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Supporting information for:

Dimolybdenum(III) Complexes of $-OSi(O^tBu)_3$, $-O_2P(O^tBu)_2$, and $-OB[OSi(O^tBu)_3]_2$ as Single-Source Molecular Precursors to Molybdenum-Containing, Multi-Component Oxide Materials.

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Table of Contents:

Crystallographic experimental details. Crystals of **1-3** and **4b-6** suitable for X-ray crystallographic analyses were grown from pentane solutions at –30 °C. Crystals of **4a** were grown via slow evaporation of C_6H_6 from a dilute solution at 25 °C. Crystals were mounted on a quartz fiber using Paratone N hydrocarbon oil. Measurements were made on a SMART CCD area detector with graphite monochromated Mo-K_α radiation. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3° counted for a total of 30.0 seconds per frame, unless otherwise noted. Data were integrated using the program SAINT (SAX Area-Detector Integration Program, V5.04; Bruker, 1995). Data were corrected for Lorentz and polarization effects and were analyzed for agreement and possible absorption using XPREP (part of the SHELXTL Crystal Structure Determination suite of programs; Bruker, 1995). An empirical absorption correction based upon comparison of redundant and equivalent reflections was applied using SADABS (Siemens Area Detector Absorption Corrections; Sheldrick, G. M., 1996). All structures were solved by direct methods and expanded using Fourier techniques (refinement based upon F^2) with all calculations performed using the SHELXTL crystallographic software package (Sheldrick, G. M. SHELXTL, V5.03; Bruker, 1994). The non-hydrogen and non-boron atoms were refined anisotropically, unless otherwise noted. Hydrogen atoms were included in calculated idealized positions, with thermal parameters based upon the carbon atom to which they were bonded, but not refined.

The structure of **4a** exhibited rotational disorder in one of the ^{t}Bu groups (the methyl carbons) and each these carbon atoms was modeled over two positions (50% occupancies) using isotropic thermal parameters. The single C_6H_6 molecule of solvation (per unit cell) was well behaved and modeled with anisotropic thermal parameters, including fixed hydrogen atoms. Complex **4b** contained a severely disordered molecule of C_5H_{12} (one per molecule of **4b**) that

was modeled over several positions with appropriate occupancies; isotropic thermal parameters were used for these carbon atoms and no hydrogen atoms were added. All other atoms in **4b** were well behaved. The structure of **5a** contained one disordered -O^{t}Bu group (Si-based) and this was modeled with the oxygen atom over two sites (50% occupancy; anisotropic) and the methyl carbon atoms as described above for **4a**. Each molecule in the asymmetric unit of the structure of **5b** contained one disordered ^{t}Bu group (Si-based) and this was modeled as above for **4a**. The molecule of C_5H_{12} (per asymmetric unit) was disordered and modeled with isotropic thermal parameters without added hydrogen atoms. Complexes **1-3** and **6** did not exhibit any disorder and there were no molecules of solvation.

Table S1. Crystallographic information for **1-3** and **6**.

	1	**2**	**3**	**6**
formula	$C_{32}H_{78}Mo_2N_4O_8Si_2$	$C_{40}H_{90}Mo_2O_{12}Si_2$	$C_{56}H_{132}B_2Mo_2N_4O_{18}Si_4$	$C_{68}H_{156}B_2Mo_2N_2O_{26}P_2Si_4$
size (mm)	0.17 × 0.16 × 0.13	0.18 × 0.15 × 0.08	0.20 × 0.16 × 0.05	0.20 × 0.15 × 0.13
color / habit	yellow / prism	red / block	yellow / block	purple / irregular
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	*C*2/c	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Z	4	2	2	2
Cell Constants:				
a (Å)	9.5645(2)	12.7732(5)	15.6091(2)	13.3363(2)
b (Å)	16.1754(2)	12.4173(5)	13.3064(3)	14.4157(1)
c (Å)	29.7612(7)	17.3864(7)	19.4502(4)	24.8246(1)
α (°)	90	90	90	94.539(1)
β (°)	90.421(1)	102.302(1)	93.721(1)	92.367(1)
γ (°)	90	90	90	93.161(1)
V (Å^3)	4604.2(2)	2694.3(2)	4031.31(13)	4745.37(8)
D_{calc} (g cm^{-3})	1.291	1.246	1.216	1.264
F_{000}	1896	1076	1580	1932
μ (cm^{-1})	6.41	5.59	4.29	4.15
2θ max. (°)	49.5	49.4	49.6	49.5
T (K)	151(2)	154(2)	145(2)	123(2)
measured refs.	10098	11663	17574	30459
unique refs.	3811	4418	6620	15270
param. / restr.	217 / 0	263 / 0	410 / 0	955 / 0
T_{max} / T_{min}	0.935 / 0.545	0.944 / 0.544	0.962 / 0.674	0.956 / 0.488
R_{int}	0.043	0.047	0.060	0.053
R_{obs} / $wR2_{obs}$	0.0352 / 0.0818	0.0333 / 0.0785	0.0381 / 0.0861	0.0470 / 0.1067
R_{all} / $wR2_{all}$	0.0565 / 0.0877	0.0518 / 0.0828	0.0727 / 0.1165	0.0947 / 0.1221
GOF_{obs}/GOF_{all}	1.074 / 0.958	1.060 / 0.931	0.911 / 1.008	1.062 / 0.903
max. / min. (e Å^{-3})	0.54 / -1.27	0.66 / -0.60	0.52 / -1.02	1.23 / -1.18

