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Synthesis of a tris(pyrazolyl)borate-stabilized molybdenum alkylidene and its hydrolysis products. Crystal structures of $TpMo(CH_2C(Me)_2Ph)(NAr)(O)$ and $[TpMo(NAr)(O)]_2O$

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Abstract

The synthesis of a tris(pyrazolyl)borate-stabilized molybdenum (VI) imido alkylidene complex, $TpMo(CHC(Me)_2Ph)(NAr)(OTf)$ (**1**) [$Ar = 2,6\text{-i-}Pr_2\text{-}C_6H_3$, $Ph = C_6H_5$, $OTf = OSO_2CF_3$], has been achieved by addition of potassium hydridotris(1-pyrazolyl)borate (KTp) to $Mo(CHC(CH_3)_2Ph)(NAr)(OTf)_2(DME)$. Stirring compound **1** over alumina in the presence of H_2O gave $TpMo(CH_2C(Me)_2Ph)(NAr)(O)$ (**2**). Alternatively, compound **1** was converted to **2** by the addition of $CsOH \cdot H_2O$ in THF. A single crystal of $[TpMo(NAr)(O)]_2O$ (**4**) was isolated from a solution of **2**. Compounds **2** and **4** have been characterized by X-ray crystallography and the bonding considerations about the molybdenum atoms are discussed.

Keywords: Molybdenum; Alkylidenes; Trispyrazolylborates

1. Introduction

The chemistry of transition metal–ligand multiple bonds is widely encountered throughout the literature, especially concerning high oxidation state metal alkylidene complexes and their role in olefin metathesis reactions [1–4]. Our efforts have focused on developing and studying metal alkylidene compounds employing ancillary chelating ligands. Previous communications from our group have described the function of hydridotris(pyrazolyl)borate (Tp) ligands [5] in the stabilization of tungsten (VI) alkylidene complexes. The Tp ligand, serving as a template to bind and stabilize the metal center, has led to the development of neutral and cationic tungsten alkylidene complexes [6–8]. These compounds serve as ring-opening metathesis polymerization (ROMP) and acyclic diene metathesis (ADMET) oligomerization catalysts in the presence of Lewis acid cocatalysts.

In this paper, we report the synthesis of an imido alkylidene complex of molybdenum that is stabilized by the Tp ligand system, $TpMo(CHC(Me)_2Ph)(NAr)(OTf)$ (**1**) ($Ar = 2,6\text{-i-}Pr_2\text{-}C_6H_3$, $Ph = C_6H_5$, $OTf = OSO_2CF_3$). The hydrolysis of compound **1** resulted in the formation of a stable molybdenum (VI) oxo imido compound, $TpMo(CH_2C(Me)_2Ph)(NAr)(O)$ (**2**). The further hydrolysis of **2** resulted in the formation of an oxo-bridged dimer $[TpMo(NAr)(O)]_2O$ (**4**). The synthesis and characterization of these compounds are described below.

2. Results and discussion

2.1. Synthesis of $TpMo(CHC(Me)_2Ph)(NAr)(OTf)$ (1)

The reaction of one equivalent of KTp with $Mo(CHC(Me)_2Ph)(NAr)(OTf)_2(DME)$ in THF at ambient temperature results in the rapid formation of $TpMo(CHC(Me)_2Ph)(NAr)(OTf)$ (**1**, Eq. 1) which is obtained as bright yellow needles from pentane. Compound **1** remains stable in air as a solid for one month

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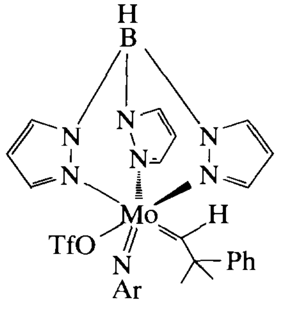
with no evidence of decomposition by ^{1}H NMR and it decomposes thermally in air at 155°C. The chelating ability of the Tp ligand and the increased steric bulk at the metal [9], as well as the formal 18 electron count at the metal, are responsible for the robust nature of compound **1**.

