DOI: 10.1021/ic101159g

Inorganic Chemistry
Article

Replacement of an Oxo by an Imido Group in Oxotransferase Model Compounds: Influence on the Oxygen Atom Transfer

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Received June 9, 2010

Treatment of [MoO(N-*t*-Bu)Cl_2(dme)] (dme = dimethoxyethane) with 2 equiv of the potassium salts of Schiff base ligands of the type KArNC(CH_3)CHC(CH_3)O afforded oxo imido molybdenum(VI) compounds [MoO(N-*t*-Bu)L_2] {**1**, with Ar = phenyl (L_{Ph}), **2** with Ar = 2-tolyl (L_{MePh}), **3** with Ar = 2,6-dimethylphenyl (L_{Me2Ph}) and **4** with Ar = 2,6-diisopropylphenyl (L_{iPr2Ph})}. We have also prepared related bisimido complexes [Mo(N-*t*-Bu)$_2L_2$ (**5** with L = L_{Ph}, **6** with L = L_{MePh}, and **7** with L = L_{Me2Ph}) by treatment of [Mo(N-*t*-Bu)$_2Cl_2$(dme)] with 2 equiv of the potassium salt of the respective ligand. **1**, **3**, **5**, and **6** were characterized via single crystal X-ray diffraction. The oxo imido complexes exhibit oxygen atom transfer (OAT) reactivity toward trimethyl phosphine. Kinetic data were obtained for **1** and **3** by UV/vis spectroscopy revealing decreased OAT reactivity in comparison to related dioxo complexes with the same Schiff base ligands and decreased reactivity of **1** versus **3**. Cyclic voltammetry was used to probe the electronic situation at the molybdenum center showing reversible reduction waves for **3** and [$MoO_2(L_{Me2Ph})_2$] at comparable potentials while **1** exhibits a significant lower potential. Density functional theory (DFT) calculations showed a higher electron density on oxygen in the oxo imido complexes.

Introduction

Molybdenum is found in a large class of enzymes capable of transferring an oxygen atom from or to a substrate referred to as mononuclear molybdoenzymes or oxotransferases.[1,2] They can be classified into three different families (*xanthine oxidase* (XO), *sulfite oxidase* (SO), and *DMSO reductase* (DMSOR) families) according to the structure of their oxidized active center. They all contain in their oxidized state a mononuclear molybdenum(VI) atom with at least one oxo ligand, but the XO family possesses a MoOS, the SO family an MoO_2, and the DMSOR family a MoO(OR) core. For this reason model chemistry for these enzymes has focused on molybdenum compounds that contain a metal core with at least one oxo group and an additional doubly bonded chalcogen atom.[3,4] Most model compounds, both functional as well as structural, possess a $[MoO_2]^{2+}$ core; however, a compound having next to the oxo a non-oxygen group would be desirable as early studies by Rappé and Goddard suggest that in dioxo systems one oxygen atom represents the actual transferable one whereas the other one takes the role of a spectator ligand.[5,6] Only a few complexes containing the interesting $[MoOS]^{2+}$ core have been prepared although they seem to be quite prone to dimerization, forming a Mo−S−S−Mo unit.[7−12]

For this reason, we aim at the preparation of molybdenum compounds $[MoOX]^{2+}$ where the additional doubly bonded unit is represented by an imido group. The imido functionality provides better steric stabilization of the metal than an oxo ligand preventing dimerization. Electronically, the Mo═O bond should be weakened as imido groups are better π donors; however, steric demand is increased.[41] Comparison of oxygen atom transfer (OAT) reactivity of various oxo imido to analogous dioxo complexes will give insights into steric and electronic influences on the OAT activity within mixed non-dioxo systems. The obtained information could

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Published on Web 09/10/2010

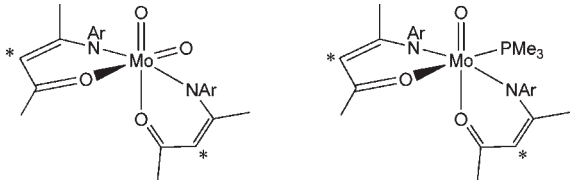


Figure 1. Molybdenum dioxo and monooxo complex with Schiff base ligands; the asterisk denotes the γ-position referred to in the text.

be relevant for a better understanding of the role of the oxo ligand in biological non-dioxo systems.

Whereas dioxo molybdenum(VI) complexes have been prepared in a very wide variety,[3,4,13−15] oxo imido Mo(VI) complexes are significantly rarer. Early work describes molybdenum oxo imido complexes mainly as byproduct,[16−20] and only recently an interesting starting material has been developed from which coordination chemistry evolved.[21−26]

Recently, we reported molybdenum dioxo complexes with Schiff base ligands as shown in Figure 1 that are active catalyst in the OAT from dimethylsulfoxide to trimethylphosphine. This well-behaved system allowed the isolation of the reduced monooxo compound after the transfer giving insights into the mechanism which proceeds via a mononuclear species with a coordinated trimethylphosphine molecule.[27,28]

Here, we report analogous complexes in which the oxo groups are replaced by one or two *t*-butyl imido functionalities. Oxygen atom transfer reactivity of the oxo imido complexes toward trimethyl phosphine was investigated and compared to data obtained with the dioxo system.

Results and Discussion

Synthesis of the Compounds. The employed β-ketiminate ligands can easily be prepared by condensation of acetylacetone and the corresponding aromatic amines in a ratio 1:1 with catalytic amounts of concentrated sulfuric acid.[29]

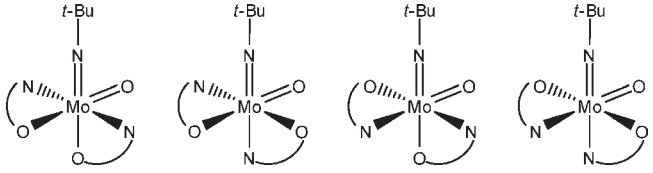
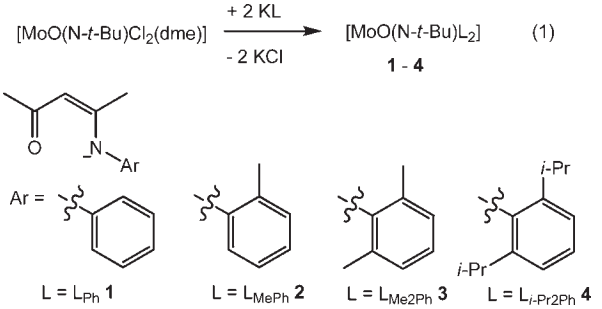


Figure 2. Four possible isomers in oxo imido compounds with two general bidentate O,N ligands.

