Experimental

All operations were carried out in a glovebox under nitrogen atmosphere. MoO_2Cl_2, 2.5M BuLi in hexanes and 2,6-di-*t*-butylphenol were used as received from Aldrich. LiO(2,6-di-*t*-BuC_6H_6) was prepared from BuLi and the alcohol in tetrahydrofuran. Acetonitrile was Aldrich anhydrous, dried over freshly activated 4Å molecular sieves. Pentane was distilled from sodium/benzophenone ketyl. C_6D_6 was deaerated using freeze-pump-thaw cycles and dried over molecular sieves. THF-d_8 was vacuum transferred from sodium/benzophenone ketyl.

Synthesis of MoO_2(O-2,6-di-*t*-BuC_6H_6)$_2$.HO-2,6-di-*t*-BuC_6H_6 (1). MoO_2Cl_2 (117.5 mg, 0.5909 mmol) and 260.7 mg LiO(2,6-*t*-BuC_6H_6) (1.228 mmol) were each dissolved in 5 mL CH_3CN. The MoO_2Cl_2 solution was added to the LiOAr solution with stirring to cause an immediate color change to deep red. The mixture was stirred for 1 hour, then the solvent removed *in vacuo*. The product was brought up in approx. 50 mL pentane, leaving black undissolved material, filtered to remove residual solid, and placed in a -35 °C freezer for 2d. The resulting solid was recrystallized from pentane to produce 94.4 mg air-sensitive orange blocky crystals of MoO_2(O-2,6-di-*t*-BuC_6H_6)$_2$.HO-2,6-*t*-BuC_6H_6 (126.9 mmol, 31.0% yield): mp 124-125 °C; IR (C_6H_6): 3636 m, 2961 s, 2874 w, 1466 w, 1426 m, 1402 s, 1395 m, 1366 w, 1264 w, 1231 w, 1206 m, 1186 s, 1119 s, 1109 m, 963 s, 941 s (Mo=O), 911 s (Mo=O), 882 w, 795 w, 748 m, 698 w, 685 s. ^{1}H NMR (thf-d_8) δ 7.32 (d, 2H, J = 7.88 Hz), 6.98 (t, 1H, J = 7.87 Hz), 1.50 (s, 18H). ^{13}C NMR (C_6D_6) δ 31.8 (^{t}Bu CH_3), 35.4 (^{t}Bu quat.), 124.4 (*p* to O), 126.1 (*m* to O), 140.0 (aryl quat.),

164.4 (*C*-O) (ArOH NMR peaks not listed). UV-vis (C_6H_6) λ_{max}= 278 (ε 7.9 x 10^3), 346 (ε 6.1 x 10^3). Anal. Calcd for $C_{42}H_{64}MoO_5$: C, 67.72; H, 8.66. Found: C, 67.61; H, 8.82.

X-Ray Crystal Structure Determination of MoO_2(O-2,6-*t*-BuC_6H_6)$_2$.HO-2,6-di-*t*-BuC_6H_6 (1). Crystals were obtained from pentane solution after 2d at -35 °C, and mailed to University of Delaware in an ampule sealed under vacuum. A suitable crystal for data collection was selected and mounted in a nitrogen flushed, thin-walled capillary. Data were collected with a Siemens P4 diffractometer equipped with a SMART/CCD detector.

The systematic absences in the diffraction data are uniquely consistent with the reported space group, which yielded chemically reasonable and computationally stable results of refinement. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. The molecule co-crystallized with one molecule of 2,6-di-*tert*-butylphenol. The phenolic hydrogen was located from the difference map and refined. There is a strong interaction between H(1) and O(4) on the order of 2.327(8) Å. All non-hydrogen atoms were refined with anisotropic displacement coefficients and the hydrogen atoms, with the exception of H(1), were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (5.1) program libary (G. Sheldrick, Siemens XRD, Madison, WI).