KTp + Mo(CHC(Me$_2$)Ph)(NAr)(OTf)(DME) $\xrightarrow{THF}$



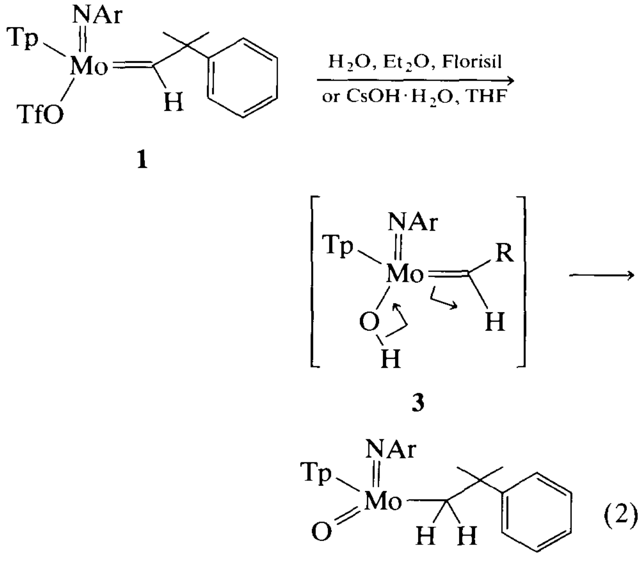
(1)

1

The ^{1}H NMR spectrum of compound **1** at 22°C is complicated by the chirality of the compound, resulting in nine distinct pyrazole proton resonances and diastereotopic methyl resonances for the neophylidene ligand and for the isopropyl groups of the aryl imido ligand. The proton signals of the isopropyl groups of the aryl imido ligand are broad, suggesting hindered rotation about the nitrogen–aryl bond. Variable temperature NMR measurements were used to measure a barrier to rotation of 15 kcal mol^{-1} for the nitrogen–carbon bond. The solution structure is assigned by nOe experiments as the *syn* isomer in which the alkylidene C(Me)$_2$Ph group is oriented towards the imido ligand [10]. The triflate ligand is covalently bound to the metal center, demonstrated by strong characteristic IR absorptions at 1202 and 633 cm^{-1} assigned to the S=O stretches [11].

2.2. Synthesis of TpMo(CH$_2$C(Me)$_2$Ph)(NAr)(O) (2)

Compound **1** in THF remains stable in the presence of H_2O over a period of 24 h. However, when a wet Et_2O solution of **1** is passed over a column of alumina, a small amount of TpMo(CH$_2$C(Me)$_2$Ph)(NAr)(O) (**2**) was observed by ^{1}H NMR. Stirring compound **1** in a slurry of Florisil in Et_2O and H_2O for 24 h afforded an orange solution of compound **2** which can be recrystallized from pentane to give orange crystals. This result compares with a previously reported reaction by our group in which a tungsten alkylidene complex, Tp′W(CCMe$_3$)Cl$_2$, is converted to the tungsten alkylidene complex, Tp′W(CHCMe$_3$)OCl, by stirring over alumina [6]. Also, the reaction of compound **1** with one equivalent of CsOH in THF gave a quantitative yield of **2**. Heating **2** in excess PMe$_3$ for 5 days at 65°C showed no reaction by ^{1}H NMR and no evidence of phosphine oxide or phosphazine.



(2)

2

The distinctive features of the ^{1}H NMR spectrum of compound **2** are the presence of an AB quartet corresponding to the diastereotopic protons of the CH$_2$C(Me)$_2$Ph ligand and the loss of the downfield alkylidene resonance of the alkylidene proton of **1**. The isopropyl groups of the aryl imido ligand are responsible for a broad multiplet due to the methine protons and two slightly broadened doublets due to the methyl protons indicating that the N–Ar bond rotates more freely than that of compound **1**. The molybdenum–oxygen bond appears as a strong absorption at 896 cm^{-1} in the IR spectrum which is within the normal range for molybdenum oxo compounds containing additional multiply bonded ligands [1].

One possible mechanism for the formation of **2** is the displacement of the triflate ligand by hydroxide to form an unobserved hydroxy-alkylidene species (**3**, Eq. 2). Subsequent proton transfer from the oxygen to the α-carbon of the alkylidene results in the favorable formation of the strong molybdenum–oxygen triple bond. The previously reported tungsten analogue of **2** was prepared by the protonation of TpW(CHC(Me)$_2$Ph) (NAr)(CH$_2$C(Me)$_2$Ph) by HBF$_4$ in the presence of H_2O to give [TpW(NHAr)(O) (CH$_2$C(Me)$_2$Ph)][BF$_4$] followed by deprotonation by NEt$_3$ [8]. This result suggests an acid-catalyzed mechanism for the formation of **2** in the Florisil preparation.