The compounds can be conveniently characterized by ^{1}H and ^{13}C NMR spectroscopy. In particular, the resonances of the γ-protons in the backbone (see Figure 1) represent an easy tool for determining the ligand's coordination to the metal core. Thus, in the ^{1}H NMR spectra resonances for the γ-protons in the free ligands can be found around 5.0 ppm, whereas upon coordination resonances shift toward lower fields (~5.2 ppm).

Well-defined starting materials for the preparation of oxo imido molybdenum compounds are scarce. A straightforward method of preparation for the *tert*-butyl imido derivative [MoO(N-*t*-Bu)Cl_2(dme)] has been described in the literature. Its synthesis involves an exchange reaction between the dioxo compound [MoO_2Cl_2(dme)] and the bisimido compound [Mo(N-*t*-Bu)$_2Cl_2$(dme)] under prolonged refluxing conditions (3 days). Purification occurs by recrystallization from toluene where the target compound [MoO(N-*t*-Bu)Cl_2(dme)] crystallizes selectively. Stoichiometry and strict oxygen- and moisture-free reaction conditions are extremely crucial, otherwise the product does not crystallize and only impure material is obtained.[21] The reaction of [MoO(N-*t*-Bu)Cl_2(dme)] with 2 equiv of the potassium salts of the ligands in cold toluene under elimination of potassium chloride affords oxo imido molybdenum(VI) compounds of the type [MoO(N-*t*-Bu)L_2] (eq 1). Crude mixtures contain some unidentified byproducts. Analytically pure material can be obtained by crystallization from pentane. For this reason and also because of a pronounced solubility in pentane isolated yields are moderate. Crystals of **1** and **3** suitable for X-ray diffraction analysis were obtained from concentrated pentane solution upon cooling to −30 °C for few days (vide infra).



Proton and carbon NMR spectra of **1**, **3**, and **4** show two sets of sharp resonances for the signals of two types of ligands consistent with the expected oxo imido compounds. Particularly indicative are the two resonances of equal intensity of the two inequivalent γ-protons in the region of 5 ppm in the ^{1}H NMR spectra and in the region of 100 ppm in the ^{13}C NMR spectra. Compound **2** can also be obtained in analytically pure form; however, it behaved differently in solution. The ^{1}H NMR spectrum is complex showing eight sets of resonances assignable to

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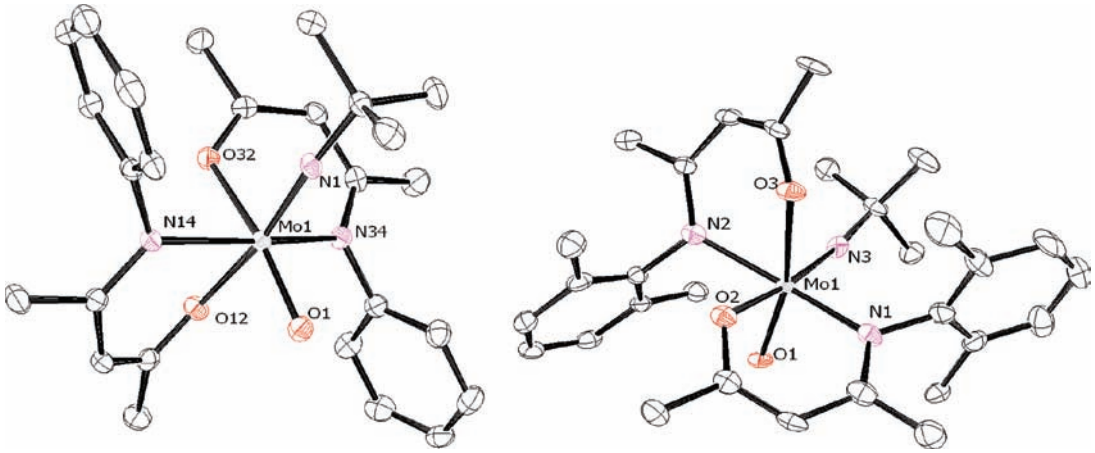

Figure 3. Molecular structures of [MoO(N-*t*-Bu)(L_{Ph})$_2$] (**1**, left) and [MoO(N-*t*-Bu)(L_{Me2Ph})$_2$] (**3**, right). Thermal ellipsoids are drawn at 50% probability level and hydrogen atoms are omitted for clarity.

the ligand; two at a time showing equal intensity. In contrast, both sterically less as well as more demanding ligands form a single isomer in solution.

In principle, four isomers as shown in Figure 2 can be envisioned explaining the observed NMR spectra. Another possibility for the found isomers could be hindered rotation about the nitrogen-aryl axis. Thus, different positions of the methyl group in compound **2** is a source of further asymmetry leading possibly to the observed isomer distribution. We found a similar behavior of this ligand in related molybdenum dioxo and rhenium oxo complexes.[28,34]

Bisimido complexes [Mo(N-*t*-Bu)$_2$L$_2$] (L = L_{Ph} **5**, L = L_{MePh} **6**, L = L_{Me2Ph} **7**) were synthesized for comparative studies. They were obtained by the reaction of [Mo(N-*t*-Bu)$_2$Cl$_2$(dme)][30] and the potassium salt of the respective ligand (eq 2). The reactions proceeded similar to those of **1** to **4** and again isolated yields were moderate because of the high solubility in pentane solution.

$$[\mathrm{Mo(N\text{-}t\text{-}Bu)_2Cl_2(dme)}] \xrightarrow[-2\ \mathrm{KCl}]{+2\ \mathrm{KL}} [\mathrm{Mo(N\text{-}t\text{-}Bu)_2L_2}] \quad (2)$$

where L = L_{Ph} **5**; L_{MePh} **6**; and L_{Me2Ph} **7**.

The analogous reaction employing the bulky ligand L_{iPr2Ph} did not yield in any product, but only a mixture of unidentified species was formed. Presumably, the steric bulk of two *t*-butyl groups on the Mo atom and two *i*-propyl groups on each ligand is too high to form the expected compound. NMR spectroscopy of complexes **5** and **7** shows them to be of symmetric nature as only one set of resonances for the ligands and only one for both *t*-butyl groups is detected in each case. This is consistent with a structure where the two nitrogen atoms of the ligands are trans to each other which was confirmed by X-ray diffraction analysis (vide infra). However again, ligand L_{MePh} gave the analytically pure compound [Mo(N-*t*-Bu)$_2$(L_{MePh})$_2$] (**6**) that behaved differently in solution. The ^{1}H NMR spectrum of **6** in benzene-d$_6$ showed sets of resonances for three isomers which corresponds to the number of possible isomers in this type of bisimido complexes.

