presence, at the core of the enzyme itself, of a molybdenum(VI) oxo unit, eventually complemented by an additional doubly bonded atom (S or O) and one or two dithiolene residues belonging to a pterin ligand. Depending on the arrangement around the metal atom, such enzymes can be classified in three major families, also differing among themselves in the geometry adopted, ranging from octahedral to trigonal-prismatic extremes: (i) xanthine oxidase, (ii) sulfite oxidase, and (iii) dimethyl sulfoxide (DMSO) reductase.[2−4]

Previous contributions from our group have focused on the introduction of a heteroatom in coordination complexes of oxomolybdenum(VI) in order to explore the influence of such a ligation in OAT reactions.[5] Although not found in biological systems, the advantage of introducing an imido functionality rather than a sulfur group is due to its better steric stabilization and, hence, prevention of in situ dimerization. Whereas molybdenum diimido[6] and dioxo[7] complexes are well documented in the literature, only a few mixed oxoimido complexes are known until now.[5,8]

Furthermore, our group has been active in exploring changes in the OAT reactivity by modification of the geometry imposed around the metal center: recently, we found that asymmetric molybdenum dioxo complexes exhibit significantly higher OAT activity than their symmetric analogues.[7a] We attributed this to different trans effects in the two systems and ruled out the involvement of a spectator oxo effect.[9] A series of trigonal-prismatic molybdenum(VI) dioxo complexes has also been reported, which featured the quite unusual η^2-pyrazolate anion as the ancillary ligand.[10]

Usually, pyrazolate ligands display η^1-bonding to a single metal ion or bridge between two metal centers.[11] Besides these common bonding modes, the unusual η^2-pyrazolate coordination where both nitrogen atoms coordinate to the same metal atom has been demonstrated in the past decade in coordination chemistry. The first η^2-pyrazolate ligation in a transition-metal complex was reported by Erker and co-workers.[12] Subsequently, it was found that sterically demanding pyrazolate ligands coordinate predominantly η^2 to electrophilic transition-

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metal centers, as shown by Winter et al.[13] and us,[10,14] and to lanthanoids, as shown by Deacon and co-workers.[15]

We have published molybdenum *cis*-dioxo complexes $[MoO_2Cl(\eta^2\text{-}t\text{-}Bu_2\text{-}pz)]$ and $[MoO_2(\eta^2\text{-}t\text{-}Bu_2\text{-}pz)_2]$ with η^2-coordinate pyrazolate ligands.[10] The small metallacycle formed by the two nitrogen atoms of the pyrazolate and the metal leads to distorted trigonal-prismatic geometries. Molybdenum oxo complexes in a trigonal-prismatic coordination environment are biologically relevant because of their resemblance to the active site of DMSO reductases.[4d] In addition, we found $[MoO_2Cl(\eta^2\text{-}t\text{-}Bu_2\text{-}pz)]$ and $[MoO_2(\eta^2\text{-}t\text{-}Bu_2\text{-}pz)_2]$ to be convenient starting materials for the synthesis of molybdenum coordination compounds by offering easier purification of the products.[7f,16] The pyrazolate ligand can be easily exchanged by any other ligand and the formed pyrazole conveniently removed by washing or sublimation. A more conventional method employing $[MoO_2Cl_2]$ leads most often to lower yields.

In the present paper, we have decided to combine the heteroatom ligation with a nonoctahedral geometry, preparing molybdenum oxoimido complexes that contain sterically demanding pyrazolate ligands and investigating their OAT properties. Here, we report the synthesis, structural characterization, and OAT behavior of $[MoO(N\text{-}t\text{-}Bu)(\eta^2\text{-}t\text{-}Bu_2\text{-}4\text{-}Rpz)_2]$ [where R = H (**1**), Br (**2**), and Me (**3**)].

EXPERIMENTAL SECTION

General Procedures. All syntheses were performed under an atmosphere of dry argon using glovebox or Schlenk techniques. The starting materials $[MoO_2Cl_2(dme)]$,[17] $[Mo(N\text{-}t\text{-}Bu)_2Cl_2(dme)]$,[6h] $[MoO(N\text{-}t\text{-}Bu)Cl_2(dme)]$,[8c] 3,5-di-*tert*-butylpyrazole (t-Bu$_2$pzH),[18] 3,5-di-*tert*-butyl-4-bromopyrazole (t-Bu$_2$-4-BrpzH),[10a] t-Bu$_2$pzK,[13g] and t-Bu$_2$-4-BrpzK[10a] were prepared according to published procedures. 3,5-Di-*tert*-butyl-4-methylpyrazole (t-Bu$_2$-4-MepzH)[19] and the corresponding potassium salt (t-Bu$_2$-4-MepzK) were prepared with slight modifications with respect to the literature procedure.[14c] All other chemicals mentioned were used as purchased from commercial sources. All of the solvents were dried by a Pure Solv MD-4-EN solvent purification system from Innovative Technology, Inc., flushed with argon, and further passed through an activated aluminum oxide column prior to use. All deuterated solvents for NMR studies were purchased from Deutero GmbH and dried over molecular sieves. NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Chemical shift values are given in parts per million (ppm). Spectra were obtained at 25 °C unless otherwise noted. IR spectra were recorded with a Bruker Alpha FT-IR spectrometer. Electron impact mass spectra were measured on an Agilent 5973 direct probe. Elemental analyses were carried out using a Heraeus Vario Elementar automatic analyzer at the Institute of Inorganic Chemistry, Graz University of Technology, Graz, Austria.