2.3. Crystal structure of TpMo(CH$_2$C(Me)$_2$Ph)(NAr)(O) (2)

The structure of compound **2** was determined by X-ray diffraction methods and a thermal ellipsoid plot

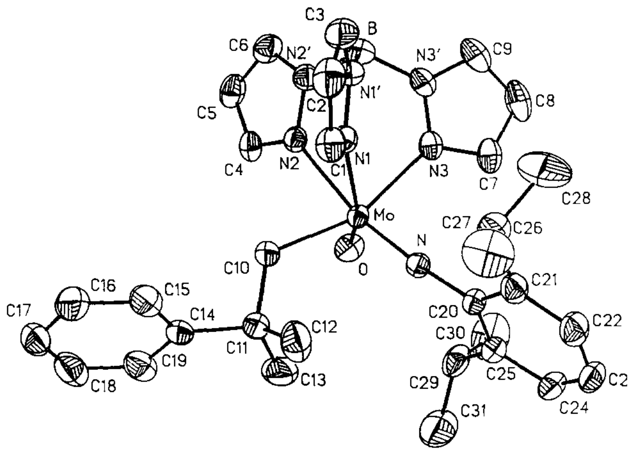


Fig. 1. Molecular structure of **2**, showing 50% thermal ellipsoids and the atomic labeling scheme.

is given in Fig. 1. Selected bond distances and angles are given in Table 1. The structure consists of well-separated molecules with a pseudooctahedral coordination geometry about the metal. The geometric constraints of the facially-bound Tp ligand force the oxo, imido, and alkyl ligands to be mutually *cis*, with a O–Mo–N angle of 103.68(9)° [12]. The N–Mo bond lengths of the chelating pyrazole rings range from 2.379(2) to 2.207(2) Å and are consistent with the decreasing *trans* influence of the ligands oxo > imido > alkyl [1].

In transition metal-oxo and -imido compounds in which the formal electron count of the metal is less than 18 electrons, triply bonded oxo and imido ligands are the preferred valence bond description by donation of a lone pair of electrons of the ligand to an empty metal d orbital of appropriate π-symmetry. In compound **2**, however, the metal has an electron count of 20 if both the oxo and the imido are triply bonded. The crystal structure of **2** shows the oxo and the imido ligands to have bond orders between two and three with metal bond lengths of 1.706(2) and 1.760(2) Å, respectively [1,13]. Also, the Mo–N–Ar bond angle, 168.07(13)°, approaches linearity, suggesting to a first approximation that the molybdenum–nitrogen bond order is greater than two. However, the steric bulk at the metal center may also contribute to the linearity of the sterically demanding aryl imido ligand. A delocalized, three center-four electron π-bonding description between the oxygen, molybdenum, and nitrogen atoms may provide the best explanation of the metal's ability to accommodate twenty electrons.

Table 1
Selected bond lengths (Å) and angles (°) for the non-H atoms of compound **2**

1	2	3	1–2	1–2–3
O	Mo	N	1.706(2)	103.68(9)
O	Mo	N1		158.69(8)
O	Mo	N2		84.04(8)
O	Mo	N3		101.76(8)
N	Mo	N1	1.760(2)	97.56(8)
N	Mo	N2		168.68(8)
N	Mo	N3		90.07(8)
N	Mo	C10		101.46(9)
N1	Mo	N2	2.379(2)	74.68(6)
N1	Mo	N3		76.13(6)
N1	Mo	C10		80.49(9)
N2	Mo	N3	2.321(2)	80.14(7)
N2	Mo	C10		85.59(8)
N3	Mo	C10	2.207(2)	155.10(8)
C10	Mo	O	2.191(2)	96.89(10)
C20	N	Mo	1.386(3)	168.07(13)
C11	C10	Mo	1.552(3)	125.5(2)