Other Physical Measurements. A Mattson Infinity Gold™ FTIR spectrometer was used to monitor the infrared spectra. NMR spectra were recorded on a Varian VXR 300 MHz instrument. Melting point determinations were done using the sealed-capillary method. Elemental analysis was performed by Atlantic Microlab, Inc, Norcross, GA.

Table 1S. Crystal data and structure refinement.

Identification code	tcu01
Empirical formula	$C_{42}H_{64}MoO_5$
Formula weight	744.87
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.4344(2) Å alpha = 90° b = 19.4277(3) Å beta = 99.1385(6)° c = 18.5445(3) Å gamma = 90°
Volume, Z	4067.27(12) $Å^3$, 4
Density (calculated)	1.216 g/cm^3
Absorption coefficient	0.362 mm^{-1}
F(000)	1592
Crystal size	0.30 x 0.20 x 0.10 mm
θ range for data collection	1.53 to 28.14°
Limiting indices	$-11 \le h \le 15$, $-24 \le k \le 25$, $-24 \le l \le 23$
Reflections collected	18681
Independent reflections	8275 (R_{int} = 0.0360)
Completeness to θ = 28.14°	83.2 %
Absorption correction	Empirical from SADABS
Max. and min. transmission	0.9647 and 0.8990
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8275 / 0 / 437
Goodness-of-fit on F^2	1.250
Final R indices [I>2σ(I)]	R1 = 0.0486, wR2 = 0.1505
R indices (all data)	R1 = 0.0650, wR2 = 0.1675
Largest diff. peak and hole	0.403 and -0.621 $eÅ^{-3}$

Table 2S. Atomic coordinates [x 10^{-}] and equivalent isotropic displacement parameters [$Å^2$ x 10^3]. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Mo(1)	1055.9(2)	6698.0(1)	6097.8(1)	20(1)
O(1)	357(2)	6263(1)	6813(1)	23(1)
O(2)	2677(2)	6809(1)	6395(1)	22(1)
O(3)	831(2)	6234(2)	5309(1)	35(1)
O(4)	391(2)	7476(1)	5902(1)	33(1)
O(5)	-2076(2)	7774(1)	5261(2)	32(1)
C(1)	-341(3)	6000(2)	7308(2)	17(1)
C(2)	-984(3)	5381(2)	7124(2)	20(1)
C(3)	-1670(3)	5133(2)	7636(2)	26(1)
C(4)	-1722(3)	5489(2)	8286(2)	30(1)
C(5)	-1077(3)	6086(2)	8446(2)	27(1)
C(6)	-347(3)	6361(2)	7977(2)	21(1)
C(7)	-1002(3)	4989(2)	6390(2)	22(1)
C(8)	-1594(3)	5454(2)	5749(2)	28(1)
C(9)	259(3)	4765(2)	6286(2)	29(1)
C(10)	-1749(3)	4324(2)	6358(2)	32(1)
C(11)	371(3)	7025(2)	8188(2)	25(1)
C(12)	1710(3)	6923(2)	8171(2)	30(1)
C(13)	-140(4)	7624(2)	7679(2)	33(1)
C(14)	290(4)	7256(2)	8976(2)	36(1)
C(15)	3900(3)	6895(2)	6542(2)	19(1)
C(16)	4617(3)	6300(2)	6733(2)	22(1)
C(17)	5844(3)	6414(2)	6922(2)	29(1)
C(18)	6333(3)	7063(2)	6906(2)	34(1)
C(19)	5613(3)	7629(2)	6690(2)	28(1)
C(20)	4383(3)	7565(2)	6509(2)	21(1)
C(21)	4111(3)	5562(2)	6722(2)	26(1)
C(22)	3242(3)	5470(2)	7271(2)	31(1)
C(23)	3515(4)	5368(2)	5928(2)	38(1)
C(24)	5111(4)	5024(2)	6932(3)	44(1)
C(25)	3614(3)	8212(2)	6270(2)	25(1)
C(26)	2987(4)	8121(2)	5472(2)	31(1)
C(27)	2729(3)	8348(2)	6800(2)	30(1)
C(28)	4386(4)	8871(2)	6272(2)	39(1)
C(29)	-2874(3)	8272(2)	4971(2)	22(1)
C(30)	-3845(3)	8030(2)	4451(2)	22(1)
C(31)	-4650(3)	8525(2)	4127(2)	28(1)
C(32)	-4525(3)	9220(2)	4303(2)	31(1)
C(33)	-3592(3)	9438(2)	4827(2)	25(1)
C(34)	-2743(3)	8978(2)	5174(2)	22(1)
C(35)	-4004(3)	7256(2)	4244(2)	27(1)
C(36)	-2944(4)	6999(2)	3881(2)	40(1)
C(37)	-5146(4)	7136(2)	3689(2)	41(1)
C(38)	-4119(4)	6811(2)	4921(2)	36(1)
C(39)	-1708(3)	9242(2)	5761(2)	25(1)
C(40)	-1805(4)	10024(2)	5897(2)	37(1)
C(41)	-489(3)	9139(2)	5509(2)	32(1)
C(42)	-1732(4)	8882(2)	6503(2)	37(1)