Table S2. Selected bond distances (Å) and angles (°) for **1**.

		Distances			
Mo(1)-O(1)	1.961(2)	Si(1)-O(2)	1.624(2)	Si(1)-O(4)	1.625(2)
Mo(1)-N(1)	1.948(3)	Si(1)-O(3)	1.628(2)	N(1)-C(1)	1.469(4)
Mo(1)-N(2)	1.928(3)	Si(1)-O(1)	1.606(2)	N(1)-C(2)	1.464(5)
Mo(1)-Mo(1A)	2.2098(5)				
		Angles			
N(2)-Mo(1)-N(1)	114.2(1)	O(1)-Mo(1)-Mo(1A)	106.0(1)	O(2)-Si(1)-O(3)	107.5(1)
N(2)-Mo(1)-O(1)	118.0(1)	O(1)-Si(1)-O(2)	105.5(1)	O(4)-Si(1)-O(3)	105.5(1)
N(1)-Mo(1)-O(1)	113.7(1)	O(1)-Si(1)-O(4)	111.1(1)	Si(1)-O(1)-Mo(1)	142.9(1)
N(2)-Mo(1)-Mo(1A)	100.3(1)	O(2)-Si(1)-O(4)	113.3(1)		
N(1)-Mo(1)-Mo(1A)	101.8(1)	O(1)-Si(1)-O(3)	114.1(1)		

Table S3. Selected bond distances (Å) and angles (°) for **2**.

		Distances			
Mo(1)-O(1)	1.931(2)	Mo(1)-Mo(1A)	2.2464(7)	Si(1)-O(3)	1.618(2)
Mo(1)-O(5)	1.863(2)	Si(1)-O(1)	1.623(2)	Si(1)-O(4)	1.623(2)
Mo(1)-O(6)	1.887(2)	Si(1)-O(2)	1.620(2)		
		Angles			
O(5)-Mo(1)-O(6)	113.1(1)	O(1)-Mo(1)-Mo(1A)	101.9(1)	Si(1)-O(1)-Mo(1)	130.6(1)
O(5)-Mo(1)-O(1)	115.8(1)	O(3)-Si(1)-O(2)	107.0(1)	O(3)-Si(1)-O(1)	113.9(1)
O(6)-Mo(1)-O(1)	117.5(1)	O(3)-Si(1)-O(4)	106.3(1)	O(2)-Si(1)-O(1)	110.8(1)
O(5)-Mo(1)-Mo(1A)	107.6(1)	O(2)-Si(1)-O(4)	114.1(1)	O(4)-Si(1)-O(1)	104.9(1)
O(6)-Mo(1)-Mo(1A)	98.0(1)				

Table S4. Selected bond distances (Å) and angles (°) for **3**.