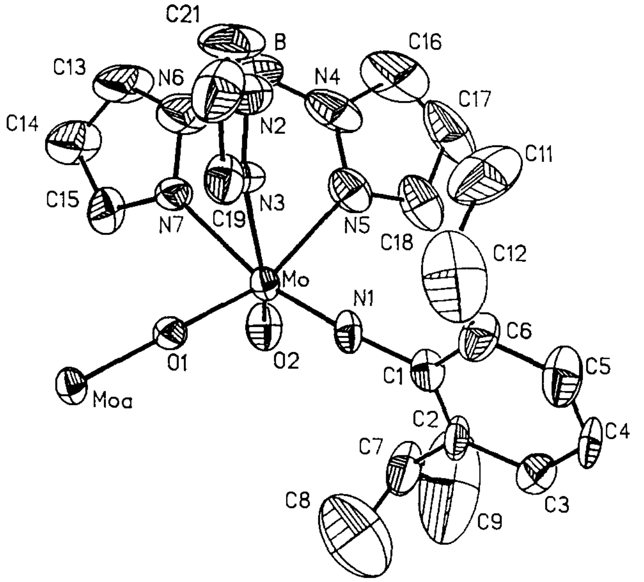


Fig. 2. Molecular structure of **4**, showing 50% thermal ellipsoids and the atomic labeling scheme. The coordination sphere around Mo_a is omitted for clarity.

2.4. *Crystal structure of [TpMo(NAr)(O)]$_2$O (4)*

A red single crystal suitable for X-ray diffraction studies was isolated from the pentane mother liquor of **2** after 2 weeks. The structure of $[TpMo(NAr)(O)]_2O$ (**4**), shown in Fig. 2, was obtained. Compound **4** appears to be a hydrolysis product of compound **2** in which the neophyl ligands of two equivalents of **2** are protonated and lost and the metal centers are bridged by an oxygen atom, most likely from H_2O. The synthesis of compound **4** was attempted in two ways. H_2O and 2,6-lutidine were added to compound **2** dissolved in THF, and H_2O and HBF_4 were added to **2** dissolved in Et_2O. Both attempts were unsuccessful with only unreacted **2** being recovered. $[TpMoOCl]_2O$, a molyb-

Table 2
Selected bond lengths (Å) and angles (°) for the non-H atoms of compound **4**

1	2	3	1–2	1–2–3
N1	Mo	N3	1.728(9)	95.3(4)
N1	Mo	N5		87.9(5)
N1	Mo	N7		165.6(4)
N1	Mo	O1		101.7(3)
N3	Mo	N5	2.342(11)	78.0(4)
N3	Mo	N7		73.6(4)
N3	Mo	O1		82.5(3)
N3	Mo	O2		158.0(4)
N5	Mo	N7	2.200(12)	80.8(4)
N5	Mo	O1		159.0(3)
N5	Mo	O2		92.2(4)
N7	Mo	O1	2.309(11)	86.3(3)
N7	Mo	O2		85.5(4)
O1	Mo	O2	1.8789(12)	103.3(3)
O2	Mo	N1	1.706(8)	104.0(4)
O1	Mo_a		1.8789(12)	
C1	N1	Mo	1.41(2)	168.1(8)
Mo	O1	Mo_a		180.(0)

denum (V) analog of **4** has been prepared by the hydrolysis of $TpMoCl_3$ [14].

The crystal structure of compound **4** shows the molecule to possess a center of inversion at the position of the bridging oxygen atom, with the oxo, imido, and other ligands being trans to one another. Selected bond distances and angles are given in Table 2. The crystal consists of well-separated molecules with the pseudooctahedral coordination geometry and metal–ligand bond lengths about the molybdenum centers not differing remarkably from those of compound **2**. The N–Mo bond lengths of the chelating pyrazole rings range from 2.342(11) to 2.200(12) Å and are consistent with the decreasing trans influence of terminal oxo > imido > bridging oxo [1]. The Mo–O1–Mo_a angle is linear as required by symmetry and the Mo–O1 bond length (1.879(1) Å) is shortened [15] suggesting the bridging oxygen can participate in stabilizing the d^0 metal centers through $p\pi$-$d\pi$ donation. However, the steric bulk about the molybdenum atoms likely contribute to the linearity of the Mo–O1–Mo_a angle.

It is concluded that the stability of the described molybdenum compounds arises from the chelating ability of the Tp ligand and the presence of coordinatively and electronically saturated metal centers. The Tp ligand provides a template on which the hydrolysis products of the metal alkylidene can be observed and characterized. The molybdenum oxo imido compounds characterized crystallographically in this paper demonstrate the effects of competition between the multiply bonded ligands for the limited number of π-symmetry metal orbitals.