Mo(1)-O(3)	1.703(2)	Mo(1)-O(4)	1.706(2)
Mo(1)-O(1)	1.857(2)	Mo(1)-O(2)	1.861(2)
O(1)-C(1)	1.405(4)	O(2)-C(15)	1.392(4)
O(5)-C(29)	1.379(4)	C(1)-C(2)	1.423(4)
C(1)-C(6)	1.426(4)	C(2)-C(3)	1.409(5)
C(2)-C(7)	1.557(4)	C(3)-C(4)	1.399(5)
C(4)-C(5)	1.380(5)	C(5)-C(6)	1.403(5)
C(6)-C(11)	1.546(5)	C(7)-C(10)	1.545(5)
C(7)-C(9)	1.547(5)	C(7)-C(8)	1.560(4)
C(11)-C(14)	1.545(5)	C(11)-C(12)	1.550(5)
C(11)-C(13)	1.553(5)	C(15)-C(20)	1.419(4)
C(15)-C(16)	1.428(4)	C(16)-C(17)	1.409(5)
C(16)-C(21)	1.544(5)	C(17)-C(18)	1.381(5)
C(18)-C(19)	1.394(5)	C(19)-C(20)	1.398(5)
C(20)-C(25)	1.559(5)	C(21)-C(22)	1.543(5)
C(21)-C(24)	1.554(5)	C(21)-C(23)	1.566(5)
C(25)-C(27)	1.541(6)	C(25)-C(26)	1.549(5)
C(25)-C(28)	1.554(5)	C(29)-C(34)	1.424(4)
C(29)-C(30)	1.430(4)	C(30)-C(31)	1.399(5)
C(30)-C(35)	1.555(5)	C(31)-C(32)	1.391(5)
C(32)-C(33)	1.390(5)	C(33)-C(34)	1.399(4)
C(34)-C(39)	1.562(4)	C(35)-C(37)	1.547(5)
C(35)-C(38)	1.546(5)	C(35)-C(36)	1.558(5)
C(39)-C(40)	1.546(5)	C(39)-C(42)	1.548(5)
C(39)-C(41)	1.552(5)		