OAT reactions were carried out by reacting freshly prepared complexes **1**−**3** and PMe_3 in a 1:4 ratio in 1 mL of dry benzene (C_6D_6).

Synthesis of Ligands. The diketone 2,2,4,6,6-pentamethyl-3,5-heptanedione was prepared with a slight modification from the literature procedure, as described in the following:[19]

To a suspension of sodium (1.7 g, 74 mmol) in 30 mL of benzene was added slowly at 5 °C 2,2,6,6-tetramethyl-3,5-heptanedione (11.48 g, 62.3 mmol). The reaction mixture was allowed to warm to room temperature and then stirred at 50 °C for 24 h. Subsequently, the reaction flask was placed in a refrigerator (8 °C) for 1 day, during which a colorless crystalline material precipitated. To this mixture was added dropwise at 5 °C methyl iodide (19.87 g, 140 mmol). The resulting solution was heated to 80 °C for 15 h. The formed yellow precipitate was filtered off, the colorless filtrate was collected in a Schlenk flask, and the solvent was removed at atmospheric pressure. The product 2,2,4,6,6-pentamethyl-3,5-heptanedione was collected by distillation at 130 °C in vacuo (1.0 mbar). Yield: 7.4 g (60%). ^{1}H NMR (C_6D_6): δ 0.979 (s, 18H, t-BuH), 1.16 (d, 3H, CCH_3), 4.07 (q, CH). ^{13}C NMR (C_6D_6): δ 15.3 (CCH_3), 27.5 (C(CH_3)$_3$), 44.2 (C(CH_3)$_3$, 49.6 (CCH_3), 211.0 (C=O).

Synthesis of 3,5-Di-*tert*-butyl-4-methylpyrazole (t-Bu$_2$-4-MepzH). This ligand was prepared following the reported procedure for t-Bu$_2$pzH[18] except that 2,2,4,6,6-pentamethyl-3,5-heptanedione was used instead of 2,2,6,6-tetramethyl-3,5-heptanedione to yield 5.4 g (95%) of the product as a white solid. ^{1}H NMR (C_6D_6): δ 1.35 (s, 18H, t-BuH), 2.20 (s, 3H, ring CH_3), 10.35 (br, 1H, NH). ^{13}C NMR (C_6D_6): δ 11.7 (ring CCH_3), 26.2 (C(CH_3)$_3$), 29.8 (C(CH_3)$_3$), 32.5 (ring CCH_3), 107.7 (CC(CH_3)$_3$).

Synthesis of Potassium 3,5-Di-*tert*-butyl-4-methylpyrazolate (t-Bu$_2$-4-MepzK). This ligand was prepared following the reported procedure[14c] except that t-Bu$_2$-4-MepzH was used instead of t-Bu$_2$-4-BrpzH to yield 0.93 g (31%) of the product as a white solid. ^{1}H NMR ($CDCl_3$): δ 1.35 (s, 18H, t-BuH), 2.22 (s, 3H, CH_3). MS: m/z 194 (M^+ − K).

General Procedure for the Synthesis of Molybdenum Oxoimido Complexes 1−3. To a stirred solution of 0.052 g (0.15 mmol) of $[MoO(N\text{-}t\text{-}Bu)Cl_2(dme)]$ in dry toluene (3 mL) were added solutions of 0.066 g (0.30 mmol) of t-Bu$_2$pzK for the preparation of complex **1**, 0.089 g (0.30 mmol) of t-Bu$_2$-4-BrpzK for complex **2**, and 0.070 g (0.30 mmol) of t-Bu$_2$-4-MepzK for complex **3** in 2 mL of toluene. The reaction mixture was allowed to stir for 12 h followed by filtration through a pad of Celite (2 cm). The filtrate was evaporated to dryness, affording complexes **1**−**3** as pale-yellow solids. The product was extracted into dry pentane, and the volatiles were removed under vacuum, giving yellow microcrystalline solids. They were dissolved in a minimum volume of dry pentane and stored at −25 °C overnight, giving yellow crystals that proved to be suitable for X-ray diffraction analysis.

