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Molybdenum Oxo–Imido Aryloxide Complexes: Oxo Analogues of Olefin Metathesis Catalysts

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The novel 16-electron molybdenum oxo–imido bis(aryloxide) complexes [$Mo(N^tBu)(O)(2,6\text{-}Me_2C_6H_3O)_2(py)$] (**1**) and [$Mo(N^tBu)(O)(2,6\text{-}{}^iPr_2C_6H_3O)_2(py)$] (**2**) have been prepared by the salt elimination reactions of [$Mo(N^tBu)(O)Cl_2(DME)$] with the appropriate lithium aryloxide and from the cycloaddition reactions of *tert*-butyl isocyanate with the appropriate molybdenum dioxo bis(aryloxide) complex [$Mo(O)_2(OAr)_2(py)_n$]. Complexes **1** and **2** are the first isolable and crystallographically characterized molybdenum oxo–imido aryloxide complexes. The geometry around the metal in complexes **1** and **2** is best described as a distorted trigonal bipyramid, with the imido and pyridine ligands occupying the axial positions and the oxo and aryloxide ligands in the equatorial plane. X-ray and IR data have confirmed that the imido ligand is the dominant π donor in the complexes, resulting in an Mo–O bond order of less than 2.5. Reaction of [$Mo(N^tBu)(O)Cl_2(DME)$] with $Li(OCH_2{}^tBu)$ instead gave the novel complex [$Mo(N^tBu)(OCH_2{}^tBu)_3Cl(py)$] (**3**).

Introduction

Transition-metal complexes containing multiply bonded ligands[1] have become increasingly important as more is understood about their structure and reactivity. The most common multiply bonded ligands are oxo,[1] imido,[1−3] and alkylidene[1,4] groups, and they have been employed either as spectator ligands to stabilize high-oxidation-state metal centers or as reactive entities. Reactive metal−ligand multiple bonds are now highly important in organic synthesis and catalysis:[1] examples include olefin metathesis,[6] carbonyl olefination,[7] cyclopropanation,[8] epoxidation,[9] asymmetric dihydroxylation,[10] hydroamination,[11] and C−H activation.[12] As part of a research program aimed at defining unprecedented bond constructions and functional group transformations, we are trying to engineer transition-metal complexes with highly reactive oxo ligands that will participate in cycloaddition reactions with unsaturated organic molecules. We anticipate that we will require an electron-deficient and coordinatively unsaturated metal center to facilitate initial π coordination of the unsaturated organic molecule and the space to accommodate the desired cycloaddition adduct. In addition, we activate the metal−oxo bond of our complexes by using a spectator ligand effect.[13,14] The isoelectronic oxo

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(1) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(2) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239.

(3) Chisholm, M. H.; Rothwell, I. P. In *Computational Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 2, p 162.

(4) (a) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (b) Schrock, R. R. *J. Chem. Soc., Dalton Trans.* **2001**, 2541.

(5) (a) Grubbs, R. H., Ed. *Handbook of Olefin Metathesis*; Wiley-VCH: Weinheim, Germany, 2003. (b) Linker, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2060. (c) Kühn, F. E.; Zhao, J.; Herrmann, W. A. *Tetrahedron: Asymmetry* **2005**, 3469. (d) Mayer, J. M. *Acc. Chem. Res.* **1998**, *31*, 441. (e) Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: Weinheim, Germany, 2000; p 357. (f) Duncan, A. P.; Bergman, R. G. *Chem. Rev.* **2002**, *2*, 431. (g) Hazari, N.; Mountford, P. *Acc. Chem. Res.* **2005**, *38*, 839.

(6) Grubbs, R. H., Ed. *Handbook of Olefin Metathesis*; Wiley-VCH: Weinheim, Germany, 2003.

(7) (a) Takeda, T. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 195. (b) Takeda, T.; Tsubouchi, A. *Modern Carbonyl Olefination*; Wiley-VCH: Weinheim, Germany, 2004; pp 151−159.

(8) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911.

(9) Linker, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2060.

(10) Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: Weinheim, Germany, 2000; p 357.

(11) (a) Duncan, A. P.; Bergman, R. G. *Chem. Rev.* **2002**, *2*, 431. (b) Hazari, N.; Mountford, P. *Acc. Chem. Res.* **2005**, *38*, 839.

(12) (a) Mayer, J. M. *Acc. Chem. Res.* **1998**, *31*, 441. (b) Slaughter, L. M.; Wolczanski, P. T.; Klinckman, T. R.; Cundari, T. R. *J. Am. Chem. Soc.* **2000**, *122*, 7953. (c) Hoyt, H. M.; Michael, F. E.; Bergman, R. G. *J. Am. Chem. Soc.* **2004**, *26*, 1018. (d) Blackmore, I. J.; Legzdins, P. *Organometallics* **2005**, *24*, 4088. (e) Weng, W.; Yang, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4700.

(13) Rappé, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 448.