All compounds **1** to **7** are extremely well soluble in all organic solvents including apolar ones such as pentane which hampers isolation in high yields. They are rather sensitive toward moisture so that even in the glovebox they can only be stored for a limited amount of time. Within weeks they decompose to blue intractable products.

Molecular Structures. Single crystals suitable for X-ray diffraction analyses were obtained from compounds **1**, **3**, **5**, and **6**. Molecular structures of compounds **1** and **3** are shown in Figure 3 and those of **5** and **6** in Figure 4. Selected bond lengths and angles are given in Tables 1 and 2 and crystallographic data and structure refinement in Table 3.

Structural analysis shows all four compounds consisting of a hexa-coordinate molybdenum(VI) atom in a distorted octahedral geometry. The metal atom is surrounded by an imido and an oxo or two imido groups and two bidentate Schiff-base ligands. The two nitrogen atoms of the latter are found in *trans* position to each other in all cases independent of the steric bulk imposed by the ligands. The substitution of one oxo ligand with one imido group results in a slight elongation of the residual Mo=O bond length, which goes from 1.710(6) (average in structurally related dioxo complexes) to 1.7259(15) Å in **1** and 1.723(4) in **3**. In compounds **1** and **3** the imido groups are linear with molybdenum−nitrogen−carbon angles of 175.63(15)° in **1** and 172.5(5)° in **3**. This is consistent with short molybdenum−nitrogen(imido) bonds of 1.7418(19) Å and 1.734(6) Å, respectively, and with the formulation of a triple bond.[32,33] The two corresponding angles in the bisimido compound **5** are Mo1−N5−C51 175.12(11)° and Mo1−N6−C61 158.15(12)°. The more acute angle is close to those found in bent imido groups where angles < 150° are typical and where the lone pair is located at nitrogen.[32,33] This is apparently due to electronic reasons as in the sterically more demanding bisimido compound **6**, both angles are in good agreement with linear imido

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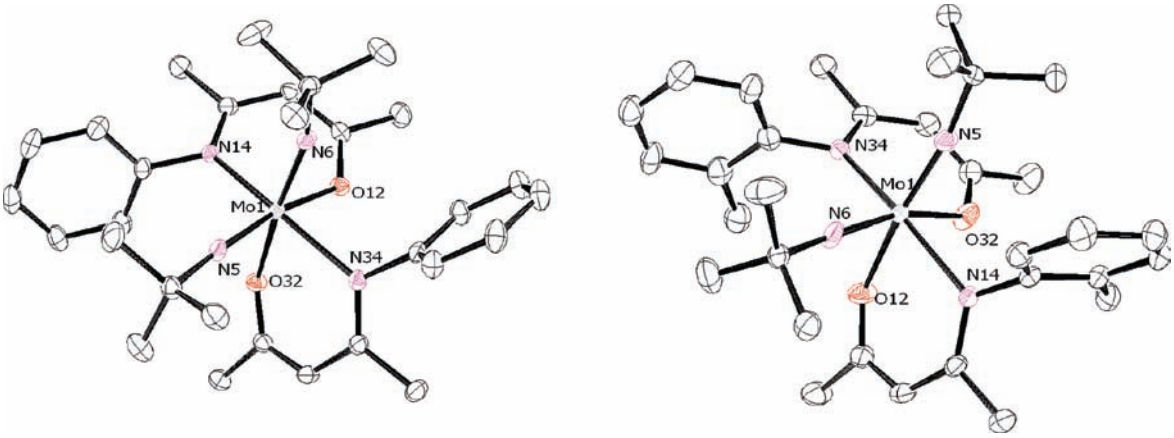


Figure 4. Molecular structures of $[Mo(N\text{-}t\text{-}Bu)_2(L_{Ph})_2]$ (**5**, left) and $[Mo(N\text{-}t\text{-}Bu)_2(L_{MePh})_2]$ (**6**, right). Thermal ellipsoids are drawn at 50% probability level and hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Compounds **1** and **3**

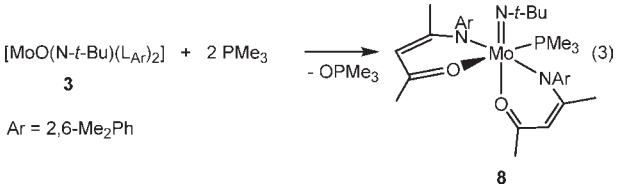
	1		**3**
Mo1−N1	1.7418(19)	Mo1−N3	1.734(6)
Mo1−O1	1.7259(15)	Mo1−O1	1.723(4)
Mo1−N14	2.1303(17)	Mo1−N1	2.144(6)
Mo1−N34	2.1728(17)	Mo1−N2	2.176(6)
Mo1−O12	2.1578(16)	Mo1−O2	2.112(4)
Mo1−O32	2.1474(15)	Mo1−O3	2.148(4)
N1−Mo1−O1	104.25(8)	N3−Mo1−O1	104.3(2)
N1−Mo1−N14	97.47(7)	N3−Mo1−N1	97.7(2)
N1−Mo1−N34	93.29(7)	N3−Mo1−N2	94.3(2)
N1−Mo1−O12	168.25(7)	N3−Mo1−O2	167.5(2)
N1−Mo1−O32	91.18(7)	N3−Mo1−O3	90.1(2)
O1−Mo1−N14	98.08(7)	O1−Mo1−N1	95.2(2)
O1−Mo1−N34	92.35(7)	O1−Mo1−N2	90.9(2)
O1−Mo1−O12	87.30(7)	O1−Mo1−O2	88.20(19)
O1−Mo1−O32	163.32(7)	O1−Mo1−O3	163.57(19)
N14−Mo1−N34	162.68(7)	N1−Mo1−N2	164.70(18)
N14−Mo1−O12	82.80(6)	N1−Mo1−O2	81.18(19)
N14−Mo1−O32	85.94(6)	N1−Mo1−O3	90.44(19)
N34−Mo1−O12	83.93(6)	N2−Mo1−O2	85.02(18)
N34−Mo1−O32	80.29(6)	N2−Mo1−O3	80.09(19)
O12−Mo1−O32	77.10(6)	O2−Mo1−O3	77.41(17)
Mo1−N1−C1	175.63(15)	Mo1−N3−C27	172.5(5)