3. Experimental details

All syntheses were performed under dry argon atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF), diethyl ether (Et_2O), toluene, and pentane were distilled from potassium or sodium benzophenone ketyl. $Mo(CHC(CH_3)_2Ph)(NAr)(OTf)_2(DME)$[4] and potassium hydrotris(1-pyrazolyl)borate (KTp)[5] were prepared according to literature methods.

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 (300 MHz) or a General Electric QE-300 (300 MHz) spectrometer. Elemental analyses were performed by the University of Florida Department of Chemistry Analytical Services. IR spectra were recorded on a Perkin Elmer 1200 series spectrometer in KBr pellets which were prepared under N_2.

3.1. *TpMo*($CHC(CH_3)_2Ph$)(*NAr*)(SO_3CF_3) (*1*)

$Mo(CHC(CH_3)_2Ph)(NAr)(OTf)_2(DME)$ (3.53 g, 4.46 mmol) and KTp (1.21 g, 4.81 mmol) were stirred in 100 ml THF at room temperature under argon. A yellowish brown solution resulted after 3 h, and the solvent was removed under reduced pressure. The product was extracted with Et_2O leaving white KOTf solids. Solvent removal, followed by washing with pentane at 0°C, gave the product as yellow solids (2.91 g, 3.82 mmol, 85.6% yield). The product may be recrystallized from Et_2O. ^{1}H NMR(C_6D_6, 22°C): δ 14.73 (s, 1H, $C\mathit{H}C(CH_3)_2Ph$); 9.19, 7.70, 7.22, 7.09, 6.99, 6.22 (each a d, 1H each, Tp ring H's, 3,5-positions); 7.34–6.66 (m, 8H, Ph, Ar); 5.84, 5.65, 5.49 (t, 1H each, Tp ring H's, 4-position); 4.81, 2.50 (each a broad sept, 1H each, $C\mathit{H}(CH_3)_2$); 2.42, 1.86 (each a s, 3H each, $CHC(C\mathit{H}_3)_2Ph$); 1.67, 0.79, −0.06 (each a broad d, 6 : 3 : 3 H, $CH(C\mathit{H}_3)_2$). ^{13}C NMR δ 333.0 ($^{1}J_{CH} = 120$ Hz, $\mathit{C}HC(CH_3)_2Ph$); 148.2, 144.0, 141.6, 137.2, 135.1, 134.8, 129.3, 129.0, 128.9, 126.7, 126.26, 106.4, 105.9, 105.4 (Tp, Ph, Ar); 56.6 ($CH\mathit{C}(CH_3)_2Ph$); 31.2, 30.3, 28.4, 28.2, 26.1, 23.9, 23.7, 23.0 ($\mathit{C}H(\mathit{C}H_3)_2$, $CHC(\mathit{C}H_3)_2Ph$). IR: $\nu_{BH} = 2523$ cm^{-1}; $\nu_{S=O} = 1202$, 633 cm^{-1}. Elemental analysis calculated for $C_{32}H_{39}BF_3MoN_7O_3S$: C, 50.21; H, 5.14; N, 12.81. Found: C, 49.96; H, 5.01; N, 12.71%.

3.2. *TpMo*($CH_2C(CH_3)_2Ph$)(*NAr*)(*O*) (*2*)

1 ml of water was added to a yellow solution of **1** (0.172 g, 0.225 mmol) in 50 ml Et_2O over 5.0 g of Florisil. After stirring for 24 h at room temperature, the solution became orange and the slurry was filtered. The solvent and excess H_2O were removed under reduced pressure to give orange solids. ^{1}H NMR showed **1** was present (10%). The product was recrys-