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and imido ligands have the potential to be six-electron donors through a σ bond and two degenerate pπ−dπ bonds to the metal. In certain configurations of complexes containing sets of multiply bonded ligands, for example, if mutually cis in a trigonal-bipyramidal geometry, the ligands compete for three molybdenum π orbitals (originating from the metal d_{xy}, d_{xz}, and d_{yz} orbitals).[15] Thus, one of the multiply bonded ligands can form a triple bond to the metal as a six-electron donor (1σ, 2π), while the other can only form a metal ligand double bond as a four-electron donor (1σ, 1π). In certain configurationally defined mixed oxo−imido complexes, one would expect the imido ligand to form the stronger π bond to the metal because of nitrogen's weaker electronegativity compared to oxygen, thus coercing the oxo ligand toward being a four-electron donor and a weaker π bond.[16]

The spectator ligand effect contributes to the high reactivity of the metal alkylidene fragment in Schrock's olefin metathesis catalyst $[Mo(CHR^1)(NR^2)(OR^3)_2]$.[17] This catalyst is a rare example of a transition-metal complex that contains two different multiply bonded ligands. The imido group acts as a six-electron donor, stabilizing the coordinatively unsaturated metal center and the olefin metathesis reaction manifold, of which cycloaddition with an alkene is the first bond-forming step. By analogy, we are interested in studying the structure and reactivity of electron-deficient and coordinatively unsaturated oxo−imido complexes of molybdenum that may undergo similar cycloaddition reactions with a range of unsaturated functionality. Most previously reported molybdenum oxo−imido complexes are 18-electron coordinatively saturated octahedral complexes, for example, the dichloride DME adducts $[Mo(NR)(O)Cl_2(DME)]$ (R = 2,4,6-$Ph_3C_6H_2$,[18] 1-adamantyl,[19] C_6F_5,[20] 2,4,6-$Me_3C_6H_2$,[21] ^{t}Bu[14,22]), the Schiff base compounds [Mo(N^{t}Bu)(O){(3,5-^{t}Bu$_2$)$_2$-salpen}] and [Mo(NAr)(O){(7-Me)$_2$salen}] (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$),[22] the oxyquinolato derivative [Mo(N ^{t}Bu)(O)(N−O)$_2$] (N−OH = 8-hydroxyquinoline),[23] and the dithiocarbamate complexes $[Mo(NR)(O)(S_2CNEt_2)_2]$ (R = Ph,[24] tosyl,[25] *p*-tolyl[26]). Two coordinatively unsaturated and electron-deficient molybdenum oxo−imido alkoxide complexes that have been reported previously, [Mo(N^{t}Bu)(O)(O^{t}Bu)$_2$][14] and [Mo(NAr)(O)(O^{t}Bu)$_2$] (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$),[27] are unstable in solution at room temperature, disproportionating to the diimido and dioxo complexes. There are no reports in the literature of isolable molybdenum or tungsten oxo−imido alkoxide or aryloxide compounds that have been crystallographically characterized. We reasoned that stable mixed oxo−imido complexes with a low coordination number could be prepared using bulky aryloxide ligands. Consequently, we report the synthesis of two 16-electron, five-coordinate, oxo−imido aryloxide complexes of molybdenum, in which the imido ligand weakens the metal−oxo bond by competing for π donation to the metal. These are the first isolable, crystallographically characterized molybdenum oxo−imido aryloxide compounds.

Experimental Section

Materials and Methods. All manipulations were performed under dry, oxygen-free nitrogen or argon using standard Schlenk techniques or in a Mbraun Unilab glovebox. THF was dried over and distilled from sodium benzophenone prior to use. Et_2O, pentane, toluene, and hexane were degassed and then dried by passing through a column of activated alumina. Complexes [Mo(N^{t}Bu)(O)Cl$_2$(DME)], [Mo(O)$_2$(2,6-Me$_2$C$_6$H$_3$O)$_2$(py)$_2$], and [Mo(O)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$(py)] were prepared as described in the literature.[22,28] The lithium aryloxides Li(2,6-Me$_2$C$_6$H$_3$O) and Li(2,6-^{i}Pr$_2$C$_6$H$_3$O) were prepared from ^{n}BuLi and the appropriate aryl alcohol in hexane at −78 °C. All other reagents were obtained from commercial suppliers and used without further purification. NMR spectra were obtained on a Bruker AMX400 or a Bruker DRX500 spectrometer. Elemental analyses were performed in the School of Chemistry, University of Nottingham, Nottingham, U.K. IR spectra were recorded as solids using an Avatar 320 FTIR spectrometer.

[Mo(N^{t}Bu)(O)(2,6-Me$_2$C$_6$H$_3$O)$_2$(py)] (1). (a) From [Mo(N^{t}Bu)(O)Cl$_2$(DME)]. A solution of [Mo(N^{t}Bu)(O)Cl$_2$(DME)] (0.48 g, 1.39 mmol) in THF (20 mL) was slowly added to a stirred solution of Li(2,6-Me$_2$C$_6$H$_3$O) (0.36 g, 2.77 mmol) in a mixture of THF (20 mL) and pyridine (3.4 mL) at −78 °C. The mixture was allowed to warm to room temperature over a period of about 2 h, during which time its color changed to dark green, and then stirred overnight. Volatiles were then removed in vacuo to give a green oily residue. The product was extracted into pentane (3 × 20 mL), giving a yellow solution that was reduced in volume to ca. 30 mL in vacuo. Cooling to −20 °C gave pale-yellow crystals of **1** (0.31 g, 45%), which were isolated in three batches.