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Compounds **5** and **6**

	5	**6**
Mo1−N5	1.7512(14)	1.755(2)
Mo1−N6	1.7622(14)	1.751(2)
Mo1−N14	2.1779(13)	2.177(2)
Mo1−N34	2.1788(14)	2.179(2)
Mo1−O12	2.1720(12)	2.1821(19)
Mo1−O32	2.1819(12)	2.1661(18)
N5−Mo1−N6	104.89(7)	106.75(11)
N5−Mo1−N14	97.83(6)	98.14(9)
N5−Mo1−N34	94.51(6)	91.77(9)
N5−Mo1−O12	165.47(6)	164.07(9)
N5−Mo1−O32	89.72(6)	90.20(9)
N6−Mo1−N14	92.85(6)	91.36(8)
N6−Mo1−N34	97.70(6)	97.65(9)
N6−Mo1−O12	89.60(6)	88.98(10)
N6−Mo1−O32	165.24(6)	162.92(9)
N34−Mo1−N14	161.15(5)	164.13(8)
N14−Mo1−O12	82.13(5)	83.62(7)
N14−Mo1−O32	82.86(5)	84.01(7)
N34−Mo1−O12	82.35(5)	83.50(7)
N34−Mo1−O32	83.01(5)	83.59(7)
O12−Mo1−O32	75.84(5)	74.19(8)
Mo1−N5−C51	175.12(11)	169.80(19)
Mo1−N6−C61	158.15(12)	175.12(18)

groups (169.80(19) and 175.12(18)°). All other bond lengths and angles in the four compounds exhibit very similar features (Table 1 and 2).

Oxygen Atom Transfer Properties. Oxygen atom transfer properties of **1**−**3** to the non-biological substrate trimethylphosphine were investigated. Thus, a solution of the corresponding compound was treated with an excess (3 equiv) of PMe_3 in benzene-d_6. Reactivity was immediately apparent as in all cases a color change from orange to green-brown occurred and no precipitate was observed. After 2 h at room temperature, ^{31}P NMR spectra were recorded revealing resonances for the phosphorus atom of excess trimethylphosphine at −61.1 ppm, for formed trimethylphosphine oxide at 32.0 ppm and additional resonances: 10.3 ppm (**1**), 7.7, 8.4, and 9.6 ppm (**2**), and 6.5 ppm (**3**). We believe the new resonances are assignable to reduced molybdenum imido compounds of the type $[Mo(N\text{-}t\text{-}Bu)(PMe_3)L_2]$ with a coordinated trimethyl phosphine molecule. This is in good agreement with our previous results employing the related dioxo compound where we also found phosphine adducts after OAT.[28] The occurrence of three resonances employing compound **2** is again explainable by isomers. To unambiguously identify the nature of the reduced species, a toluene solution of compound **3** was treated with 2 equiv of trimethyl phosphine. After workup green-brown compound $[Mo(N\text{-}t\text{-}Bu)(PMe_3)(LMe_2)_2]$ (**8**) was isolated in moderate yield (eq 3).



Compound **8** exhibits a single resonance in the ^{31}P NMR spectrum at 6.5 ppm which is identical to that found in the above-described NMR experiment. Proton and carbon NMR spectra are also consistent with a structure shown in eq 3 so that we are confident that the mononuclear compound **8** is formed. Molybdenum(IV) imido compounds are relatively rare, and only recently

Table 3. Crystallographic Data and Structure Refinement of Compound [MoO(N-*t*-Bu)(L_{Ph})$_2$] (**1**), [MoO(N-*t*-Bu)(L_{Me2Ph})$_2$] (**3**), [Mo(N-*t*-Bu)$_2$(L_{Ph})$_2$] (**5**), and [Mo(N-*t*-Bu)$_2$(L_{MePh})$_2$] (**6**)

	1	**3**	**5**	**6**
empirical formula	$C_{26}H_{33}MoN_3O_3$	$C_{30}H_{43}MoN_3O_3$	$C_{30}H_{42}MoN_4O_2$	$C_{32}H_{46}MoN_4O_2$
Fw	531.49	589.61	586.62	614.67
temperature, K	95	100(2)	95	95
wavelength, Å	0.71069	0.71073	0.71069	0.71069
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2/c$
unit cell dimens				
a, Å	10.960(2)	9.992(2)	9.6105(16)	20.584(3)
b, Å	20.887(2)	11.645(2)	11.4339(18)	9.0773(13)
c, Å	11.6976(18)	13.350(3)	14.540(2)	19.137(3)
α, deg		89.34(3)	84.994(13)	
β, deg	106.305(17)	85.90(3)	79.468(13)	117.604(11)
y. deg		73.58(3)	70.033(12)	
volume, Å^3	2570.1(7)	1486.1(5)	1475.8(4)	3168.7(9)
Z	4	2	2	4
density (calcd), Mg/m^3	1.374	1.318	1.320	1.288
absorp coeff, mm^{-1}	0.541	0.475	0.476	0.447
F(000)	1104	620	616	1296
cryst size, mm^3	0.22 × 0.20 × 0.16	0.32 × 0.26 × 0.16	0.34 × 0.24 × 0.20	0.30 × 0.20 × 0.16
θ range for data collection	2.66 to 26.00°	1.82 to 24.50°	2.60 to 30.00°	2.51 to 28.00°
index ranges	$-2 \le h \le 13$	$-11 \le h \le 11$	$-13 \le h \le 13$	$-27 \le h \le 27$
	$-25 \le k \le 2$	$-13 \le k \le 13$	$-16 \le k \le 15$	$-1 \le k \le 11$
	$-14 \le l \le 14$	$-15 \le l \le 15$	$-13 \le l \le 20$	$-19 \le l \le 25$
no. of reflns collected	7210	10238	9521	9279
no. of indep reflns	4395 [*R*(int) = 0.0206]	4899 [*R*(int) = 0.0719]	7945 [*R*(int) = 0.0241]	6621 [*R*(int) = 0.0229]
completeness to θ_{max}	99.9%	98.9%	99.7%	99.9%
max. and min transmn		0.9279 and 0.8629		
goodness-of-fit on F^2	1.032	1.119	1.074	1.075
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0276	R1 = 0.0732	R1 = 0.0301	R1 = 0.0416
	wR2 = 0.0609	wR2 = 0.1553	wR2 = 0.0741	wR2 = 0.0871
R indices (all data)	R1 = 0.0353	R1 = 0.0951	R1 = 0.0340	R1 = 0.0516,
	wR2 = 0.0647	wR2 = 0.1659	wR2 = 0.0764	wR2 = 0.0916
larges diff peak and hole, e/ Å^3	0.407 and −0.340	755511 0.971 and −1.305	755728 0.461 and −0.439	755510 1.092 and −0.463	755509
CCDC dep. number				

were phosphine containing Mo(IV) imido complexes reported in the literature.[35,36]

Kinetic studies of the oxygen atom transfer reaction shown in eq 3 with compound **1** and **3** were carried out by UV/vis spectroscopy. The reaction was performed under pseudo-first order conditions with excesses of trimethylphosphine over molybdenum compounds in the range of 100 to 200 equiv. UV/vis spectra were recorded every 30 s between 400 and 800 nm (see Supporting Information).