		Distances			
Mo(1)-O(1)	2.005(2)	Mo(1)-Mo(1A)	2.2107(7)	B(1)-O(2)	1.365(5)
Mo(1)-N(1)	1.935(3)	B(1)-O(1)	1.348(5)	B(1)-O(3)	1.388(5)
Mo(1)-N(2)	1.936(3)				
		Angles			
N(1)-Mo(1)-N(2)	112.9(1)	N(2)-Mo(1)-Mo(1A)	100.7(1)	O(2)-B(1)-O(3)	118.3(4)
N(1)-Mo(1)-O(1)	115.8(1)	O(1)-Mo(1)-Mo(1A)	103.5(1)	O(1)-B(1)-O(3)	119.4(4)
N(2)-Mo(1)-O(1)	119.0(1)	B(1)-O(1)-Mo(1)	121.8(2)	B(1)-O(2)-Si(1)	154.7(3)
N(1)-Mo(1)-Mo(1A)	101.3(1)	O(1)-B(1)-O(2)	122.2(4)	B(1)-O(3)-Si(2)	140.1(3)

Table S5. Crystallographic information for **4a-5b**.

	4a	**4b**	**5a**	**5b**
formula	$C_{36}H_{84}Mo_2N_2O_{16}P_4$ •C_6H_6	$C_{36}H_{84}Mo_2N_2O_{16}P_4$ •C_5H_{12}	$C_{44}H_{102}Mo_2N_2O_{16}P_2Si_2$	$C_{44}H_{102}Mo_2N_2O_{16}P_2Si_2$ •$^1/_2C_5H_{12}$
size (mm)	0.16 × 0.10 × 0.08	0.23 × 0.20 × 0.19	0.22 × 0.16 × 0.14	0.15 × 0.11 × 0.08
color / habit	red / block	yellow / block	red / prism	yellow / prism
crystal system	monoclinic	orthorhombic	monoclinic	triclinic
space group	$P2_1/c$	$Pccn$	$C2/m$	$P\bar{1}$
Z	2	4	2	4
Cell Constants:				
a (Å)	10.6499(2)	15.6706(1)	15.764(1)	12.714(6)
b (Å)	19.0944(5)	16.8518(3)	20.947(2)	21.769(9)
c (Å)	15.0019(3)	24.3821(3)	10.0739(8)	25.00(1)
α (°)	90	90	90	81.542(7)
β (°)	105.227(1)	90	106.907(2)	76.190(7)
γ (°)	90	90	90	88.013(8)
V ($Å^3$)	2943.6(1)	6438.8(2)	3182.8(4)	6646(5)
D_{calc} (g cm^{-3})	1.348	1.227	1.279	1.261
F_{000}	1256	2512	1300	2684
μ (cm^{-1})	5.94	5.42	5.38	5.18
2θ max. (°)	46.2	49.5	49.4	49.5
T (K)	146(2)	142(2)	129(2)	142(2)
measured refs.	11772	27199	7116	33663
unique refs.	4200	5413	2697	21092
param. / restr.	295 / 0	299 / 0	175 / 0	1235 / 0
T_{max} / T_{min}	0.977 / 0.561	0.928 / 0.612	0.962 / 0.592	0.962 / 0.587
R_{int}	0.055	0.079	0.052	0.092
R_{obs} / $wR2_{obs}$	0.0461 / 0.1041	0.0384 / 0.1018	0.0437 / 0.1027	0.0586 / 0.1066
R_{all} / $wR2_{all}$	0.0812 / 0.1127	0.0708 / 0.1103	0.0661 / 0.1103	0.1920 / 0.1373
GOF_{obs}/GOF_{all}	1.070 / 0.909	1.159 / 1.014	1.051 / 0.974	1.087 / 0.805
max. / min. (e $Å^{-3}$)	0.65 / -0.71	0.51 / -0.93	1.82 / -1.16	0.81 / -1.02

Table S6. Selected bond distances (Å) and angles (°) for **4a**.

	Distances	
Mo(1)-O(1) 2.094(4)	P(1)-O(1) 1.509(4)	P(2)-O(5) 1.509(4)
Mo(1)-N(1) 1.920(4)	P(1)-O(2) 1.557(4)	P(2)-O(6) 1.556(4)
Mo(1)-O(5) 2.074(3)	P(1)-O(3) 1.552(4)	P(2)-O(7) 1.547(4)
Mo(1)-O(4A) 2.074(3)	P(1)-O(4) 1.533(4)	P(2)-O(8) 1.481(4)
Mo(1)-Mo(1A) 2.2335(9)		
	Angles	
N(1)-Mo(1)-O(5) 146.8(2)	O(5)-Mo(1)-Mo(1A) 110.0(1)	O(5)-Mo(1)-O(1) 83.0(1)
N(1)-Mo(1)-O(4A) 96.6(2)	O(4A)-Mo(1)-Mo(1A)94.0(1)	P(1)-O(1)-Mo(1) 118.6(2)
O(4A)-Mo(1)-O(1) 168.7(1)	O(1)-Mo(1)-Mo(1A) 93.1(1)	P(1)-O(4)-Mo(1A) 119.4(2)
O(5)-Mo(1)-O(4A) 86.3(2)	N(1)-Mo(1)-Mo(1A) 102.8(1)	P(2)-O(5)-Mo(1) 120.8(2)
N(1)-Mo(1)-O(1) 90.4(2)		