(b) From [Mo(O)$_2$(2,6-Me$_2$C$_6$H$_3$O)$_2$(py)$_2$]. To a stirred solution of [Mo(O)$_2$(2,6-Me$_2$C$_6$H$_3$O)$_2$(py)$_2$] (0.366 g, 0.693 mmol) in PhMe (15 mL) was added ^{t}BuNCO (0.069 g, 0.693 mmol). The reaction mixture was heated at 70 °C for 16 h, after which time the color of the orange solution had darkened. The solution was allowed to cool to room temperature, and all volatiles were removed in vacuo. The residue was dissolved in pentane (20 mL) and cooled to −20 °C overnight, giving pale-yellow crystals of **1** (0.081 g, 23%).

Mp: 122−126 °C. ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ 9.08 (br d, J = 3.6 Hz, 2H, *o*-py), 6.96 (d, J = 7.6 Hz, 4H, *m*-ArO), 6.88 (t, J = 7.6 Hz, 1H, *p*-py), 6.77 (t, J = 7.6 Hz, 2H, *p*-ArO), 6.61 (t, J = 7.4 Hz, 2H, *m*-py), 2.56 (s, 12H, Me), 0.69 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz): δ 168.8 (C−O), 150.0, 138.3, 129.2, 126.8, 124.9, 121.9 (remaining aromatics), 73.3 (N−*C*Me$_3$), 29.4

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(14) Gibson, V. C.; Graham, A. J.; Jolly, M.; Mitchell, J. P. *Dalton Trans.* **2003**, 4457.

(15) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 321

(16) Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1994**, 1607.

(17) Schrock, R. R. In *Handbook of Olefin Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; p 15.

(18) Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Dalton Trans.* **1996**, 4265.

(19) Copley, R. C. B.; Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Marshall, E. L.; Wang, W.; Whittle, B. *Polyhedron* **1996**, *15*, 3001.

(20) Rufanov, K. A.; Zarubin, D. N.; Ustynyuk, N. A.; Gourevitch, D. N.; Sundermeyer, J.; Churakov, A. V.; Howard, J. A. K. *Polyhedron* **2001**, *21*, 379.

(21) Galindo, A.; Montilla, F.; Pastor, A.; Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Ruiz, C. *Inorg. Chem.* **1997**, *36*, 2379.

(22) Ramnauth, R.; Al-Juaid, S.; Motevalli, M.; Parkin, B. C.; Sullivan, A. C. *Inorg. Chem.* **2004**, *43*, 4072.

(23) Tackacs, T.; Cavell, R. G. *Inorg. Chem.* **1994**, *33*, 2635.

(24) Maatta, E. A.; Wentworth, R. A. D. *Inorg. Chem.* **1979**, *18*, 2409.

(25) Harlan, E. W.; Holm, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 186.

(26) Devore, D. D.; Maatta, E. A. *Inorg. Chem.* **1985**, *24*, 2846.

(27) Bazan, G. C.; Schrock, R. R.; O'Regan, M. B. *Organometallics* **1991**, *10*, 1062.

(28) Hanna, T. A.; Ghosh, A. K.; Ibarra, C.; Mendez-Rojas, M. A.; Rheingold, A. L.; Watson, W. H. *Inorg. Chem.* **2004**, *43*, 1511.

(CH_3), 18.3 (CH_3). IR (cm^{-1}): 1603w, 1590w, 1476m, 1466m, 1447m, 1404w, 1377w, 1358w, 1264m, 1237m, 1220m, 1213s, 1198vs, 1160w, 1134w, 1092m, 1072w, 1039w, 1010w, 931w, 917w, 901vs, 860sh, 853vs, 776m, 765s, 756s. ν(M═O) is assigned as 901 cm^{-1}. Elem anal. Calcd for $C_{25}H_{32}MoN_2O_3$: C, 59.27; H, 6.37; N, 5.53. Found: C, 60.26; H, 6.43; N, 5.35.

[Mo(N^{t}Bu)(O)(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$(py)] (2). (a) From [Mo(N^{t}Bu)(O)Cl$_2$(DME)]. In an identical procedure for the preparation of **1**, [Mo(N^{t}Bu)(O)Cl$_2$(DME)] (0.74 g, 2.14 mmol) gave, after cooling to −20 °C for several days, pale-yellow crystals of **2** (0.63 g, 48%), which were isolated in three batches.

(b) From [Mo(O)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$(py)]. To a stirred solution of [Mo(O)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$(py)] (0.175 g, 0.312 mmol) in PhMe (15 mL) was added ^{t}BuNCO (0.031 g, 0.312 mmol). The mixture was heated to 70 °C for 16 h, during which the color of the solution changed from orange to yellow-green. The mixture was allowed to cool to room temperature, and all volatiles were removed in vacuo. The residue was dissolved in pentane (10 mL) and cooled to −20 °C for 3 days, giving yellow crystals of **2** (0.095 g, 49%).