tallized from pentane to give orange crystals. (0.098 g, 0.155 mmol, 69% yield). Alternatively, **1** (0.098 g, 0.128 mmol) in 10 ml of THF was added to a stirring mixture of $CsOH \cdot H_2O$ (0.025 g, 0.149 mmol) in 50 ml THF at room temperature. After 12 h, the solution became orange-yellow. The THF was removed under reduced pressure, and the product was extracted in pentane leaving white solids. Solvent removal resulted in an orange solid. ^1H NMR showed that **1** had been quantitatively converted to **2**. ^1H NMR: δ (8.35, 7.90, 7.42, 7.31, 7.24, 7.10 (each a d, 1H each, Tp ring H's, 3,5-positions); 7.55–7.00 (m, 8H, Ph, Ar); 5.93, 5.79, 5.37 (each a t, 1H each, Tp ring H's, 4-position); 4.63 (broad m, 2H, $C\mathit{H}(CH_3)_2$); 3.27, 2.87 (each a d, 1H each, $^2J_{HH} = 13$ Hz, $C\mathit{H}_2C(CH_3)_2Ph$); 1.87, 1.81 (each a s, 3H each, $CH(\mathit{CH}_3)_2$); 1.35, 0.93 (each a d, 6H each, $CH(\mathit{CH}_3)_2$). ^{13}C NMR: δ 154.1, 152.7, 151.2, 144.2, 143.5, 143.0, 136.1, 134.7, 134.3, 130.0, 128.2, 126.3, 125.1, 123.6, 105.9, 105.7, 104.8, 71.1 ($^1J_{CH} = 125.1$ Hz, $\mathit{C}H_2C(CH_3)_2Ph$), 43.0, 32.6, 32.4, 27.6, 24.6, 23.7. IR: $\nu_{Mo=O} = 896\ cm^{-1}$. Elemental analysis calculated for $C_{31}H_{40}BMoN_7O$: C, 58.78; H, 6.36; N, 15.48. Found: C, 58.60; H, 6.40; N, 15.10%.

Table 3
Fractional coordinates and equivalent isotropic [a] thermal parameters (Å^2) for the non-H atoms of compound **2**

Atom	*x*	*y*	*z*	*U*
Mo	0.20884(2)	0.298290(10)	0.174370(10)	0.03119(7)
O	0.0254(2)	0.2613(2)	0.19504(12)	0.0504(7)
N	0.3054(2)	0.27178(14)	0.27027(12)	0.0351(6)
N1	0.4195(2)	0.3583(2)	0.09393(12)	0.0390(6)
N1′	0.4165(2)	0.3103(2)	0.00279(13)	0.0418(7)
N2	0.1068(2)	0.31379(14)	0.03037(12)	0.0375(6)
N2′	0.1443(2)	0.2737(2)	−0.05291(12)	0.0434(7)
N3	0.2095(2)	0.13961(14)	0.08514(13)	0.0401(6)
N3′	0.2263(2)	0.1219(2)	−0.00661(14)	0.0447(7)
B	0.2707(3)	0.2217(2)	−0.0546(2)	0.0468(10)
C1	0.5591(3)	0.4348(2)	0.1224(2)	0.0473(9)
C2	0.6456(3)	0.4363(2)	0.0510(2)	0.0565(11)
C3	0.5519(3)	0.3566(2)	−0.0235(2)	0.0548(11)
C4	−0.0080(3)	0.3492(2)	0.0107(2)	0.0452(8)
C5	−0.0456(3)	0.3321(2)	−0.0860(2)	0.0570(10)
C6	0.0531(3)	0.2840(2)	−0.1229(2)	0.0543(10)
C7	0.1845(3)	0.0397(2)	0.1097(2)	0.0544(10)
C8	0.1861(4)	−0.0409(2)	0.0339(3)	0.0706(13)
C9	0.2120(3)	0.0132(2)	−0.0376(2)	0.0634(12)
C10	0.2650(3)	0.4820(2)	0.2165(2)	0.0405(8)
C11	0.3082(3)	0.5531(2)	0.3189(2)	0.0449(8)
C12	0.4612(5)	0.5544(3)	0.3642(3)	0.078(2)
C13	0.1901(6)	0.5041(3)	0.3774(3)	0.082(2)
C14	0.3207(3)	0.6740(2)	0.31301(14)	0.0422(8)
C15	0.4389(4)	0.7409(2)	0.2766(2)	0.0581(11)
C16	0.4480(5)	0.8485(3)	0.2670(2)	0.0731(14)
C17	0.3386(5)	0.8914(3)	0.2935(2)	0.075(2)
C18	0.2220(4)	0.8279(3)	0.3302(2)	0.0708(14)
C19	0.2115(3)	0.7203(3)	0.3395(2)	0.0574(11)
C20	0.3595(2)	0.2283(2)	0.33968(14)	0.0365(7)
C21	0.5094(3)	0.2262(2)	0.3455(2)	0.0437(8)
C22	0.5586(3)	0.1817(2)	0.4158(2)	0.0544(10)
C23	0.4647(4)	0.1386(2)	0.4770(2)	0.0577(11)
C24	0.3204(3)	0.1395(2)	0.4706(2)	0.0540(10)
C25	0.2623(3)	0.1842(2)	0.4026(2)	0.0444(9)
C26	0.6094(3)	0.2685(3)	0.2761(2)	0.0569(11)
C27	0.7628(5)	0.3568(4)	0.3227(4)	0.093(2)
C28	0.6306(6)	0.1712(5)	0.2079(4)	0.100(2)
C29	0.1017(3)	0.1844(3)	0.3968(2)	0.0606(12)
C30	−0.0115(5)	0.0652(5)	0.3606(5)	0.104(3)
C31	0.0709(7)	0.2412(6)	0.4902(4)	0.106(3)