Table S7. Selected bond distances (Å) and angles (°) for **4b**.

	Distances	
Mo(1)-O(1) 2.152(2)	P(1)-O(1) 1.513(3)	P(2)-O(5) 1.525(3)
Mo(1)-N(1) 1.911(3)	P(1)-O(2) 1.565(3)	P(2)-O(6) 1.471(3)
Mo(1)-O(5) 2.041(2)	P(1)-O(3) 1.561(3)	P(2)-O(7) 1.581(3)
Mo(1)-O(4A) 2.055(3)	P(1)-O(4) 1.530(3)	P(2)-O(8) 1.589(3)
Mo(1)-Mo(1A) 2.2171(6)		
	Angles	
O(5)-Mo(1)-Mo(1A) 107.4(1)	N(1)-Mo(1)-O(5) 93.8(1)	O(4A)-Mo(1)-O(1) 83.0(1)
O(5)-Mo(1)-O(4A) 150.7(1)	N(1)-Mo(1)-O(4A) 97.2(1)	O(5)-Mo(1)-O(1) 79.1(1)
O(4A)-Mo(1)-Mo(1A) 96.0(1)	N(1)-Mo(1)-O(1) 163.6(1)	P(1)-O(1)-Mo(1) 117.1(2)
N(1)-Mo(1)-Mo(1A) 104.8(1)	P(1)-O(4)-Mo(1A) 118.7(2)	P(2)-O(5)-Mo(1) 140.4(2)
O(1)-Mo(1)-Mo(1A) 91.5(1)		

Table S8. Selected bond distances (Å) and angles (°) for **5a**.[a]

	Distances	
Mo(1)-O(1) 1.998(4)	P(1)-O(4) 1.515(3)	Si(1)-O(2*) 1.537(5)
Mo(1)-N(1) 1.939(4)	P(1)-O(5) 1.569(3)	Si(1)-O(2C*) 1.537(5)
Mo(1)-O(4) 2.105(3)	Si(1)-O(1) 1.585(4)	Si(1)-O(2) 1.804(5)
Mo(1)-Mo(1A) 2.236(1)	Si(1)-O(3) 1.610(4)	Si(1)-O(2C) 1.804(5)
	Angles	
N(1)-Mo(1)-Mo(1A)103.9(1)	N(1)-Mo(1)-O(1) 143.6(2)	O(1)-Mo(1)-O(4) 84.98(7)
O(1)-Mo(1)-Mo(1A)112.5(1)	N(1)-Mo(1)-O(4) 92.67(7)	Si(1)-O(1)-Mo(1) 132.7(2)
O(4)-Mo(1)-Mo(1A)94.05(7)	O(4)-Mo(1)-O(4A) 105.5(1)	P(1)-O(4)-Mo(1) 118.3(2)

[a]O(2) was disordered over 2 positions modeled with 50% occupancy: O(2) and O(2*).

Table S9. Selected bond distances (Å) and angles (°) for a molecule in the asymmetric unit of **5b**.