Mp: 117−121 °C. ^{1}H NMR (C_6D_6, 500 MHz): δ 9.26 (br d, J = 4.8 Hz, 2H, *o*-py), 7.13 (d, J = 7.9 Hz, 4H, *m*-ArO), 6.97 (t, J = 7.9 Hz, 2H, *p*-ArO), 6.84 (t, J = 7.3 Hz, 1H, *p*-py), 6.65 (t, J = 7.3 Hz, 2H, *m*-py), 3.93 [sep, J = 6.6 Hz, 4H, *C*H(CH$_3$)$_2$], 1.38 [d, J = 6.6 Hz, 12H, CH(*C*H$_3$)$_2$], 1.37 [d, J = 6.6 Hz, 12H, CH(*C*H$_3$)$_2$], 0.74 (s, 9H, ^{t}Bu). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ 166.2 (C−O), 150.0, 138.2, 136.9, 124.8, 123.9, 122.3 (aromatics), 73.5 (N−*C*Me$_3$), 29.7, 28.2, 24.9, 23.9. IR (cm^{-1}): 1602w, 1590w, 1465w, 1458w, 1444w, 1425m, 1379w, 1359w, 1324w, 1253m, 1237w, 1217m, 1193s, 1153w, 1139w, 1115m, 1071w, 1040w, 1012w, 934w, 899vs, 886s, 861s, 854vs, 799m, 792m, 767m, 752s. ν(M═O) is assigned as 899 cm^{-1}. Elem anal. Calcd for $C_{33}H_{48}MoN_2O_3$: C, 64.05; H, 7.82; N, 4.53. Found: C, 63.78; H, 7.94; N, 4.43.

[Mo(N^{t}Bu)(OCH$_2$^{t}Bu)$_3$Cl(py)] (3). A solution of [Mo(N^{t}Bu)(O)Cl$_2$(DME)] (0.500 g, 1.45 mmol) in Et$_2$O (30 mL) was slowly added to a stirred solution of Li(OCH$_2$^{t}Bu) (0.273 g, 2.90 mmol) in a mixture of Et$_2$O (30 mL) and pyridine (1 mL) at −78 °C. The mixture was allowed to warm to room temperature over a period of about 2 h and then stirred overnight. Volatiles were then removed in vacuo to give a green oily residue. The residue was dissolved in pentane (ca. 10 mL), filtered, and cooled to −20 °C for 1 week, giving pale-yellow crystals of **3** (0.293 g, 37%).

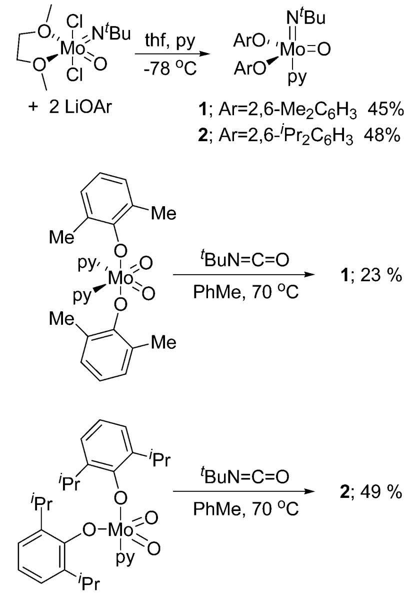
Mp: 101−104 °C. ^{1}H NMR (C_6D_6, 400 MHz): δ 9.23 (br d, J = 3.7 Hz, 2H, *o*-py), 6.90 (t, J = 7.6 Hz, 1H, *p*-py), 6.71 (t, J = 6.9 Hz, 2H, *m*-py), 4.70 (br, 6H, OC*H*$_2$^{t}Bu), 1.46 (s, 9H, N^{t}Bu), 1.00 (s, 27H, OCH$_2$^{t}Bu). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz): δ 150.6 (*o*-py), 137.9 (*p*-py), 123.8 (*m*-py), 92.4 (br, OCH$_2$), 75.3 (N−*C*Me$_3$), 35.4, 31.9, 27.7. IR (cm^{-1}): 1391w, 1361w, 1303w, 1259w, 1231m, 1215m, 1057vs, 1051vs, 1039s, 1019vs, 939m, 964m, 851w, 821w, 801m, 760m, 753m, 722m. Elem anal. Calcd for $C_{24}H_{47}ClMoN_2O_3$: C, 53.08; H, 8.72; N, 5.16. Found: C, 50.87; H, 8.61; N, 4.99.[29]

X-ray Crystallography. All single-crystal diffraction data were collected using graphite-monochromated Mo Kα X-radiation on SMART APEX CCD area detector diffractometer equipped with an Oxford Cryostream cooling device. All data were collected at 150 K. Details of the individual data collections and refinements are given in Table 1. All structures were solved using *SHELXS-97* by direct methods. All structures were refined by least-squares full-matrix refinement against F^2 using *SHELXL-97* and all fully occupied non-hydrogen atoms refined with anisotropic atomic displacement parameters (adps). Hydrogen atoms were geometrically placed and refined as part of a riding model, except those of the methyl groups of complex **1** bound to sp^2-hydridized atoms, which were located from difference Fourier syntheses and refined as rigid rotors. In complex **3**, disorder present in the methyl carbon atoms of two of the *tert*-butyl groups, C1 and C12, was modeled over two sites with occupancies of 0.55 and 0.45 and of 0.60 and 0.40, respectively. Geometric restraints were applied, and partially occupied atom sites were refined with isotropic adps.