[a] For anisotropic atoms, *U* value is U_{eq}, calculated as $U_{eq} = 1/3\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*A_{ij}$ where A_{ij} is the dot product of the ith and jth direct space unit cell vectors.

3.3. X-ray data collection, structure refinement and refinement for $TpMo(CH_2C(CH_3)_2Ph)(NAr)(O)$ (2) and $[TpMo(NAr)(O)]_2O$ (4)

Compound **2**: $C_{31}H_{40}BN_7OMo$, $M_r = 633.45$, Triclinic, $P\bar{1}$, $a = 9.419(1)$, $b = 12.816(1)$, $c = 14.698(2)$ Å, $\alpha = 100.73(1)°$, $\beta = 94.71(1)°$, $\gamma = 108.89(1)°$, $V = 1629.5(3)$ Å^3, $Z = 2$, $D_{calc.} = 1.291$ g cm^{-3}, Mo Kα ($\lambda = 0.71073$ Å), T = 298 K. Compound **4**: $C_{42}H_{54}B_2N_{14}O_3Mo_2$, $M_r = 1016.49$, Monoclinic, $P2_1/n$, $a = 11.419(4)$, $b = 17.597(5)$, $c = 12.320(4)$ Å, $\beta = 98.16(3)°$, $V = 2451(1)$ Å^3, $Z = 2$, $D_{calc} = 1.378$ g cm^{-3}, Mo Kα ($\lambda = 0.71073$ Å), T = 298 K. Data were collected at room temperature on a Siemens R3m/V diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation ($\lambda = 0.71073$ Å). 32 reflections from each structure with $20.0° \leq 2\theta \leq 22.0°$ were used to refine the cell parameters. 7953 and 3402 reflections, for **2** and **4** respectively, were collected using the ω-scan method (**2**: 2θ range 3–55°, 1.2° scan range and 4–8° scan speed depending on intensity; **4**: 2θ range 3–45°, 1.2° scan range and 3–6° scan speed depending on intensity). Four reflections (110, $12\bar{2}$, $02\bar{1}$, $\bar{1}12$) for **2**, and ($0\bar{2}\bar{2}$), $1\bar{1}0$, 120, $10\bar{1}$) for **4**, were measured every 96 reflections to monitor instrument and crystal stability (maximum corrections on I were 2%, respectively). Absorption corrections were applied based on measured crystal faces using SHELXTL PLUS [16]. Absorption coefficients: **2**, $\mu = 0.44$ mm^{-1} (min. and max. transmission factors are 0.882 and 0.904, respectively); **4**, $\mu = 0.56$ mm^{-1} (min. and max. transmission factors are 0.940 and 0.958, respectively).

The structures were solved by the heavy atom method in SHELXTL PLUS from which the positions of the Mo atoms were obtained. The rest of the non-H atoms were obtained from subsequent Difference Fourier maps. The structures were refined in SHELXTL PLUS using full-matrix least squares. All of the non-H atoms were refined with anisotropic thermal parameters. All of the non-methyl H atoms in **2** were located

Table 4
Fractional coordinates and equivalent isotropic [a] thermal parameters (Å^2) for the non-H atoms of compound **4**