*[MoO(N-t-Bu)(t-Bu$_2$pz)$_2$] (**1**).* Yield: 0.069 g (85%). ^{1}H NMR (C_6D_6): δ 1.31 (s, 36H, t-BuH), 1.41 (s, 9H, NC(CH_3)$_3$), 6.22 (s, 2H, ring H). ^{13}C NMR (C_6D_6): δ 29.6 (NC(CH_3)$_3$), 30.3 (C(CH_3)$_3$), 32.0 (C(CH_3)$_3$), 73.8 (NC(CH_3)$_3$), 104.3 (ring CH), 160.6 (CC(CH_3)$_3$). IR (cm^{-1}): 913 (s, Mo=O). MS(EI): m/z 543 (12%; $[M]^+$), 528 (60%; $[M - (CH_3)]^+$). Anal. Calcd for $C_{26}H_{47}N_5OMo$: C, 57.65; H, 8.76; N, 12.93. Found: C, 57.30; H, 8.70; N, 12.84.

*[MoO(N-t-Bu)(t-Bu$_2$-4-Brpz)$_2$] (**2**).* Yield: 0.085 g (81%). ^{1}H NMR (C_6D_6): δ 1.28 (s, 9H, NC(CH_3)$_3$), 1.41 (s, 36H, t-BuH). ^{13}C NMR (C_6D_6): δ 28.6 (C(CH_3)$_3$), 29.4 (NC(CH_3)$_3$), 33.1 (C(CH_3)$_3$), 74.6 (NC(CH_3)$_3$), 94.7 (ring CBr), 156.0 (CC(CH_3)$_3$). IR (cm^{-1}): 909 (s, Mo=O). MS(EI): m/z 701 (10%; $[M]^+$), 686 (45%; $[M - (CH_3)]^+$). Anal. Calcd for $C_{26}H_{45}N_5Br_2OMo$: C, 44.65; H, 6.50; N, 10.02. Found: C, 45.14; H, 6.53; N, 10.07.

*[MoO(N-t-Bu)(t-Bu$_2$-4-Mepz)$_2$] (**3**).* Yield: 0.068 g (80%). ^{1}H NMR (C_6D_6): δ 1.34 (s, 36H, t-Bu), 1.37 (s, 9H, NC(CH_3)$_3$), 2.17 (s, 6H, ring CH_3). ^{13}C NMR (C_6D_6): δ 12.5 (ring CH_3), 29.9 (C(CH_3)$_3$), 30.1 (NC(CH_3)$_3$), 33.2 (C(CH_3)$_3$), 73.6 (NC(CH_3)$_3$), 115.6 (ring CCH$_3$)), 156.6 (CC(CH_3)$_3$). IR: 905 (s, Mo=O). MS(EI): m/z 571 (24%; $[M]^+$), 556 (100%; $[M - (CH_3)]^+$). Anal. Calcd for $C_{28}H_{51}N_5OMo$: C, 59.03; H, 9.04; N, 12.30. Found: C, 58.70; H, 8.85; N, 12.37.

X-ray Crystallographic Determination. Single crystals of the complexes were analyzed on a four-cycle Stoe diffractometer with graphite-monochromated Mo Kα radiation (0.710 73 Å) at 100 K. The structures were solved by direct methods (*SHELXS-97*)[20] and refined by full-matrix least-squares techniques against F^2 (*SHELXL-97*).[20] The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. In complex **1**, the hydrogen atoms H14 and H24 were put at the external bisector of the C−C−C angle at a C−H distance of 0.95 Å, but the individual isotropic displacement parameters were left free to refine. The hydrogen atoms of the methyl groups were refined with common isotropic displacement parameters for the hydrogen atoms of the same *tert*-butyl group and idealized geometries with tetrahedral angles, enabling rotation around the C−C bond, and C−H distances of 0.98 Å.

Computational Details. The OAT reaction between complexes **1**−**3** and PMe_3 was calculated using the hybrid density functional B3-LYP,[21] as implemented in the *TURBOMOLE*[22] program. All

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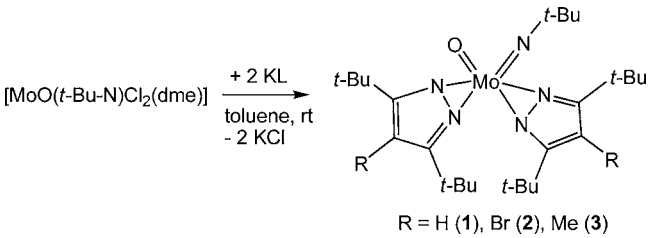
geometries were first optimized in the gas phase with the standard double-ζ quality basis set def2-SVP[23] for all atoms except molybdenum, which was treated with an effective core potential and its corresponding basis set (ecp-28-mwb-SVP). Further optimizations were performed by employing the COSMO solvation model (benzene: r_{solv} = 2.60 Å, ε_r = 2.28) with the larger basis sets ecp-28-mwb-TZVP for molybdenum and with def2-TZVP[23b,24] for all other atoms. The nature of all stationary points was confirmed by vibrational analysis. Input geometries were derived from crystal structures by replacing the bulky *tert*-butyl groups of the pyrazolates by hydrogen atoms and the *tert*-butyl group of the imido functionality by methyl to save computational costs.