Table 1. Crystallographic Data and Summary of Data Collection and Structural Refinement

	1	2	3
chem formula	$C_{25}H_{32}MoN_2O_3$	$C_{33}H_{48}MoN_2O_3$	$C_{24}H_{47}ClMoN_2O_3$
M_r	504.47	616.67	543.03
cell syst	monoclinic	monoclinic	triclinic
space group	$P2_1$	$P2_1/c$	$P\bar{1}$
a (Å)	9.3920(12)	12.4469(8)	13.7787(8)
b (Å)	8.3861(12)	12.7781(8)	14.7479(9)
c (Å)	15.617(2)	20.8685(13)	15.4947(9)
α (deg)	90.00	90.00	74.810(1)
β (deg)	92.332(2)	97.716 (1)	86.015(1)
γ (deg)	90.00	90.00	81.253(1)
V (Å^3)	1229.0(5)	3289.0(4)	3001.8(3)
Z	2	4	4
D_x (Mg m^{-3})	1.365	1.245	1.202
radiation type	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	0.56	0.43	0.55
T (K)	150(2)	150(2)	150(2)
R [$I > 2\sigma(I^2)$]	0.025	0.032	0.032
$wR(F^2)$	0.062	0.082	0.085
S	1.07	1.03	1.01

Scheme 1. Synthesis of Molybdenum Oxo−Imido Bis(aryloxide) Complexes



Results and Discussion

The novel complexes **1** and **2** were prepared via two routes (Scheme 1). First, they were prepared from the salt elimination reaction of [Mo(N^{t}Bu)(O)Cl$_2$(DME)] and the appropriate lithium aryloxide at −78 °C in THF. Following removal of the volatiles in vacuo, the product was extracted into pentane. Cooling the pentane solution to −20 °C gave **1** and **2** as yellow crystalline solid in 45 and 48% yield, respectively, in several batches. Second, complexes **1** and **2** were prepared

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(29) Satisfactory microanalysis could not be obtained because of the highly air-sensitive nature of the compound.

by heating the appropriate metal dioxo aryloxide compound and *tert*-butyl isocyanate at 70 °C for 16 h. In this second route, one of the Mo═O fragments of the dioxo complex undergoes a [2 + 2] cycloaddition reaction with the N═C bond of the isocyanate. A retro-cycloaddition extrudes CO_2 to give the oxo−imido product. As for the salt elimination route, complexes **1** and **2** were subsequently isolated from pentane solutions in 23% and 49% yields, respectively. The relatively moderate yields of the crystalline products from the two routes are, in part, compromised by their high solubility in pentane and also because of the formation of unidentifiable minor byproducts in the crude mixture. The ^1H and $^{13}C\{^1H\}$ NMR spectra for **1** and **2** were consistent with the expected molybdenum oxo−imido bis(aryloxide) compounds, with one pyridine molecule coordinated to the metal center in each case. Spectra for both complexes indicate that the two aryloxide ligands are equivalent by NMR spectroscopy, although for compound **2**, two inequivalent methyl groups of the isopropyl moieties were observed.

Single-crystal X-ray diffraction structures of **1** and **2** are shown in Figure 1, and Table 1 summarizes the data collection and refinement. Selected bond lengths and angles are given in Table 2. The geometry around the metal centers of **1** and **2** is best described as a distorted trigonal bipyramid. In both complexes, molybdenum is coordinated to axial *tert*-butylimido and pyridine ligands, with the oxo and *cis*-aryloxide ligands in the equatorial plane. In this respect, **1** and **2** differ from the analogous trigonal-bipyramidal dioxo complex $[Mo(O)_2(2,6\text{-}^iPr_2C_6H_3O)_2(py)]$,[28] in which the two oxo ligands and one of the aryloxide groups occupy the equatorial plane; the other aryloxide ligand and pyridine are found in the axial coordination sites. Moreover, in the dioxo compounds $[Mo(O)_2(2,6\text{-}^iPr_2C_6H_3O)_2(py)]$ and $[Mo(O)_2(2,6\text{-}Me_2C_6H_3O)_2(py)_2]$, the difference in steric bulk of the two aryloxide ligands demands a difference in the number of coordinated pyridine molecules.[28] This change in coordination number is not observed between **1** and **2**.

The strong trans influence of the imido group in **1** and **2** distorts the imido−metal−cis ligand angles to greater than 90°; the N(imido)−metal−O(aryloxide) angles are in the range 97.82(8)−98.60(6)°, and the N(imido)−metal−O(oxo) angles are 103.83(9)° and 104.73(7)°. The angle between two cis multiply bonded ligands is expected to be much larger than 90° and is almost always between 102 and 112° in d^0 complexes.[1] There is also distortion in the equatorial plane, with the O(oxo)−metal−O(aryloxide) angles being less than 120° [in the range 110.53(6)−113.28(8)°], presumably in order to reduce steric interactions between the 2,6-dimethyl or 2,6-diisopropyl substituents of the aryloxide.

The crystal structure determinations of **1** and **2** enable a comparison to be made between the π basicity of the oxo and *tert*-butylimido ligands. The almost linear Mo−N−C bond angles of 165.82(18)° for **1** and 173.46(15)° for **2** suggest that the imido nitrogen is sp-hybridized and the ligand is a six-electron donor (Mo≡N bond). Therefore, the oxo ligand is probably a four-electron donor, and the Mo═O bond order tends toward 2. This competition between π donors is also demonstrated by the metal−ligand distances.