The second-order rate constants, evaluated by plotting ln α versus time (α = $(A_t - A_\infty)/(A_0 - A_\infty)$, *A* = absorbance) at several [PMe_3]/[Mo] ratios, were found to be 9.34×10^{-4} L mol^{-1} s^{-1} for **1** and 1.83×10^{-3} L mol^{-1} s^{-1} for **3**. The data of compound **3** can be compared to those of the analogous dioxo system [MoO_2(L_{Me2Ph})$_2$] (4.1×10^{-3} L mol^{-1} s^{-1}), which is faster by a factor of 2.[28] Steric hindrance of the *tert*-butylimido group in **3** is significantly higher than that of an oxo group, and the increase in sterics around the Mo center should disfavor the entrance of the incoming phosphine, that is regarded as the first step in the associative mechanism leading to phosphine oxide formation with concomitant reduction of the metal. The electronic effect induced by the substitution of an oxo by an N-*t*-Bu group was investigated by cyclic voltammetry. Both compounds **3** and [MoO_2(L_{Me2Ph})$_2$] show a reversible reduction wave (Mo(VI)/Mo(V)) at $E_{1/2}$ = −1.60 V for **3** and −1.59 V (vs Fc/Fc$^+$) for [MoO_2(L_{Me2Ph})$_2$] (see Supporting Information). Despite the better donor capabilities of an imido group versus an oxo group,[41] in the two compounds no relevant electronic difference seems to be discernible. Thus, the slower kinetics of the oxo imido compound can be attributed to a steric influence of the *tert*-butyl substituents. To determine the extent of the steric effect on the transfer, kinetics of the sterically less demanding oxo imido compound **1** were investigated. Quite surprisingly, compound **1** exhibits slower transfer kinetics compared to **3** by a factor of 2. This is probably due to the electron-donating capability of the two methyl groups of L_{Me2Ph} in compound **3** as compared to the unsubstituted ligand in **1**. This leads to a higher electron density on the oxo atom in **3** pointing to a significant contribution of the second resonance structure in Mo═O ↔ M—Ō. This is supported by cyclic voltammetry that shows a significant difference in the reduction potential between **1** and **3**. Whereas **3** has a reversible reduction wave (Mo(VI)/Mo(V)) at $E_{1/2}$ = −1.60 V, **1** presents an irreversible wave at −1.82 V giving evidence for the trend of **1** being harder to reduce. The absence of electron-donating substituents in **1** decreases the reaction rate enough to counter balance the increase expected by the larger coordination pocket. Thus, substitution on the aromatic ring within the Schiff base ligand more strongly affects the electronic rather than the steric influence on the transfer reaction.

To aid our understanding of relative influences of steric and electronic effects on the OAT, density functional theory

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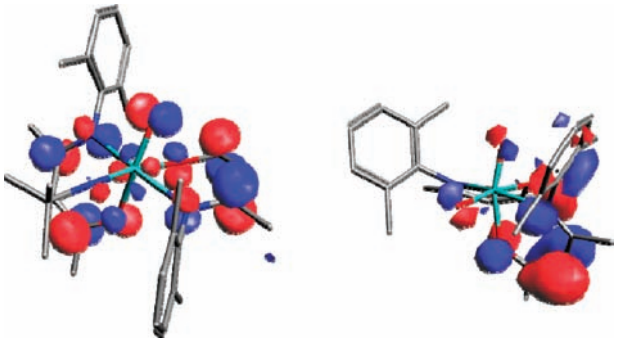

Figure 5. HOMO of [MoO(N-*t*-Bu)(L_{Me2Ph})$_2$] (**3**, left) and [MoO_2-(L_{Me2Ph})$_2$] (right).

Figure 6. HOMO of [Mo(N-*t*-Bu)(L_{Me2Ph})$_2$(PMe_3)] (**8**).

(DFT) calculations were performed on the oxo imido complex [MoO(N-*t*-Bu)(L_{Me2Ph})$_2$] (**3**) and the OAT product [Mo(N-*t*-Bu)(PMe_3)(L_{Me2Ph})$_2$] (**8**). In addition, the related dioxo complex [MoO_2(L_{Me2Ph})$_2$] was included in the theoretical study for comparison. Figure 5 shows the highest occupied molecular orbitals (HOMO) of the dioxo as well as of the oxo imido complex. Whereas the HOMO of the dioxo complex was found to be localized essentially on the Schiff base ligands, the one in **3** has a significant p contribution on the oxo atom. The HOMO on complex **8** shows to have no contribution on the phosphorus atom (Figure 6). These findings are consistent with the expected electron-donating capability of an aliphatic imido group which results in an elongation of the molybdenum oxo bond (as evidenced by the long bond found by X-ray crystallography) and a higher electron density on the oxo atom. Comparison to these theoretical data to cyclic voltammetry points to a push−pull interplay between oxo and imido which cannot be resolved experimentally.

Conclusion

A series of molybdenum oxo imido and bisimido complexes of the type [MoO(N-*t*-Bu)L_2] (**1**−**4**) and [Mo(N-*t*-Bu)$_2L_2$] (**5**−**7**) that contain L = β-ketiminate ligands were synthesized. They exhibit octahedral structures with the two nitrogen atoms of the ligand being trans to each other elucidated by X-ray diffraction analyses. Comparison to the related dioxo compound[28] reveals an increase in the bond lengths of the molybdenum oxo bonds upon substitution of the second oxo by the imido groups. NMR studies of **1**, **3**, **4**, **5**, and **7** in benzene-d_6 confirm the structures found by X-ray diffraction in solution. In contrast, compounds **2** and **6** with ortho tolyl substitutents at the ligand were found to be mixtures of isomers in solution. Reaction of **3** with trimethyl phosphine led to the isolation of the reduced molybdenum(IV) imido compound **8** after oxygen atom transfer. Kinetics of this transfer employing **1** and **3** were investigated by UV/vis spectroscopy under pseudo-first order conditions revealing a decreased rate in comparison to the related dioxo complex [MoO_2(L_{Me2Ph})$_2$]. Keeping constant the oxo imido environment showed compound **1** to be slower than **3**. Furthermore, cyclic voltammetry revealed essentially identical reduction potential for **3** and [MoO_2(L_{Me2Ph})$_2$] while a significant lower potential was found for **1**. The electronic influence of the N-*t*-Bu group was additionally investigated by DFT calculations revealing higher electron density on oxygen. Considering just the electronic effect of the imido group, a faster transfer reaction was expected.[41] The present findings show the steric effect of the *t*-Bu imido group to be dominating. However, comparison of the two slower oxo imido complexes **1** and **3** has revealed a profound electronic influence of the substitution pattern at the Schiff base ligand. Because of the overruling steric effects of the *t*-Bu substituent on the imido ligand, the spectator oxo effect cannot be investigated by the presented system. Complexes featuring imido groups with different electronic and steric effects are thus in need, which we are currently investigating.