O(3)-Mo(1)-O(4)	106.55(13)	O(3)-Mo(1)-O(1)	110.47(11)
O(4)-Mo(1)-O(1)	109.14(12)	O(3)-Mo(1)-O(2)	108.81(12)
O(4)-Mo(1)-O(2)	110.50(11)	O(1)-Mo(1)-O(2)	111.26(10)
C(1)-O(1)-Mo(1)	170.3(2)	C(15)-O(2)-Mo(1)	174.2(2)
O(1)-C(1)-C(2)	118.4(3)	O(1)-C(1)-C(6)	118.1(3)
C(2)-C(1)-C(6)	123.5(3)	C(3)-C(2)-C(1)	116.6(3)
C(3)-C(2)-C(7)	119.4(3)	C(1)-C(2)-C(7)	123.9(3)
C(4)-C(3)-C(2)	121.1(3)	C(5)-C(4)-C(3)	120.4(3)
C(4)-C(5)-C(6)	122.5(3)	C(5)-C(6)-C(1)	115.9(3)
C(5)-C(6)-C(11)	120.4(3)	C(1)-C(6)-C(11)	123.7(3)
C(10)-C(7)-C(9)	106.3(3)	C(10)-C(7)-C(2)	111.9(3)
C(9)-C(7)-C(2)	111.3(3)	C(10)-C(7)-C(8)	106.6(3)
C(9)-C(7)-C(8)	111.7(3)	C(2)-C(7)-C(8)	109.0(3)
C(14)-C(11)-C(6)	111.9(3)	C(14)-C(11)-C(12)	105.4(3)
C(6)-C(11)-C(12)	112.0(3)	C(14)-C(11)-C(13)	106.6(3)
C(6)-C(11)-C(13)	109.7(3)	C(12)-C(11)-C(13)	111.2(3)
O(2)-C(15)-C(20)	119.2(3)	O(2)-C(15)-C(16)	118.1(3)
C(20)-C(15)-C(16)	122.8(3)	C(17)-C(16)-C(15)	116.3(3)
C(17)-C(16)-C(21)	120.4(3)	C(15)-C(16)-C(21)	123.3(3)
C(18)-C(17)-C(16)	121.9(3)	C(17)-C(18)-C(19)	120.2(3)
C(18)-C(19)-C(20)	121.6(3)	C(19)-C(20)-C(15)	117.0(3)
C(19)-C(20)-C(25)	119.8(3)	C(15)-C(20)-C(25)	123.1(3)
C(22)-C(21)-C(16)	112.3(3)	C(22)-C(21)-C(24)	106.3(3)
C(16)-C(21)-C(24)	111.3(3)	C(22)-C(21)-C(23)	111.3(3)
C(16)-C(21)-C(23)	110.0(3)	C(24)-C(21)-C(23)	105.5(3)
C(27)-C(25)-C(26)	112.2(3)	C(27)-C(25)-C(28)	106.8(3)
C(26)-C(25)-C(28)	105.9(3)	C(27)-C(25)-C(20)	110.8(3)
C(26)-C(25)-C(20)	109.5(3)	C(28)-C(25)-C(20)	111.6(3)
O(5)-C(29)-C(34)	122.5(3)	O(5)-C(29)-C(30)	115.2(3)

C(34)-C(29)-C(30)	122.2(3)	C(31)-C(30)-C(29)	116.8(3)
C(31)-C(30)-C(35)	121.0(3)	C(29)-C(30)-C(35)	122.2(3)
C(32)-C(31)-C(30)	122.0(3)	C(33)-C(32)-C(31)	119.9(3)
C(32)-C(33)-C(34)	121.8(3)	C(33)-C(34)-C(29)	117.2(3)
C(33)-C(34)-C(39)	120.3(3)	C(29)-C(34)-C(39)	122.5(3)
C(37)-C(35)-C(38)	106.5(3)	C(37)-C(35)-C(36)	107.3(3)
C(38)-C(35)-C(36)	110.1(3)	C(37)-C(35)-C(30)	111.2(3)
C(38)-C(35)-C(30)	111.1(3)	C(36)-C(35)-C(30)	110.4(3)
C(40)-C(39)-C(42)	106.8(3)	C(40)-C(39)-C(41)	105.5(3)
C(42)-C(39)-C(41)	110.7(3)	C(40)-C(39)-C(34)	111.7(3)
C(42)-C(39)-C(34)	110.6(3)	C(41)-C(39)-C(34)	111.4(3)

Symmetry transformations used to generate equivalent atoms:

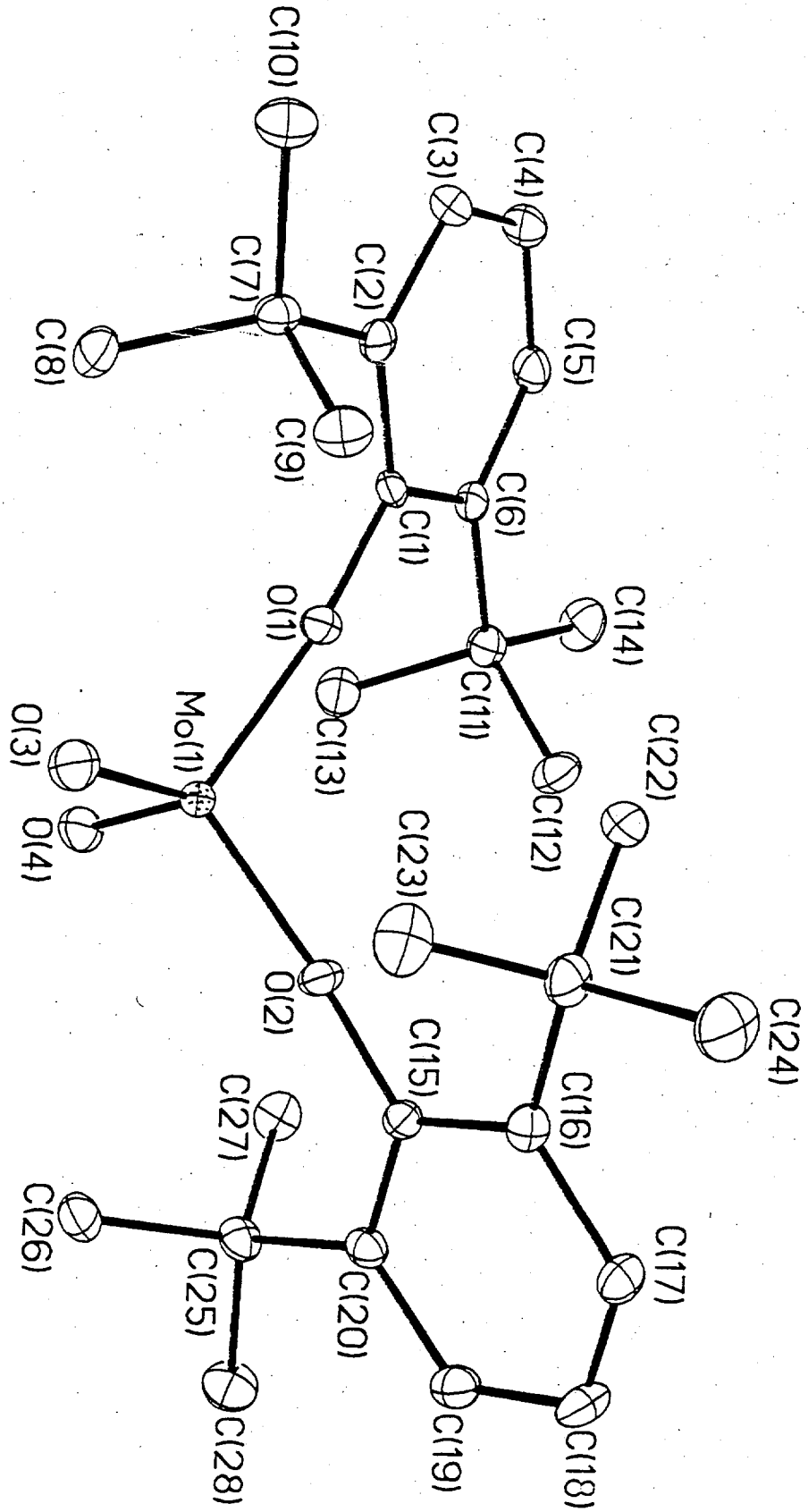
Table 4S. Anisotropic displacement parameters ($A^2 \times 10^3$)

