Supporting Information

Synthesis, Characterization, X-ray and Electronic Structures of Diethyl Ether and 1,2-Dimethoxyethane Adducts of Molybdenum(IV) Chloride and Tungsten(IV) Chloride

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Materials and Methods

General Comments

All chemical manipulations were carried out using standard Schlenk and glovebox techniques in ultrahigh purity (UHP) nitrogen environments. 3Å molecular sieves were purchased from Fisher Scientific and dried at 150 °C for 24 h before pumping into the glovebox. Basic alumina (50-200 μm) was purchased from Acros Organics and was activated by heating to 220 °C while pumping under vacuum (5 x 10^{-3} torr) for 12 h. Diethyl ether and hexanes were collected from an mBraun solvent purification system (SPS). 1,2-dimethoxyethane (TCI) was pumped into the glovebox upon delivery and dried over activated basic alumina for 24 h prior to use. Molybdenum pentachloride (99.5%) was used as received from Beantown Chemical. Tungsten tetrachloride (97%) was used as received from Strem Chemicals. Allyltrimethylsilane (> 98%) was purchased from TCI and dried over 3Å molecular sieves for 24 h prior to use. The purity of the organic reagents was checked via ^{1}H NMR. Elemental analyses (C, H, Cl) were performed by Galbraith Laboratories, Inc., Knoxville, TN. ^{1}H NMR spectra were collected on a Bruker Avance III HD 600 equipped with a cryoprobe. UV-Vis measurements were conducted with an Agilent Cary 60 spectrophotometer using an air-free cuvette sealed under UHP N_2.

Synthesis

$MoCl_4(OEt_2)_2$ (**1**). Inside the glovebox, $MoCl_4(OEt_2)_2$ was prepared as described by Persson and Andersson.[1] The only deviation from their reported procedure was that the addition of allyltrimethylsilane to the $MoCl_5$/diethyl ether suspension was done at -35 °C inside the glovebox instead of -78 °C. Starting with 9.3 g of $MoCl_5$, 12 g (90% yield, based on $MoCl_5$) of rust orange powder was isolated on a medium porosity filter frit and washed first with 2 x 30 mL of diethyl ether and then 30 mL of hexanes prior to drying under reduced pressure. We note that green $MoOCl_3(OEt_2)_2$ is present as a byproduct (< 10%), but it is highly soluble in diethyl ether and readily separated from the desired $MoCl_4(OEt_2)_2$.[2] ^{1}H NMR (600 MHz, toluene-d_8; δ, ppm): 21.55 (s, 4H), 8.76 (s, 6H).
$MoCl_4$(dme) (**2**). Inside the glovebox, $MoCl_4$(dme) was prepared by dissolving $MoCl_4(OEt_2)_2$ in minimal dme (~10 mL per gram of solid). The solid adduct is isolated in ≥ 90% yield from the dme solution by slowly adding an equal volume of pentane. The solid is isolated by filtration, washed with pentane, and dried under reduced pressure. ^{1}H NMR (600 MHz, toluene-d_8; δ, ppm): 16.32 (s, 6H), 1.17 (s, 4H). Anal., Calcd. for $C_4H_{10}O_2Cl_4Mo$: C, 14.65; H, 3.06; Cl, 43.25. Found: C, 14.51; H, 2.87; Cl, 43.17.
$WCl_4(OEt_2)_2$ (**3**). Scintillation vial-scale reactions to obtain $WCl_4(OEt_2)_2$ were conducted as described by Shaw, *et al.*[3] Inside the glovebox, commercial (Strem Chemicals) WCl_4 was ground with an agate mortar and pestle for several minutes. Then, 100 mg of the ground WCl_4 were added to a scintillation vial along with 20 mL of dry diethyl ether. The vial was left to sit in the glovebox overnight which led to the formation of dark yellow, crystalline $WCl_4(OEt_2)_2$ in the bottom of the vial amidst some unreacted WCl_4. ^{1}H NMR (500 MHz, toluene-d_8; δ, ppm): 14.42 (q, 4H, CH_2), 5.08 (t, 6H, CH_3).
WCl_4(dme) (**4**). Inside the glovebox, commercial WCl_4 was ground as noted above. Then, a 125 mL Erlenmeyer flask was charged with 5 g of the freshly ground powder and approximately 100 mL of dme and left to stir, at room temperature, overnight in the glovebox. The solution gradually changes from a purple suspension to a verdant green solution that may appear to have a blue hint due to small amounts of unreacted WCl_4. The next day, the solution was filtered through a layer of Celite on a 30 mL fine porosity frit to remove any unreacted WCl_4. The solution was then stripped, affording 6.2 g of brown solid WCl_4(dme) (97%). ^{1}H NMR (600 MHz, toluene-d_8; δ, ppm): 9.93 (s, 6H), 0.77 (s, 4H). Anal., Calcd. for $C_4H_{10}O_2Cl_4W$: C, 11.55; H, 2.42; Cl, 34.10. Found: C, 11.39; H, 2.24; Cl, 34.16.