Experimental Section

General Procedures. All manipulations were carried out under dry argon using standard Schlenk line or glovebox techniques. All solvents were dried by a solvent purification system from innovative technology inc. and flushed with argon prior to use. Ligands,[29] [Mo(N-*t*-Bu)$_2$$Cl_2$(dme)][30] and [$MoO_2Cl_2$][31] were prepared according to literature procedures. All other chemicals mentioned were used as purchased from commercial sources.

Samples for mass spectrometry were measured on an Agilent Technologies 5795C inert XL MSD spectrometer and all NMR spectra on a Bruker Avance 300 MHz spectrometer. 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. UV/vis spectra were recorded on a Varian Cary 50 spectrophotometer which was connected to a Hellma fiber optics all-quartz immersion probe.

X-ray diffraction data were collected on a Stoe four-circle (**1**, **5**, and **6**) or on a Bruker AXS-SMART APEX CCD (**3**) diffractometer using graphite-monochromated MoKa radiation (0.71073 Å). The data for all compounds were reduced, corrected for Lorentz and polarization effects and for absorption using SAINT[42] and SADABS[43] programs, respectively. The structures were solved by direct methods (SHELXS-97)[44] and refined by full-matrix least-squares method.[45] If not noted otherwise, all non-hydrogen atoms were refined anisotropically; hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles.

Gas-phase single point calculations of the different complexes were done using the B3LYP[37,38] DFT method as implemented in TURBOMOLE program.[39] All atoms except Mo were treated with a standard triple-ζ quality basis (def2-TZVP). The effective core potential ecp-28-mwb was used for Mo with the corresponding triple-ζ quality basis set ecp-28-mwb-TZVP. Input geometries were created from crystal structures, wherever possible,

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or were obtained by replacing an oxo atom with a preoptimized PMe_3 model. Molecular orbitals were visualized using the Gabedit software.[40]

General Procedure for the Preparation of the Oxo Imido and Bis Imido Molybdenum Complexes. All ligands were transformed into their potassium salt prior to complexation to molybdenum according to the following general procedure: approximately 2 g of the ligand and an approximate 3-fold excess of KH were placed in a Schlenk flask equipped with a bubbler, and 30 mL of THF were added. The corresponding suspension was stirred overnight at room temperature during which the evolution of hydrogen was apparent. The suspension was filtered over Celite, and the solvent was removed in vacuo. The thus obtained salt was used without further purification.

The potassium salt of the respective ligand (2 equiv) was suspended in 10 mL of cold toluene (approximately −20 °C). A cold solution of [MoO(N-*t*-Bu)Cl_2(dme)] or [Mo(N-*t*-Bu)$_2$$Cl_2$-(dme)] in 10 mL of toluene was added dropwise. The yellow to orange mixtures were left to stir at room temperature for 2 h followed by centrifugation at 13000 rpm for 4 min. The toluene solution was syringed out and the volatiles were removed in vacuo. The thus obtained yellow to orange solids were dissolved in pentane and crystallized by slow evaporation of the solvent. The yellow to orange products were filtered off and washed with small amounts of cold pentane. Crystals suitable for X-ray diffraction analysis were obtained by recrystallization from pentane.

Synthesis of Oxo Imido Complexes. Synthesis of [MoO(N-*t*-Bu)-(L_{Ph})$_2$] (1). The compound was prepared following the general procedure employing 0.200 g (0.58 mmol) of [MoO(N-*t*-Bu)Cl_2-(dme)] and 0.247 g (1.16 mmol) of KL_{Ph} giving 0.117 g (38%) of **1**. ^{1}H NMR (benzene-d_6): δ 1.05 (s, 9H, (H_3C)$_3$C), 1.41 (s, 3H, H_3C), 1.51 (s, 3H, H_3C), 1.97 (s, 3H, H_3C), 1.98 (s, 3H, H_3C), 5.06 (s, 1H, γ-*H*), 5.23 (s, 1H, γ-*H*), 6.80−7.45 (m, 10H, *H*-Ar) ppm. ^{13}C NMR (benzene-d_6): δ = 23.96 (*C*H_3), 24.08 (*C*H_3), 26.2 (*C*H_3), 27.2 (*C*H_3), 29.0 ((*C*H_3)$_3$C), 71.2 (*C*Me$_3$), 101.6 (γ-*C*), 102.6 (γ-*C*), 125.2, 125.3, 125.6, 126.4, 128.8, 155.1, 157.3, 168.8 (C=N), 169.3 (C=N), 182.9 (C=O), 185.0 (C=O) ppm. Mass (EI, *m*/*z*, (%)): 533 (30%) [M]$^+$, 462 (20%) [M − NtBu)]$^+$. Anal. Calcd. for $C_{26}H_{33}MoN_3O_3$: C, 58.76; H, 6.26; N, 7.91%. Found: C, 58.61; H, 6.31; 7.68%.

Synthesis of [MoO(N-*t*-Bu)(L_{MePh})$_2$] (2). The compound was prepared following the general procedure employing 0.200 g (0.58 mmol) of [MoO(N-*t*-Bu)Cl_2(dme)] and 0.263 g (1.15 mmol) of KL_{MePh} giving 0.115 g (35%) of **2**. Proton NMR spectroscopy revealed four isomers in solution: isomer A (40%): ^{1}H NMR (benzene-d_6): δ 1.06 (s, 9H, (H_3C)$_3$C), 1.32 (s, 3H, H_3C), 1.44 (s, 3H, H_3C), 1.81 (s, 3H, H_3C), 1.88 (s, 3H, H_3C), 2.40 (s, 3H, H_3C), 2.60 (s, 3H, H_3C), 5.07 (s, 1H, γ-*H*), 5.17 (s, 1H, γ-*H*), 6.83−7.50 (m, *H*-Ar) ppm; isomer B (24%): ^{1}H NMR (benzene-d_6): δ 1.00 (s, 9H, (H_3C)$_3$C), 1.34 (s, 3H, H_3C), 1.40 (s, 3H, H_3C), 1.77 (s, 3H, H_3C), 1.98 (s, 3H, H_3C), 2.20 (s, 3H, H_3C), 2.44 (s, 3H, H_3C), 5.07 (s, 1H, γ-*H*), 5.13 (s, 1H, γ-*H*), 6.83−7.50 (m, *H*-Ar) ppm; isomer C (20%): ^{1}H NMR (benzene-d_6): δ 1.03 (s, 9H, (H_3C)$_3$C), 1.30 (s, 3H, H_3C), 1.46 (s, 3H, H_3C), 1.89 (s, 3H, H_3C), 1.92 (s, 3H, H_3C), 2.40 (s, 3H, H_3C), 2.44 (s, 3H, H_3C), 5.04 (s, 1H, γ-*H*), 5.17 (s, 1H, γ-*H*), 6.83−7.50 (m, *H*-Ar) ppm; isomer D (16%): ^{1}H NMR (benzene-d_6): δ 0.97 (s, 9H, (H_3C)$_3$C), 1.32 (s, 3H, H_3C), 1.47 (s, 3H, H_3C), 1.90 (s, 3H, H_3C), 1.99 (s, 3H, H_3C), 2.23 (s, 3H, H_3C), 2.57 (s, 3H, H_3C), 5.11 (s, 1H, γ-*H*), 5.15 (s, 1H, γ-*H*), 6.83−7.50 (m, *H*-Ar) ppm. Mass (EI, *m*/*z*, (%)): 561 (15) [M]$^+$, 490 (15) [M − NtBu]$^+$. Anal. Calcd. for $C_{28}H_{37}MoN_3O_3$: C, 60.10; H, 6.66; N, 7.51%. Found: C, 59.60; H, 6.36; N, 7.89%.