	U11	U22	U33	U23	U13	U12
Mo(1)	17(1)	24(1)	18(1)	3(1)	2(1)	-2(1)
O(1)	22(1)	26(1)	20(1)	2(1)	4(1)	-6(1)
O(2)	15(1)	21(1)	30(1)	2(1)	3(1)	-2(1)
O(3)	34(2)	52(2)	20(1)	-4(1)	5(1)	-12(1)
O(4)	23(1)	37(1)	39(1)	17(1)	4(1)	5(1)
O(5)	25(1)	20(1)	46(2)	-1(1)	-12(1)	2(1)
C(1)	16(1)	19(1)	17(1)	7(1)	3(1)	3(1)
C(2)	16(1)	18(1)	25(2)	4(1)	-1(1)	3(1)
C(3)	27(2)	23(2)	28(2)	8(1)	2(2)	-4(1)
C(4)	24(2)	41(2)	28(2)	8(2)	10(2)	-2(2)
C(5)	26(2)	36(2)	19(2)	4(1)	5(1)	2(1)
C(6)	19(2)	23(2)	20(2)	4(1)	0(1)	3(1)
C(7)	21(2)	18(2)	27(2)	0(1)	4(1)	-2(1)
C(8)	27(2)	30(2)	25(2)	-2(1)	-3(2)	-4(1)
C(9)	26(2)	29(2)	33(2)	-5(1)	10(2)	0(1)
C(10)	34(2)	24(2)	41(2)	-4(2)	10(2)	-4(2)
C(11)	27(2)	27(2)	21(2)	-1(1)	2(2)	-3(1)
C(12)	23(2)	39(2)	27(2)	-6(2)	2(2)	-7(2)
C(13)	38(2)	26(2)	34(2)	-1(2)	-1(2)	-1(2)
C(14)	39(2)	42(2)	26(2)	-10(2)	1(2)	-2(2)
C(15)	17(2)	25(2)	15(1)	-1(1)	4(1)	0(1)
C(16)	22(2)	24(2)	21(2)	-1(1)	4(1)	4(1)
C(17)	20(2)	34(2)	32(2)	4(2)	3(2)	7(1)
C(18)	17(2)	45(2)	39(2)	0(2)	0(2)	-5(2)
C(19)	25(2)	29(2)	30(2)	-1(1)	6(2)	-5(1)
C(20)	24(2)	22(2)	18(1)	-1(1)	5(1)	-4(1)
C(21)	24(2)	21(2)	32(2)	3(1)	1(2)	6(1)
C(22)	24(2)	32(2)	37(2)	13(2)	1(2)	-3(1)
C(23)	45(2)	27(2)	39(2)	-6(2)	-2(2)	7(2)
C(24)	38(2)	28(2)	65(3)	8(2)	1(2)	10(2)
C(25)	31(2)	18(2)	27(2)	2(1)	4(2)	-3(1)
C(26)	36(2)	30(2)	26(2)	7(1)	3(2)	-2(2)
C(27)	30(2)	27(2)	32(2)	-5(1)	6(2)	6(1)
C(28)	45(2)	21(2)	50(2)	5(2)	4(2)	-10(2)
C(29)	20(2)	22(2)	22(2)	4(1)	-1(1)	5(1)
C(30)	20(2)	25(2)	22(2)	-1(1)	4(1)	-2(1)
C(31)	22(2)	37(2)	23(2)	1(1)	-3(2)	2(2)
C(32)	29(2)	29(2)	34(2)	10(2)	0(2)	8(2)
C(33)	30(2)	18(2)	29(2)	5(1)	8(2)	3(1)
C(34)	23(2)	21(2)	23(2)	2(1)	5(1)	-4(1)
C(35)	25(2)	27(2)	28(2)	-7(1)	1(2)	-3(1)
C(36)	33(2)	37(2)	50(2)	-15(2)	8(2)	-2(2)
C(37)	36(2)	42(2)	40(2)	-12(2)	-5(2)	-3(2)
C(38)	40(2)	26(2)	41(2)	-5(2)	7(2)	-3(2)
C(39)	26(2)	23(2)	25(2)	-1(1)	3(2)	-1(1)
C(40)	35(2)	26(2)	48(2)	-10(2)	2(2)	-7(2)
C(41)	25(2)	30(2)	41(2)	-2(2)	1(2)	-3(2)
C(42)	44(2)	39(2)	25(2)	-1(2)	-2(2)	-12(2)