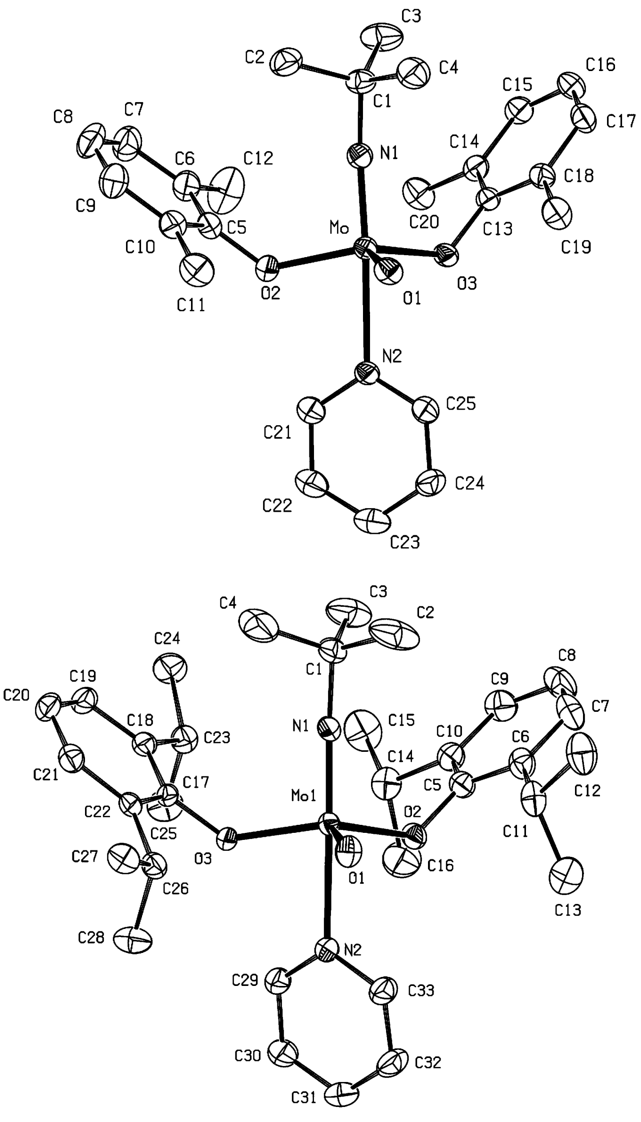

Figure 1. ORTEP views of **1** and **2** (50% probability). Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

	1	**2**
Mo−O1	1.7120(16)	1.7139(13)
Mo−N1	1.736(2)	1.7395(17)
Mo−O2	1.9445(16)	1.9347(13)
Mo−O3	1.9439(16)	1.9455(13)
Mo−N2	2.401(2)	2.3773(17)
O1−Mo-N1	103.83(9)	104.73(7)
O1−Mo−O2	113.28(8)	110.53(6)
O1−Mo−O3	111.36(8)	112.95(6)
O1−Mo−N2	86.72(8)	88.15(6)
N1−Mo−O2	98.18(8)	97.99(7)
N1−Mo−O3	97.82(8)	98.60(6)
N1−Mo−N2	169.45(8)	167.00(7)
O2−Mo−O3	126.83(7)	127.14(6)
O2−Mo−N2	76.97(7)	75.38(6)
O3−Mo−N2	78.25(6)	77.46(5)
C1−N1−Mo	165.82(18)	173.46(15)

The Mo−N1 bond lengths of 1.736(2) and 1.7395(17) Å, in **1** and **2**, respectively, are typical for Mo−imido bonds; the Mo−O1 bond lengths of 1.7120(16) and 1.7139(13) Å lie at the higher end of the range of 1.62−1.75 Å that is usually observed for metal−oxo bonds involving second- or thirdrow transition metals.[1] In addition, these metal−oxo distances are greater than those found in the series of dioxo compounds $[Mo(O)_2(OAr)_2(py)_n]$ (Ar = 2,4,6-$^tBu_3C_6H_2$, $n = 0$; Ar = 2,6-$^iPr_2C_6H_3$, $n = 1$; Ar = 2,6-$Me_2C_6H_3$, $n = 2$), where the range for d(Mo═O) is 1.682(2)−1.701(4) Å.[28] The Schiff base complex $[Mo(N^tBu)(O)\{(3,5\text{-}^tBu_2)_2salpen\}]$, which is the only other crystallographically characterized molybdenum oxo *tert*-butylimido complex, contains bond lengths between the metal and the multiply bonded ligands similar to those found in **1** and **2**: d(Mo═N) were 1.740(4) and 1.731(4) Å for the two distinct molecules found in the unit cell, while d(Mo═O) were 1.720(4) and 1.723(5) Å. The Mo−O(aryloxide) bond lengths in the two oxo−imido complexes **1** and **2** are between 1.9347(13) and 1.9455(13) Å; these values are similar to those found in the related dioxo aryloxide complexes, where the range is 1.8502(19)−1.964(4) Å.[28]

IR spectra recorded for **1** and **2** also give information about the relative π basicity of the *tert*-butylimido and oxo ligands. Although metal−imido stretching bands are expected in the range 1200−1000 cm^{-1}, identification of this stretch is problematic; often the metal−nitrogen vibrational mode is coupled with metal−ligand or N−R modes and commonly obscured by other vibrations.[1,3] Conversely, metal−oxo stretching bands can be identified clearly. Stretches for terminal monooxo complexes of molybdenum[1] (with a formal bond order of 3) usually fall within the range 920−1100 cm^{-1}, dioxo complexes (bond order 2.5) 875−970 cm^{-1}, and trioxo complexes (bond order 2) 870−935 cm^{-1}. For **1**, the very strong band ν(M═O) is found at 901 cm^{-1}, whereas for **2**, ν(M═O) occurs at 899 cm^{-1}; the wavenumbers of these vibrations are, therefore, consistent with a Mo−O bond order of less than 3. Moreover, the metal−oxo stretches in **1** and **2** are at lower wavenumbers than those found in the related *cis*-dioxo compounds $[Mo(O)_2(2,6\text{-}Me_2C_6H_3O)_2py_2]$, $[Mo(O)_2(2,6\text{-}^iPr_2C_6H_3O)_2py]$, and $[Mo(O)_2(2,4,6\text{-}^tBu_3C_6H_2O)_2]$, which have ν(M═O) in the range 915−965 cm^{-1}. These data provide further evidence that the *tert*-butylimido group is the stronger π donor of the two multiply bonded ligands. Indeed, the metal−oxo bond order appears to be less than 2.5.