RESULTS AND DISCUSSION

Three pyrazole ligands were prepared according to literature procedures.[10a,18,19] The sterically demanding *tert*-butyl groups in the 3 and 5 positions have to be present in all molecules in order to enforce η^2-coordination to the molybdenum atom and thus decrease the tendency for the formation of polynuclear complexes. Variation within the ligand system then occurred in the 4 position, ranging from the unsubstituted ligand (H**L1**) to one with an electron-withdrawing bromide (H**L2**) and one with an electron-donating methyl group (H**L3**). Potassium salts of all ligands were obtained by the addition of excess potassium hydride as white solids. They serve as excellent pyrazolate transfer reagents to the molybdenum atom.

Synthesis of the Oxoimido Complexes. Treatment of the [MoO(N-*t*-Bu)Cl_2(dme)] precursor with the potassium salts *t*-Bu_2-4-RpzK (K**L1**−K**L3**) in a 1:2 stoichiometric ratio in dry toluene led to the formation of complexes of the type [MoO(N-*t*-Bu)(*t*-Bu_2-4-Rpz)$_2$] [R = H (**1**), Br (**2**), and Me (**3**)] in good yields (Scheme 1). All compounds were isolated as pale-yellow crystalline solids by the evaporation of toluene and purified by recrystallization from pentane at −25 °C.

Scheme 1. Synthesis of Oxoimido Complexes 1−3



The large amount of *tert*-butyl groups in the pyrazolate complexes **1**−**3** renders them readily soluble in common organic solvents such as pentane, toluene, dichloromethane, and acetonitrile. In the solid state, all complexes are found to be stable in an argon atmosphere, but they readily decompose in the presence of moisture, leading to the formation of blue solids. In a pentane solution, decomposition occurs after 1 week, as is apparent by precipitation of the free ligands as colorless crystalline solids. For example, in a crystallization attempt of complex **3** in pentane, the obtained colorless crystals proved to be the ligand *t*-Bu_2-4-MepzH (see the Supporting Information). Thus, complexes **1**−**3** are extremely sensitive toward substitution reactions. This represents a drawback concerning the stability; however, it is an advantage if they are used as starting materials for the preparation of further complexes. We have previously used the dioxo complexes containing pyrazolate ligands [$MoO_2(\eta^2$-*t*-Bu_2pz$)_2$] as starting materials with significant success.[7f,16] The heterocycle represents a convenient leaving group because the formed side product, *t*-Bu_2pzH, can easily be removed by washing with pentane or by sublimation. We observe a smaller tendency to reductive degradation, which is sometimes observed by other, more conventional methods for the introduction of ligands (the addition of KL or LH and a base to metal halogenides). Furthermore, an additional benefit of using pyrazolate complexes **1**−**3** as molybdenum sources is their high solubility in pentane, heptane, etc., whereas the normally used dihalogenide precursor [MoO(N-*t*-Bu)Cl_2(dme)] is insoluble in the aforementioned solvents.

Complexes **1**−**3** were fully characterized by ^{1}H and ^{13}C NMR and IR spectroscopy as well as by electron-impact mass spectrometry. Elemental analyses agree well with the expected formula. Furthermore, single crystals suitable for X-ray diffraction analysis were obtained for all compounds, allowing determination of their molecular structures (vide infra).

The ^{1}H NMR spectra of complexes **1**−**3** at room temperature show a singlet between 1.31 and 1.41 ppm integrating for 36 protons assignable to the protons of the four *t*-Bu groups. In static structures, the *t*-Bu groups should give rise to four resonances. Thus, the occurrence of one singlet points to a dynamic behavior in solution, presumably by rotation of the heterocycle (thereby exchanging the two nitrogen atoms) as well as exchange of the two cycles themselves. However, low-temperature ^{1}H NMR spectroscopy performed with complex **1** in $CDCl_3$ down to −30 °C did not resolve the singlet. Similarly, the ^{13}C NMR spectra display one resonance for the four carbon atoms ($CC(CH_3)_3$) of the *t*-Bu groups.