	Distances	
Mo(1)-N(1) 1.922(7)	Mo(1)-O(9) 1.992(6)	Mo(2)-O(6) 2.138(6)
Mo(1)-O(1) 2.135(5)	Mo(2)-N(2) 1.937(8)	Mo(2)-O(13) 1.981(6)
Mo(1)-O(5) 2.101(6)	Mo(2)-O(2) 2.128(6)	Mo(1)-Mo(2) 2.245(2)
	Angles	
N(1)-Mo(1)-O(1) 159.8(3)	O(9)-Mo(1)-Mo(2) 110.5(2)	O(6)-Mo(2)-Mo(1) 94.5(2)
N(1)-Mo(1)-O(5) 95.6(3)	N(2)-Mo(2)-O(2) 93.4(3)	O(13)-Mo(2)-Mo(1) 109.5(2)
N(1)-Mo(1)-O(9) 93.1(3)	N(2)-Mo(2)-O(6) 158.2(3)	P(1)-O(1)-Mo(1) 118.5(3)
O(1)-Mo(1)-O(5) 81.7(2)	N(2)-Mo(2)-O(13) 95.1(3)	P(1)-O(2)-Mo(2) 119.5(3)
O(1)-Mo(1)-O(9) 80.9(2)	O(2)-Mo(2)-O(6) 79.6(2)	P(2)-O(5)-Mo(1) 119.8(3)
O(5)-Mo(1)-O(9) 151.7(2)	O(2)-Mo(2)-O(13) 152.7(2)	P(2)-O(6)-Mo(2) 117.3(4)
N(1)-Mo(1)-Mo(2) 106.3(2)	O(6)-Mo(2)-O(13) 83.0(2)	Si(1)-O(9)-Mo(1) 136.1(4)
O(1)-Mo(1)-Mo(2) 93.9(2)	N(2)-Mo(2)-Mo(1) 106.5(2)	Si(2)-O(13)-Mo(2) 138.6(4)
O(5)-Mo(1)-Mo(2) 92.8(2)	O(2)-Mo(2)-Mo(1) 92.7(2)	

Table S10. Selected bond distances (Å) and angles (°) for **6**.

			Distances		
Mo(1)-N(1)	1.921(3)	Mo(2)-N(2)	1.927(3)	B(1)-O(10)	1.401(6)
Mo(1)-O(1)	2.082(3)	Mo(2)-O(2)	2.109(3)	B(1)-O(11)	1.388(6)
Mo(1)-O(5)	2.109(3)	Mo(2)-O(6)	2.078(3)	B(2)-O(18)	1.338(6)
Mo(1)-O(9)	2.027(3)	Mo(2)-O(18)	2.022(3)	B(2)-O(19)	1.384(6)
Mo(1)-Mo(2)	2.2505(5)	B(1)-O(9)	1.321(6)	B(2)-O(20)	1.379(6)
			Angles		
N(1)-Mo(1)-O(1)	89.1(1)	N(2)-Mo(2)-O(18)	143.5(1)	O(18)-B(2)-O(20)	123.9(4)
N(1)-Mo(1)-O(5)	89.2(1)	O(2)-Mo(2)-O(6)	169.6(1)	O(19)-B(2)-O(20)	115.4(4)
N(1)-Mo(1)-O(9)	142.7(1)	O(2)-Mo(2)-O(18)	82.7(1)	P(1)-O(1)-Mo(1)	119.2(2)
O(1)-Mo(1)-O(5)	171.2(1)	O(6)-Mo(2)-O(18)	87.8(1)	P(1)-O(2)-Mo(2)	119.2(2)
O(1)-Mo(1)-O(9)	89.1(1)	N(2)-Mo(2)-Mo(1)	101.3(1)	P(2)-O(5)-Mo(1)	119.2(2)
O(5)-Mo(1)-O(9)	82.7(1)	O(2)-Mo(2)-Mo(1)	92.8(1)	P(2)-O(6)-Mo(2)	118.6(2)
N(1)-Mo(1)-Mo(2)	100.6(1)	O(6)-Mo(2)-Mo(1)	95.1(1)	B(1)-O(9)-Mo(1)	162.4(3)
O(1)-Mo(1)-Mo(2)	94.5(1)	O(18)-Mo(2)-Mo(1)	114.6(1)	B(1)-O(10)-Si(1)	133.1(3)
O(5)-Mo(1)-Mo(2)	91.8(1)	O(9)-B(1)-O(10)	124.6(5)	B(1)-O(11)-Si(2)	173.6(3)
O(9)-Mo(1)-Mo(2)	116.0(1)	O(9)-B(1)-O(11)	121.5(5)	B(2)-O(18)-Mo(2)	164.8(3)
N(2)-Mo(2)-O(2)	89.4(1)	O(10)-B(1)-O(11)	113.9(4)	B(2)-O(19)-Si(3)	167.6(3)
N(2)-Mo(2)-O(6)	95.8(1)	O(18)-B(2)-O(19)	120.7(5)	B(2)-O(20)-Si(4)	133.9(3)