Table 3S. Hydrogen coordinates ( ) and isotropic displacement parameters (Å^2 x 10^3).

	x	y	z	U(eq)
H(1)	-1490(40)	7910(20)	5460(20)	49(15)
H(3B)	-2104	4718	7539	32
H(4B)	-2205	5320	8619	36
H(5A)	-1128	6318	8890	32
H(8A)	-2401	5571	5822	42
H(8B)	-1623	5207	5286	42
H(8C)	-1131	5877	5737	42
H(9A)	588	4455	6684	43
H(9B)	767	5172	6291	43
H(9C)	222	4525	5818	43
H(10A)	-1397	4010	6746	48
H(10B)	-1764	4102	5882	48
H(10C)	-2559	4439	6426	48
H(12A)	1822	6762	7685	45
H(12B)	2030	6581	8538	45
H(12C)	2126	7361	8277	45
H(13A)	-112	7499	7170	50
H(13B)	332	8041	7804	50
H(13C)	-963	7711	7740	50
H(14A)	616	6895	9319	54
H(14B)	-541	7337	9022	54
H(14C)	744	7682	9087	54
H(17A)	6350	6034	7065	34
H(18A)	7163	7123	7042	41
H(19A)	5966	8069	6666	33
H(22A)	3627	5615	7758	47
H(22B)	3015	4984	7286	47
H(22C)	2535	5751	7119	47
H(23A)	4092	5421	5594	57
H(23B)	2838	5673	5775	57
H(23C)	3243	4890	5920	57
H(24A)	5526	5120	7425	66
H(24B)	5673	5049	6585	66
H(24C)	4766	4561	6918	66
H(26A)	2533	8537	5314	46
H(26B)	2449	7725	5443	46
H(26C)	3581	8042	5153	46
H(27A)	2255	8756	6640	45
H(27B)	3165	8424	7293	45
H(27C)	2206	7949	6804	45
H(28A)	3876	9266	6118	59
H(28B)	4954	8810	5932	59
H(28C)	4816	8951	6765	59
H(31A)	-5301	8382	3775	34
H(32A)	-5078	9545	4067	37
H(33A)	-3528	9912	4951	30
H(36A)	-2872	7288	3458	60
H(36B)	-3083	6521	3723	60
H(36C)	-2212	7027	4235	60

H(37A)	-5831	7305	3894	61
H(37B)	-5241	6643	3585	61
H(37C)	-5090	7385	3236	61
H(38A)	-4777	6983	5151	54
H(38B)	-3382	6837	5271	54
H(38C)	-4272	6332	4770	54
H(40A)	-1769	10274	5442	55
H(40B)	-1148	10170	6271	55
H(40C)	-2559	10123	6063	55
H(41A)	-484	9380	5045	49
H(41B)	-352	8647	5443	49
H(41C)	138	9325	5879	49
H(42A)	-1084	9058	6866	55
H(42B)	-1636	8384	6447	55
H(42C)	-2490	8974	6667	55


C(10)
C(3)
C(4)
C(7)
C(2)
C(8)
C(5)
C(9)
C(6)
C(1)
O(1)
C(14)
C(11)
C(13)
Mo(1)
O(3)
C(12)
C(22)
O(4)
C(23)
C(21)
C(24)
O(2)
C(15)
C(16)
C(27)
C(17)
C(26)
C(25)
C(20)
C(19)
C(18)
C(28)