The reaction of [MoO(N-*t*-Bu)Cl_2(dme)] with only 1 equiv of *t*-Bu_2-pzK in toluene led to a mixture of more than two compounds, as evidenced by ^{1}H NMR spectroscopy. We were not able to separate a single compound because of their similar solubility behavior. However, just once, during a purification attempt by crystallization, a single crystal suitable for X-ray crystallography could be picked out of the mixture (see the Supporting Information). Analysis revealed an unexpected molybdenum compound, [Mo(N-*t*-Bu)Cl_2(*t*-Bu_2pz$)_2$], containing one imido, two chloro, and two η^2-pyrazolate ligands, whereas an oxo group is absent. Its formation is unclear, but reactions in which the oxo group is replaced by two chloro ligands are known in the literature.[25] For example, [MoO(NPh)(Et_2dtc$)_2$] (Et_2dtc = diethyldithiocarbamate) in the presence of gaseous HCl leads to the formation of [Mo(NPh)Cl_2(Et_2dtc)$_2$·$CHCl_3$].[25b] Although several attempts were made to reproduce the compound rationally, we were not able to isolate this material in bulk. However, we feel that the information is important because it demonstrates the sensitivity of the systems toward any protic conditions, justifying the rigorous anhydrous and nonprotic conditions needed for the preparation of compounds **1**−**3**.

Molecular Structures of the Oxoimido Complexes. The solid-state structures of complexes **1**−**3** were determined by single-crystal X-ray diffraction analyses. Crystals suitable for the analyses were obtained by recrystallization from pentane at −25 °C. Complexes **1**−**3** exhibit similar structural features. For this reason, only a molecular view of complex **1** is shown in Figure 1, whereas those of **2** and **3** can be found in the Supporting Information (Figures S1 and S2). Crystal data of all compounds are given in Table 1 and selected bond lengths and angles in Table 2. In the unit cells of compounds **2** and **3**, two independent molecules are found with very similar structural

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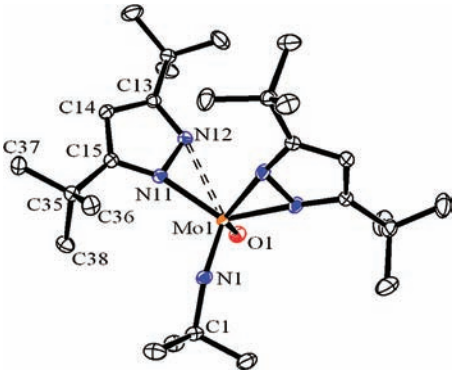

Figure 1. ORTEP drawing of complex **1** with an atom labeling scheme (ellipsoids at the 50% probability level). All hydrogen atoms have been omitted for clarity.

Table 1. Crystallographic Data for 1−3

	1	2	3
empirical formula	$C_{26}H_{47}MoN_5O$	$C_{26}H_{45}Br_2MoN_5O$	$C_{28}H_{51}MoN_5O$
fw	541.63	699.43	569.68
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.6391(14)	11.7782(6)	11.8054(4)
b (Å)	12.251(2)	15.5201(8)	15.3574(6)
c (Å)	14.203(3)	17.9310(9)	17.8372(6)
α (deg)	65.037(12)	104.523(2)	104.4582(16)
β (deg)	72.924(12)	90.810(2)	90.4678(14)
γ (deg)	76.939(12)	100.914(3)	100.7104(17)
V (Å^3)	1443.4(5)	3109.1(3)	3071.85(19)
Z	2	4	4
ρ_{calc} (g/cm^3)	1.246	1.494	1.232
cryst size (mm^3)	0.26 × 0.22 × 0.18	0.36 × 0.30 × 0.04	0.20 × 0.20 × 0.16
F(000)	576	1424	1216
μ(Mo Kα) (mm^{-1})	0.479	3.018	0.454
T (K)	95	100	100
θ range (deg)	2.72−30.00	1.76−26.00	2.02−26.00
reflns collected	9344	26100	24726
indep reflns	8412	12055	12014
R(int)	0.0233	0.0406	0.0223
data/param/restraints	8412/330/0	12055/671/0	12014/699/0
R1[a]/wR2[b], [$I > 2\sigma(I)$]	0.0285/0.0655	0.0468/0.1159	0.0313/0.0743
R1[a]/wR2[b], (all data)	0.0332/0.0678	0.0702/0.1255	0.0451/0.0809
GOF (F^2)	1.056	1.018	1.030
CCDC dept number	828736	828737	828738

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

features. For this reason, only one of each is discussed in the following section.