Atom	x	y	z	U
Mo	0.16020(9)	0.02776(6)	0.03017(9)	0.0367(3)
N1	0.1558(8)	0.0995(5)	0.1252(8)	0.042(4)
N2	0.1798(14)	0.1127(8)	−0.2016(12)	0.078(7)
N3	0.1094(11)	0.1056(7)	−0.1235(9)	0.051(5)
N4	0.3714(13)	0.0773(7)	−0.0966(14)	0.088(7)
N5	0.3337(10)	0.0717(7)	0.0021(11)	0.067(5)
N6	0.2447(11)	−0.0201(9)	−0.2022(11)	0.085(6)
N7	0.1874(9)	−0.0446(6)	−0.1206(8)	0.052(5)
O1	0.0	0.0	0.0	0.042(4)
O2	0.2229(7)	−0.0468(4)	0.1058(7)	0.058(3)
B	0.288(2)	0.065(2)	−0.202(2)	0.093(11)
C1	0.1760(11)	0.1528(7)	0.2115(11)	0.044(5)
C2	0.2047(12)	0.1275(7)	0.3207(11)	0.054(5)
C3	0.2250(13)	0.1819(10)	0.4031(12)	0.074(7)
C4	0.2230(13)	0.2583(9)	0.3771(14)	0.073(7)
C5	0.1941(13)	0.2811(8)	0.2725(14)	0.075(7)
C6	0.1685(12)	0.2314(8)	0.1863(11)	0.060(6)
C7	0.209(2)	0.0430(9)	0.3476(12)	0.092(8)
C8	0.098(2)	0.0170(12)	0.373(2)	0.21(2)
C9	0.304(2)	0.0221(11)	0.432(2)	0.28(2)
C10	0.133(2)	0.2577(9)	0.075(2)	0.096(9)
C11	0.238(2)	0.2820(11)	0.0203(13)	0.132(12)
C12	0.038(2)	0.3174(10)	0.0594(15)	0.137(11)
C13	0.248(2)	−0.0769(11)	−0.2747(14)	0.109(9)
C14	0.188(2)	−0.1391(10)	−0.2420(14)	0.098(9)
C15	0.1520(12)	−0.1171(8)	−0.1440(12)	0.063(6)
C16	0.484(2)	0.1006(14)	−0.081(2)	0.129(13)
C17	0.514(2)	0.1123(13)	0.027(2)	0.127(13)
C18	0.4221(15)	0.0916(9)	0.079(2)	0.084(8)
C19	0.0172(14)	0.1480(8)	−0.1510(12)	0.061(6)
C20	0.027(2)	0.1858(10)	−0.247(2)	0.098(10)
C21	0.127(2)	0.1619(11)	−0.277(2)	0.105(11)

[a] For anisotropic atoms, the U value is U_{eq} calculated as $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* A_{ij}$ where A_{ij} is the dot product of the ith and jth direct space unit cell vectors.

from a Difference Fourier map and were refined without any constraints. The methyl H atoms were calculated in idealized positions and their thermal parameters were fixed. In **4**, all of the H atoms were calculated in idealized positions and their thermal parameters were fixed. The boron H atom was located from a Difference Fourier map and was refined without any constraints. 530 and 299 parameters for **2** and **4**, respectively, were refined and $\Sigma w(|F_o| - |F_c|)^2$ was minimized; $w = 1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0.5\ kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$, I(intensity) = $(I_{peak} - I_{background})$(scan rate), and $\sigma(I) = (I_{peak} + I_{background})^{1/2}$ (scan rate), k is the correction due to decay and Lp effects, 0.02 is a factor used to down-weight intense reflections and to account for instrument instability. $R = 0.0323$ and $wR = 0.0411$ for **2**, and $R = 0.0619$ and $wR = 0.063$ for **4**, in the last cycle of refinement using 6765 and 1738 reflections [with $I > 2\sigma(I)$], for **2** and **4**, respectively. The linear absorption coefficient was calculated from values from the International Tables for X-ray Crystallography [17]. The final atomic coordinates for the non-hydrogen of compounds **2** and **4** are given in Tables 3 and 4, respectively. Scattering factors for non-hydrogen atoms were taken from Cromer and Mann [18] with anomalous-dispersion corrections from Cromer and Liberman [19], while those of hydrogen atoms were from Stewart et al. [20].

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Supplementary material available

Details of the X-ray crystal structure determinations of **2** and **4**, including atomic coordinates for hydrogen atoms, thermal parameters, and structure factor tables are available from the Cambridge Crystallographic Data Centre.

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