Synthesis of [MoO(N-*t*-Bu)(L_{Me2Ph})$_2$] (3). The compound was prepared following the general procedure employing 0.200 g (0.58 mmol) of [MoO(N-*t*-Bu)Cl_2(dme)] and 0.2785 g (1.15 mmol) of KL_{Me2Ph} giving 0.118 g (35%) of **3**. ^{1}H NMR (benzene-d_6): δ 0.99 (s, 9H, (H_3C)$_3$C), 1.26 (s, 3H, H_3C), 1.44 (s, 3H, H_3C), 1.73 (s, 3H, H_3C), 1.94 (s, 3H, H_3C), 2.33 (s, 3H, H_3C), 2.40 (s, 3H, H_3C), 2.49 (s, 3H, H_3C), 2.69 (s, 3H, H_3C), 5.10 (s, 1H, γ-*H*), 5.12 (s, 1H, γ-*H*), 6.90−7.11 (m, 6H, *H*-Ar) ppm. ^{13}C NMR (benzene-d_6): δ = 18.9 (*C*H_3), 19.5 (2 *C*H_3), 21.1 (*C*H_3), 23.3 (*C*H_3), 23.5 (*C*H_3), 25.6 (*C*H_3), 25.8 (*C*H_3), 29.3 ((*C*H_3)$_3$C), 71.9 (*C*Me$_3$), 101.8 (γ-*C*), 103.3 (γ-*C*), 125.7, 125.8, 128.0, 128.8, 129.1, 129.5, 129.2, 132.78, 132.82, 134.1, 151.5, 156.1, 169.1 (C=N), 170.4 (C=N), 182.7 (C=O), 184.2 (C=O) ppm. Mass (EI, *m*/*z*, (%)): 589 (10) [M]$^+$, 518 (10) [M − NtBu]$^+$. Anal. Calcd. for $C_{30}H_{41}MoN_3O_3$: C, 61.32; H, 7.03; N, 7.15%. Found: C, 61.21; H, 6.99; N, 7.00%.

Synthesis of [MoO(N-*t*-Bu)($L_{i\text{-}Pr2Ph}$)$_2$] (4). The compound was prepared following the general procedure employing 0.200 g (0.58 mmol) of [MoO(N-*t*-Bu)Cl_2(dme)] and 0.3451 g (1.16 mmol) of $KL_{i\text{-}Pr2Ph}$ giving 0.114 g (28%) of **4**. ^{1}H NMR (benzene-d_6): δ 0.95 (s, 9H, (H_3C)$_3$C), 1.11 (d, 3H, CH(CH_3)$_2$), 1.17 (d, 3H, CH(CH_3)$_2$), 1.18 (d, 3H, CH(CH_3)$_2$), 1.20 (d, 3H, CH(CH_3)$_2$), 1.38 (d, 3H, CH(CH_3)$_2$), 1.38 (s, 3H, H_3C), 1.43 (d, 3H, CH(CH_3)$_2$), 1.51 (s, 3H, H_3C), 1.67 (d, 3H, CH(CH_3)$_2$), 1.72 (d, 3H, CH(CH_3)$_2$), 1.72 (s, 3H, H_3C), 1.89 (s, 3H, H_3C), 3.06 (hept, 1H, C*H*Me$_2$), 3.81 (hept, 1H, C*H*Me$_2$), 4.02 (hept, 1H, C*H*Me$_2$), 4.08 (hept, 1H, C*H*Me$_2$), 5.08 (s, 2H, γ-*H*), 7.08 (m, 3H, *H*-Ar) 7.19 (s, 3H, *H*-Ar) ppm. ^{13}C NMR (benzene-d_6): δ 23.8, 24.62, 24.65, 24.75, 25.5, 25.6, 25.8, 25.9, 26.0, 26.2, 26.8, 27.5, 27.6, 27.7, 28.3, 28,4, 30.7 ((*C*H_3)$_3$C), 72.9 (*C*Me$_3$), 101.3 (γ-*C*), 103.6 (γ-*C*), 123.8, 124.0, 124.9, 125.5, 126.5, 126.7, 141.2, 143.0, 143.5, 144.0, 150.0, 155.5, 170.6 (C=N), 172.5 (C=N), 182.0 (C=O), 183.7 (C=O) ppm. Anal. Calcd. for $C_{38}H_{57}MoN_3O_3$: C, 65.22; H, 8.21; N, 6.00%. Found: C, 65.31; H, 8.10; N, 6.22%.

Synthesis of [Mo(N-*t*-Bu)$_2$(L_{Ph})$_2$] (5). The compound was prepared following the general procedure employing 0.399 g (1 mmol) of [Mo(N-*t*-Bu)$_2$$Cl_2$(dme)] and 0.427 g (2 mmol) of KL_{Ph} giving 0.126 g (22%) of **5**. ^{1}H NMR (benzene-d_6): δ 1.03 (s, 18H, (H_3C)$_3$C), 1.51 (s, 6H, H_3C), 2.06 (s, 6H, H_3C), 5.10 (s, 2H, γ-*H*), 6.90−7.14 (m, 8H, *H*-Ar), 7.78 (d, 2H, *H*-Ar) ppm; ^{13}C NMR (benzene-d_6): δ 23.7 (*C*H_3), 27.0 (*C*H_3), 29.0 ((*C*H_3)$_3$C), 69.6 (*C*Me$_3$), 100.8 (γ-*C*), 124.6, 125.1, 127.0, 128.0, 128.4, 158.1, 167.7 (C=N), 182.7 (C=O). Mass (EI, *m*/*z*, (%)): 588 (12) [M]$^+$, 517 (5) [M − NtBu)]$^+$. Anal. Calcd. for $C_{30}H_{42}MoN_4O_2$: C, 61.42; H, 7.22; N, 9.55%. Found: C, 61.34; H, 7.20; N, 9.51%.