All three compounds were found to exhibit rare geometries because of the η^2-coordinate pyrazolate ligands. The molybdenum atoms in complexes **1**−**3** are coordinated by an oxo, an imido, and two η^2-coordinate pyrazolate ligands. Taking the middle point of the N−N bonds in the pyrazolate ligands as the coordinating site, they exhibit distorted tetrahedral geometries. When the four nitrogen atoms are considered as the sites of coordination instead, the complexes are six-coordinate with highly distorted geometries. This is best described by the largest angles between two ligands: e.g., O1−Mo1−N22 varying between of 133.43(5) and 135.87(17)° and N1−Mo1−N12 between 138.19(5) and 142.22(18)°. These bond angles are severely deviating from those found in an octahedral environment and are closer to those in a trigonal-prismatic geometry. Anyway, no matter how the geometries of the compounds are described, they both feature the absence of a ligand trans to the oxo functionality in comparison to an octahedral structure, in which the presence of the trans ligand has a strong effect. The occurrence of a (distorted) trigonal-prismatic geometry has biological significance because it was found that trigonal-prismatic transition states play a crucial role in biological OAT reactions.[26] The small N−Mo−N bite angles [between 36.18(16)° and 37.08(16)°] of the η^2-coordinate pyrazolate ligands assist the central metal ion to attain what could be seen as a trigonal-prismatic geometry. The Mo−N distances of the heterocycles are similar, albeit not equal. In a given complex, the differences in the Mo−N(pz) distances are in one of the two ligands significantly larger than in the other. This type of bonding variation is common for η^2-pyrazolate ligands and is often reported in the literature.[10,13−15] Presumably, the pyrazolate anion not being fully aromatic [see, for example, N11−C15 1.3703(18) Å vs N12−C13 1.3332(18) Å] leads to different electron densities at the two nitrogen atoms. Depending on the difference of the Mo−N bond lengths, the heterocycle is described as being η^2-, slipped-η^2- or η^1-coordinate.[13] For example, in compound **1**, the Mo1−N21 bond length is 2.0336(13) Å and the corresponding Mo1−N22 is 2.4962(13) Å. This represents the largest difference within a given ligand of all three complexes and, thus, this particular ligand coordination is better described as η^1. The smallest difference in the Mo−N distances is found in the same complex **1** in the second pz ligand [Mo1−N11 2.1836(13) Å and Mo1−N12 2.0738(13) Å], which is indicative for a true η^2 coordination. This demonstrates the variability of the ligand system and is consistent with the dynamic behavior found in solution. Nevertheless, the steric demand of the 3,5-*t*-Bu groups prevents bridging modes preferably observed with less bulky pz ligands.[11]

Table 2. Selected Bond Lengths (Å) and Angles (deg) of 1−3

	1	2 (both molecules)	3 (both molecules)
Mo1═O1	1.7057(11)	1.701(4)/1.706(4)	1.7027(17)/1.7017(17)
Mo1═N1	1.7375(13)	1.723(4)/1.722(4)	1.726(2)/1.728(2)
Mo1−N11	2.0336(13)	2.053(4)/2.050(4)	2.050(2)/2.069(2)
Mo1−N12	2.4962(13)	2.309(4)/2.314(4)	2.310(2)/2.303(2)
Mo1−N21	2.0738(13)	2.070(5)/2.075(4)	2.073(2)/2.050(2)
Mo1−N22	2.1836(13)	2.206(4)/2.192(4)	2.189(2)/2.187(2)
O1−Mo1−N1	104.89(6)	103.3(2)/103.6(2)	103.35(9)/103.48(9)
N11−Mo1−N12	33.65(5)	36.18(16)/36.12(15)	36.30(7)/36.30(7)
N21−Mo1−N22	37.71(5)	37.08(16)/37.16(16)	37.09(8)/37.18(8)
N11−Mo1−N21	130.34(5)	127.33(17)/128.13(17)	128.25(8)/128.64(8)
N12−Mo1−N22	85.03(5)	86.09(16)/85.02(16)	86.22(8)/85.07(8)
Mo1−N1−C1	152.30(11)	150.4(4)/151.2(4)	151.51(18)/151.73(18)

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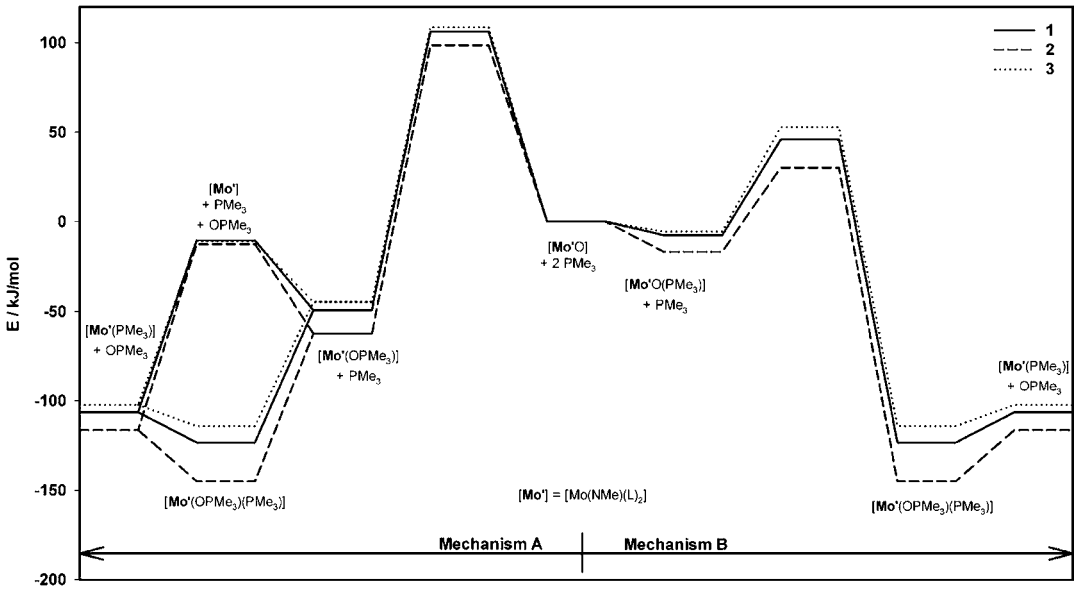