Despite complexes **1** and **2** being isolable and stable in solution at room temperature, both decompose after refluxing in toluene for 24 h. Variable-temperature ^1H NMR spectra were recorded for both complexes in benzene-d_6 up to 70 °C. There was no evidence on the NMR time scale for dissociation of the pyridine ligand. Unlike for the rhenium oxo−imido complexes $[(CH_3)Re(NR)_{3-n}(O)_n]$, there was no evidence for the formation of dimers or oligomers in solution with bridging oxo or imido groups.[30] NMR spectra recorded after cooling of the samples to room temperature showed no changes from the original spectra.

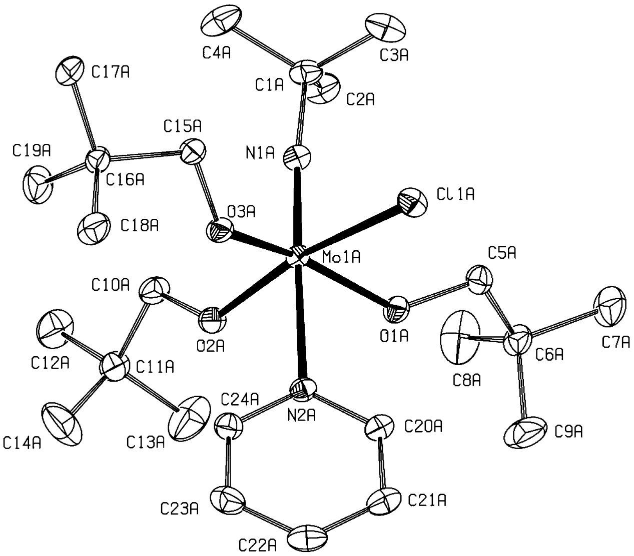

Figure 2. ORTEP view of one of the independent molecules of **3** (50% probability). Hydrogen atoms have been omitted for clarity.

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

Mo1−N1	1.7194(19)	Mo1A−N1A	1.716(2)
Mo1−O1	1.8967(16)	Mo1A−O3A	1.8995(17)
Mo1−O3	1.8999(16)	Mo1A−O2A	1.9000(16)
Mo1−O2	1.9049(16)	Mo1A−O1A	1.9080(16)
Mo1−N2	2.3504(18)	Mo1A−N2A	2.3604(19)
Mo1−Cl1	2.5008(6)	Mo1A−Cl1A	2.4989(6)
N1−Mo1−O1	99.97(8)	N1A−Mo1A−O3A	99.85(8)
N1−Mo1−O3	99.83(8)	N1A−Mo1A−O2A	101.14(8)
O1−Mo1−O3	156.68(7)	O3A−Mo1A−O2A	94.25(8)
N1−Mo1−O2	100.04(8)	N1A−Mo1A−O1A	99.23(8)
O1−Mo1−O2	94.62(8)	O3A−Mo1A−O1A	156.77(8)
O3−Mo1−O2	93.95(7)	O2A−Mo1A−O1A	94.94(7)
N1−Mo1−N2	179.45(8)	N1A−Mo1A−N2A	177.52(8)
O1−Mo1−N2	79.57(7)	O3A−Mo1A−N2A	79.69(7)
O3−Mo1−N2	80.68(7)	O2A−Mo1A−N2A	81.33(7)
O2−Mo1−N2	79.72(7)	O1A−Mo1A−N2A	80.67(7)
N1−Mo1−Cl1	93.28(7)	N1A−Mo1A−Cl1A	91.29(7)
O1−Mo1−Cl1	83.34(6)	O3A−Mo1A−Cl1A	83.33(6)
O3−Mo1−Cl1	83.34(5)	O2A−Mo1A−Cl1A	167.58(5)
O2−Mo1−Cl1	166.67(5)	O1A−Mo1A−Cl1A	83.12(5)
N2−Mo1−Cl1	86.96(5)	N2A−Mo1A−Cl1A	86.24(5)
C1−N1−Mo1	176.60(17)	C1A−N1A−Mo1A	173.80(18)

The molybdenum oxo−imido alkoxide complex $[Mo(N^tBu)(O)(OCH_2{}^tBu)_2]$ was prepared by Osborn et al. from $[Mo(N^tBu)(O)Cl_2(MeCN)_2]$ by treatment with lithium neopentoxide and characterized on the basis of ^1H NMR and IR spectroscopies.[31] We were interested in obtaining this compound to investigate the reactivity of the oxo ligand in cycloaddition reactions with unsaturated organic molecules. Our attempts to prepare this complex from $[Mo(N^tBu)(O)Cl_2(DME)]$, however, were unsuccessful. In an attempt to prepare a molybdenum oxo−imido alkoxide complex, $[Mo(N^tBu)(O)Cl_2(DME)]$ was treated with 2 equiv of lithium neopentoxide in a solution of ether with excess pyridine at −78 °C. Upon workup, pale-yellow crystals were isolated from pentane at −20 °C (37%), the moderate yield again a reflection on the high solubility of this complex and minor byproducts in the crude mixture. The pale-yellow crystals were identified by single-crystal X-ray diffraction to be **3**; one of the two independent molecules of **3** found in the unit cell is shown in Figure 2. Instead of $[Mo(N^tBu)(O)(OCH_2{}^tBu)_2(py)_n]$ (**4**) being formed, 3 equiv of the alkoxide have substituted for one chloride and the oxo ligand, eliminating 1 equiv of LiCl and Li_2O.