Synthesis of [Mo(N-*t*-Bu)$_2$(L_{MePh})$_2$] (6). The compound was prepared following the general procedure employing 0.399 g (1 mmol) of [Mo(N-*t*-Bu)$_2$$Cl_2$(dme)] and 0.455 g (2 mmol) of KL_{MePh} giving 0.122 g (20%) of **6**. NMR spectroscopy revealed three isomers in solution: isomer A ^{1}H NMR (benzene-d_6) δ (43%): 1.08 (s, 18H, (H_3C)$_3$C), 1.41 (s, 6H, H_3C), 1.90 (s, 6H, H_3C), 2.58 (s, 6H, H_3C), 5.07 (s, 2H, γ-*H*), 6.9 − 7.8 (m, overlapping Ar); isomer B (46%): 1.02 (s, 9H, (H_3C)$_3$C), 1.03 (s, 9H, (H_3C)$_3$C), 1.40 (s, 3H, H_3C), 1.44 (s, 3H, H_3C), 1.93 (s, 3H, H_3C), 2.01 (s, 3H, H_3C), 2.29 (s, 3H, H_3C), 2.59 (s, 3H, H_3C), 5.08 (s, 1H, γ-*H*), 5.09 (s, 1H, γ-*H*); 6.9 − 7.8 (m, overlapping Ar); isomer C (11%): 0.99 (s, 18H, (H_3C)$_3$C), 1.43 (s, 6H, H_3C), 2.03 (s, 6H, H_3C), 2.28 (s, 6H, H_3C), 5.12 (s, 1H, γ-*H*), 6.9 − 7.8 (m, overlapping Ar). Anal. Calcd. for $C_{32}H_{46}MoN_4O_2$: C, 62.53; H, 7.54; N, 9.11%. Found: C, 62.35; H, 7.16; N, 9.66%;

Synthesis of [Mo(N-*t*-Bu)$_2$(L_{Me2Ph})$_2$] (7). The compound was prepared following the general procedure employing 0.399 g (1 mmol)

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of [Mo(N-*t*-Bu)$_2$Cl$_2$(dme)] and 0.483 g (2 mmol) of KL_{Me2Ph} giving 0.127 g (20%) of **7**. ^{1}H NMR (benzene-d_6): δ 1.05 (s, 18H, (H_3C)$_3$C), 1.36 (s, 6H, H_3C), 1.90 (s, 6H, H_3C), 2.46 (s, 6H, H_3C), 2.59 (s, 6H, H_3C), 5.09 (s, 2H, γ-*H*), 6.83−7.30 (m, 6H, *H*-Ar) ppm. ^{13}C NMR (benzene-d_6): δ 19.7 (CH$_3$), 22.9 (CH$_3$), 23.2 (CH$_3$), 25.7 (CH$_3$), 30.2 ((CH$_3$)$_3$C), 71.2 (CMe$_3$), 102.0 (γ-*C*), 125.4, 129.0, 129.1, 131.7, 134.8, 154.6, 169.0 (C═N), 181.8 (C═O) ppm. Mass (EI, *m*/*z*, (%)): 644 (3) $[M]^+$. Anal. Calcd. for $C_{34}H_{50}MoN_4O_2$: C, 63.54; H, 7.84; N, 8.72%. Found: C, 63.54; H, 7.82; N, 8.15%.

Synthesis of [Mo(N-*t*-Bu)(L_{Me2Ph})$_2$(PMe_3)] (8). Compound [MoO(N-*t*-Bu)(L_{Me2Ph})$_2$] (**3**) (0.100 g, 0.170 mmol) was dissolved in 10 mL of toluene. Trimethyl phosphine (25 mg, 0.34 mmol) was added by syringe at room temperature upon which a color change from orange to deep brown occurred. The mixture was stirred at room temperature for 24 h, and subsequently the solvent was removed in vacuo. Washing of the brown powder with pentane gave the product in moderate yield (47 mg, 43%). ^{1}H NMR (benzene-d_6): δ 0.62 (d, 9H, PMe_3 J_{PH} = 6.86 Hz), 0.98 (s, 3H, H_3C), 1.16 (s, 9H, (H_3C)$_3$C), 1.39 (s, 3H, H_3C), 1.78 (s, 3H, H_3C), 1.82 (s, 3H, H_3C), 2.29 (s, 3H, H_3C), 2.31 (s, 3H, H_3C), 2.40 (s, 3H, H_3C), 2.61 (s, 3H, H_3C), 4.84 (s, 1H, γ-*H*), 5.31 (s, 1H, γ-*H*), 6.80−7.12 (m, 6H, *H*-Ar) ppm. ^{13}C NMR (benzene-d_6): δ = 18.2 (PMe_3), 20.0 (CH$_3$), 20.7 (2 CH$_3$), 22.8 (CH$_3$), 23.1 (CH$_3$), 23.4 (CH$_3$), 24.1 (CH$_3$), 25.4 (CH$_3$), 26.2 ((CH$_3$)$_3$C), 70.7 (CMe$_3$), 100.0 (γ-*C*), 100.6(γ-*C*), 124.2, 124.7, 129.0, 129.2, 129.7, 130.4,134.2, 134.8,154.8, 156.0, 166.1 (C═N), 166.7 (C═N), 175.1 (C═O), 181.6 (C═O) ppm. ^{31}P NMR (benzene-d_6): δ = 6.5 (PMe$_3$).

General Procedure for Kinetic Experiments. In a typical experiment 30 mg of complex **3** were dissolved in 5 mL of toluene (passed over alox) in a 3-necked Schlenk flask. Under a stream of Argon the fiber optic probe was immersed in the solution. Via a syringe, the required amount of PMe_3 was added and enough toluene was introduced as to keep the final volume of the solution the same throughout all the kinetic experiments. The measurement was started immediately after the addition.

Acknowledgment. Financial support by the Austrian Science Foundation FWF P19309-N19 is gratefully acknowledged.

Supporting Information Available: Crystallographic data in cif format. Figures of UV/vis spectra for the reduction of 3 kinetic plots and data for the reduction of **1** and **3**. Cyclic voltammograms of **1** and **3**. EI mass spectra of **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.