Figure 2. Energy profile for OAT from complexes **1**−**3** to PMe_3. Energies are given in kJ/mol relative to the reactants at the B3LYP def2-SVP level of theory.

The Mo═O bond distances of Mo1−O1 are in the range of 1.701(4)−1.705(11) Å for complexes **1**−**3**, which is normal for molybdenum oxoimido systems.[5,8] Mo−N bond lengths of the imido groups (Mo═N) are varying in the range of 1.7057(11)−1.7375(13) Å for complexes **1**−**3**. These values are consistent with those of reported similar molybdenum oxoimido compounds.[5,8] Complexes containing a metal−imido bond can be classified into two different groups according to the geometry of the M−N−C bond angle: linear (180−160°) and bent (150−130°).[6f,8d,27] The bond angles in the range of 160−150° belong to the semibent geometry class.[28] The Mo1−N1−C1 bond angles deviate significantly from linearity [152.30(11)° for **1**, 150.4(4)° for **2**, and 151.51(18)° for **3**]. These values are bordering on a bent geometry, and the imido ligand in complexes **1**−**3** is better described as a sp^2-hybridized four-electron donor. In oxoimido complexes, linear bonding modes are far more common than bent ones.[8] An example of the latter is represented by complex $[Mo(NPh)_2(S_2CNEt_2)_2]$,[6g] which was found to exhibit one linear and one bent imido group. Its mixed oxoimido analogue $[MoO(NPh)(Et_2dtc)_2]$ is not structurally characterized.[25b] We have recently reported oxoimido complexes with ketiminate ligands that exhibit linear imido groups.[5] Thus, complexes **1**−**3** represent rare examples of structurally characterized molybdenum oxoimido species with a bent imido moiety. Presumably, the steric hindrance of two *t*-Bu groups in the 3 and 5 positions leads to the observed metal imido angle. Such steric hindrance, in the case of the *t*-Bu group C35−C38, also seems to "protect" an otherwise empty coordination site on the molybdenum atom, with the C36 atom pointing directly toward the metal center. However, in complex **1**, this distance is significantly longer (4.145 Å) than those in complexes **2** and **3** (3.847 and 3.840 Å), respectively (vide infra).

OAT Studies. Complexes **1**−**3** were designed to study the OAT reactivity to phosphines. A comparison of their reactivity to that of the previously investigated dioxo system[10] would provide valuable information on the influence of the second group next to the oxygen atom that is actually transferred (spectator oxo effect). Thus, oxoimido compounds **1**−**3** were reacted with 4 equiv of trimethylphosphine in 1.0 mL of dry benzene-d_6. Upon the addition of phosphine, the color of the solution changed from yellow to deep green, pointing to reduction of the compounds. The samples were subjected to ^{31}P NMR spectroscopy at room temperature, immediately after their preparation. The three ^{31}P NMR spectra reveal, next to the resonance for excess PMe_3 (−62.6 ppm), one at 32.4 ppm for $OPMe_3$ and additional resonances at 2.96 (**1**), 12.02 (**2**), and 26.22 (**3**) ppm, respectively, characteristic for the formation of PMe_3-coordinated molybdenum(IV) adducts of the type $[Mo(N\text{-}t\text{-}Bu)(pz)_2(PMe_3)]$. This is in line with our previous observation in oxoimido complexes where after OAT monophosphine adducts $[Mo(N\text{-}t\text{-}Bu)(L)_2(PMe_3)]$ (L = *β*-ketiminate) are formed.[5] On the other hand, in dioxo pyrazolate complexes, the OAT leads to $[MoO(t\text{-}Bu_2pz)_2(PR_3)_2]$ (R = Me, Et) with two coordinated phosphines.[10] Thus, the formation of a bis(phosphine) adduct in the present complexes cannot be ruled out, in particular considering the similar ^{31}P NMR shifts of **1** (2.96 ppm) and $[MoO(t\text{-}Bu_2pz)_2(PMe_3)_2]$ (0.96 ppm).[10] The downfield shift in going from the oxo to the imido derivative is consistent with what we have already observed in the *β*-ketiminate complexes ($[MoX(L)_2(PMe_3)]$; X = O, −5.7 ppm,[7c] or X = N-*t*-Bu, +6.5 ppm).[5] Moreover, the longer distance between C36 and Mo1 in the solid state for complex **1** might, in principle, allow for formation of the bis(phosphine) derivative. Unfortunately, kinetic data of the OAT of the compounds allowing a meaningful comparison to the dioxo system $[MoO_2(t\text{-}Bu_2pz)_2]$ could, however, not be obtained. All attempts were hampered by concomitant decomposition of the system. Nonetheless, these investigations demonstrate the capability of **1**−**3** for OAT activity.