The geometry around the molybdenum center in **3** is a distorted octahedron (Table 3). The three alkoxide ligands occupy a meridian, ensuring that pyridine, as the most weakly

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(30) (a) Gisdakis, P.; Rösch, N.; Bencze, É.; Mink, J.; Gonçalves, I. S.; Kühn, F. E. *Eur. J. Inorg. Chem.* **2001**, 981. (b) Herrmann, W. A.; Ding, H.; Kühn, F. E.; Scherer, W. *Organometallics* **1998**, *17*, 2751.

bound ligand, is trans to the *tert*-butylimido group. As for **1** and **2**, the ligands cis to the imido are bent away from the multiply bonded ligand, with the N(imido)−Mo−O(alkoxide) angles lying in the range 99.23(8)−101.14(8)°. The N(imido)−Mo−Cl angles of 93.28(7) and 91.29(7)° are smaller; these are allowed by the long Mo−Cl bond lengths of 2.5008(6) and 2.4989(6) Å. The metal−imido distances of 1.7194(14) and 1.716(2) Å in the two independent molecules are shorter than those in **1** and **2**. Correspondingly, the Mo−N−C angles of the metal−imido fragment are slightly more linear, at 176.60(17) and 173.80(18)°. These changes are to be expected upon removal of the competing π donation from the oxo ligand.

In the formation of complex **3**, the metal−oxo bond is cleaved in the presence of a metal−chloride bond. This reactivity was unexpected, but by analogy with Hanna's synthesis of molybdenum oxo aryloxides $[Mo(O)(OAr)_{4-n}Cl_n]$ ($n = 0-2$, Ar = 2,6-$^iPr_2C_6H_3$ or 2,6-$Me_2C_6H_3$) from MoO_2Cl_2,[28] the mechanism shown in eqs 1−4 seems likely.

$$2LiOCH_2{}^tBu + H_2O \rightarrow 2HOCH_2{}^tBu + Li_2O \qquad (1)$$

$$[Mo(N^tBu)(O)Cl_2(DME)] + 2HOCH_2{}^tBu \rightarrow [Mo(N^tBu)(OCH_2{}^tBu)_2Cl_2] + H_2O + DME \qquad (2)$$

$$[Mo(N^tBu)(OCH_2{}^tBu)_2Cl_2] + LiOCH_2{}^tBu + py \rightarrow \mathbf{3} + LiCl \qquad (3)$$

$$[Mo(N^tBu)(O)Cl_2(DME)] + 3LiOCH_2{}^tBu + py \rightarrow \mathbf{3} + Li_2O + LiCl + DME \qquad (4)$$

The initial step involves the conversion of the lithium alkoxide to the alcohol by water (eq 1). A total of 2 equiv of the alcohol can then be added across the Mo═O bond (eq 2), releasing water and forming two metal−alkoxide bonds. The final step (eq 3) is a salt elimination reaction to give **2**. Therefore, the overall reaction (eq 4) is catalytic in water. Attempts to prepare complex **4** from the reaction of $[Mo(O)_2(OCH_2{}^tBu)_2(py)_n]$ and *tert*-butyl isocyanate proved unsuccessful.

Conclusion

In conclusion, the novel molybdenum oxo−imido bis(aryloxide) complexes **1** and **2** have been prepared by the salt elimination reactions of $[Mo(N^tBu)(O)Cl_2(DME)]$ with the appropriate lithium aryloxide or from the cycloaddition reactions of *tert*-butyl isocyanate with the appropriate molybdenum dioxo bis(aryloxide) complex $[Mo(O)_2(OAr)_2(py)_n]$. Reaction of $[Mo(N^tBu)(O)Cl_2(DME)]$ with $Li(OCH_2{}^tBu)$ instead resulted in cleavage of the metal−oxo linkage to give the novel complex **3**. Complexes **1** and **2** are the first isolable and crystallographically characterized molybdenum oxo−imido aryloxide complexes. In addition, they are coordinatively unsaturated 16-electron complexes in which we expect the oxo ligand to be highly nucleophilic. X-ray crystallographic studies and IR data have confirmed that the imido ligand is the dominant π donor in the complexes, resulting in an Mo−O bond order of less than 2.5. We are currently investigating the cycloaddition reactions of the Mo═O bond with unsaturated organic molecules.

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Supporting Information Available: ^1H and ^{13}C NMR spectra (PDF) and X-ray crystallographic data (CIF) for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) Ehrenfeld, D.; Kress, J.; Moore, B. D.; Osborn, J. A.; Schoettel, G. *J. Chem. Soc., Chem. Commun.* **1987**, 129.