Theoretical Calculations. In order to gain insight into the influence of the substituents on the OAT reactivity given the absence of kinetic data, theoretical calculations were performed on the complexes. Two mechanisms (A and B) for the OAT reaction between compounds **1**−**3** (abbreviated as [**Mo**'O] in Figure 2) and PMe_3 were calculated with density functional theory (DFT) at the B3-LYP level of theory[21,22] in order to

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investigate the electronic influence of their different substituents. The COSMO solvation model was employed to take solvent effects into account.

An approaching molecule PMe_3 can either directly attack the oxo group to form a coordinated phosphine oxide intermediate species [**Mo′**$(OPMe_3)$] (mechanism A) or coordinate to the molybdenum atom, forming [**Mo′**$O(PMe_3)$] (mechanism B). The coordination to molybdenum is energetically a barrier-less process where the compounds gain 6−17 kJ/mol depending on the substituent in the 4 position of the heterocycle. Direct OAT from **1**−**3** to PMe_3 requires 100−110 k/mol (mechanism A), whereas the attack of a second molecule PMe_3 on the oxo group of the phosphine adduct species ([**Mo′**$O(PMe_3)$] according to mechanism B) requires only 47−58 kJ/mol. According to mechanism A, the coordinated phosphine oxide molecule in [**Mo′**$(OPMe_3)$] can be replaced by PMe_3, in either an associative or a dissociative process, forming the reduced phosphine-coordinated species [**Mo′**(PMe_3)], with the latter being more energetically favored. The same species is formed by releasing $OPMe_3$ from [**Mo′**$(OPMe_3)(PMe)_3$] according to mechanism B.

Given the lower energy barrier found in mechanism B, coordination of a phosphine to molybdenum prior to the OAT reaction seems to be favored. However, the theoretical calculations comparing all complexes **1**−**3** do not indicate a significant difference in their reactivity. Hence, the electronic influence of the different substituents in the 4 position seems to be relatively low.

CONCLUSION

In summary, the unusual η^2 coordination of three different pyrazolate ligands in molybdenum oxoimido complexes has been established. The obtained complexes exhibit the general formula [MoO(N-*t*-Bu)(*t*-Bu_2-4-Rpz)$_2$] [R = H (**1**), Br (**2**), and Me (**3**)]. Structural characterization by X-ray diffraction analyses confirms the *endo*-bidentate coordination. Unusual nonoctahedral geometries around the molybdenum center were found in all cases, which could be seen as distorted trigonal-prismatic considering the pyrazolate ligands as bidentate. This is biologically relevant because of the occurrence of trigonal-prismatic geometries in the transition states of oxygen-transferring enzymes. Compound **1**−**3** are capable of transferring an oxygen atom to trimethylphosphine but were, however, found to be sensitive toward hydrolysis, preventing an in-depth kinetic investigation of the OAT reactivity. The substituents in the 4 position of the heterocycle seem to have little or no influence on the OAT reaction, as indicated by DFT calculations.

The ease of substitution of the pyrazolate ligands, despite being a drawback for the stability, proves to be an advantage in substitution reactions by other more stabilizing ligands, as is found in the case of the dioxo complexes.[7f,16] Complexes **1**−**3** are highly soluble in nonpolar solvents, which is not the case with other molybdenum oxoimido starting materials. Thus, complexes **1**−**3** would be a superior precursor to expand the synthesis of mixed molybdenum oxoimido complexes with various ligand types. This approach promises to open up a new frontier in the synthesis of mixed molybdenum oxoimido complexes that possess significant steric and electronic control on the metal center. Further investigations to explore this chemistry are currently in progress in our laboratory.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, ORTEP drawings, additional crystallographic data, and X-ray crystallographic determination. This material is available free of charge via the Internet at http://pubs.acs.org.

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