Single Crystal X-ray Diffraction Studies

Single crystals of **1** suitable for X-ray diffraction studies were obtained via the dissolution of the red-orange product in a minimal amount of toluene to obtain a saturated solution. This solution was then allowed to sit in the glovebox freezer (-35 °C) overnight, during which time dark red trapezoidal crystals of **1** formed. Single crystals of **2** were obtained by charging a Celite/glass wool plug in a disposable pipette with ca. 100 mg of $MoCl_4(OEt_2)_2$ and passing ~3 mL of dme over the solid into a medium sized vial. This vial of freshly prepared $MoCl_4$(dme) was then placed inside of a 22 mL scintillation vial charged with ~5 mL of hexane and sealed. This vapor diffusion crystallization was allowed to sit, unperturbed, in the glovebox at room temperature for three days, providing well-formed orange needles of **2**. Single crystals of **4** were obtained by taking approximately 700 mg of freshly ground WCl_4 and allowing it to sit in a scintillation vial charged with approximately 10 mL of fresh dme overnight. Well-formed, yellow blocks were observed amidst a bed of unreacted WCl_4. X-Ray diffraction studies of **1** were conducted on a Rigaku XtaLAB Mini III two-circle diffractometer using a Mo Kα (λ = 0.71073 Å) fine-focus sealed X-ray tube source and a graphite monochromator detector at 298.1(5) K. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the XL refinement package using Least Squares minimization.[4-6] X-Ray diffraction studies of **2** and **4** were conducted on a Rigaku XtaLAB Synergy, single source at offset/far, HyPix diffractometer with Mo Kα (λ = 0.71073 Å) micro-focus sealed X-ray tube PhotonJet source and a mirror detector at 100 K. Using Olex2, the structures were solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the XL refinement package using Least Squares minimization.[4-6]

Magnetic Susceptibility

Gouy magnetic susceptibility measurements were conducted on a benchtop MSB MK1, calibrated with an aqueous solution of $MnCl_2$ (Sherwood Scientific, Ltd). Samples of MCl_4(dme) (M = Mo. W) were loaded into Gouy tubes inside the glovebox and capped with rubber stoppers. The measurements were conducted at 25 °C. A 122 mg sample of **2** was packed to a height of 1.90 cm in the sample tube, which produced a blank reading of -36 cgs. Both the sample and the tube produced a reading of +346 cgs. A 181 mg sample of **4** was packed to a height of 2.03 cm in a second sample tube, which produced a blank reading of -36 cgs. Both the sample and the tube produced a reading of +135 cgs. SQUID magnetometry measurements were obtained with a 7 Tesla Quantum Design Superconducting Quantum Interference Device (MPMS3). Approximately 65 mg of MCl_4(dme) (M = Mo, W) powder were added to a capsule in an argon glovebox. This capsule was then removed from the glovebox and quickly inserted into the MPMS for temperature dependent susceptibility measurements down to 2 K.

Computational Methods

Optimizations and frequency analyses were performed using the Gaussian (G09[7]) suite. A sizable integration grid (keyword Int=UltraFineGrid) was used in all cases. The title molecules as well as *cis*–$MCl_4(OEt_2)_2$ (M = Mo, W) were initially fully optimized as spin singlets and spin triplets at the UM06L+GD3/def2-SVP level, then at the UM06L+GD3/def2-TZVP level.[8-10] Convergence of the spin singlet wavefunctions for the MCl_4L_2 required use of a quadratic converger (Keyword SCF=XQC). Stationary points were confirmed as minima using frequency calculations.

The restricted singlet wavefunctions showed RHF → UHF instabilities. Consequently, subsequent optimizations using different local DFT approaches were performed with the molecules as unrestricted spin triplets (Supporting Information, Table S14). These were done to provide computational "error bars" for the energetics and bond distances.[11] Local DFT models were employed based on findings from Truhlar and co-workers that they perform better than hybrid models for transition metal compounds/complexes.[12] Frontier α orbitals from the triplet calculations were visualized using Avogadro.[13]

We noted that the three DFT models employed gave different predictions of *cis*/*trans* preferences for $MoCl_4(OEt_2)_2$. To arbitrate this, we performed optimizations and DLPNO-UCCSD(T)//UM06-2X+GD3/def2-TZVP and DLPNO-UCCSD(T)//UPBEPBE+GD3/def2-TZVP single point energy calculations[14-16] on *cis*– and *trans*–$MCl_4(ORR')_2$ (M = Mo, W; ORR' = OH_2, OMeH, OMe_2) and DLPNO-UCCSD//UM06-2X+GD3/def2-TZVP and DLPNO-UCCSD//UPBEPBE+ GD3/def2-TZVP single point energy calculations on *cis*– and *trans*–$MCl_4(OEt)_2$ using the ORCA program.[17-18] (The latter were too resource-intensive to allow calculating coupled cluster triples corrections). These employed auxiliary basis sets for Coulomb and correlation corrections.[19-20] The single point energies differed little regardless of the starting structure (see Supporting Information Table S14) or inclusion of triples corrections. They agreed best overall with the UPBEPBE-determined energies and *cis*/*trans* preferences. Consequently, energetics discussed below will involve the DLPNO-UCCSD//UPBEPBE+GD3/def2-TZVP data.

Absorption spectra were modeled using time-dependent density functional theory (TDDFT). Only the title molecules were examined. Several models were employed to determine which performed best (Supporting Information, Tables S15-S16). Very low energy *d-d* transitions were expected, so the number of states to be included in the calculations was set to 25. This ensured that transitions between 300–700 nm (the experimental spectrum limits) were included, with some loss of accuracy due to intruder states. The lowest energy transitions analyzed as *d-d* transitions, with energies 2000–5000 nm. The title molecules were also optimized and TD-analyzed at the ULC-BLYP/def2-TZVP and ULC-M06L/def2-TZVP levels with a self-consistent reaction field modeling the toluene solvent (Keyword SCRF Solvent=toluene). The overlaid experimental and theoretical UV-Vis graphic was generated using Kaleidagraph for Macintosh.[21]

X-Ray Crystallography

Table S1. Crystallographic data for all crystalline habits **1-3**.

	1	**2**	**4**
Empirical formula	$C_8H_{20}Cl_4MoO_2$	$C_4H_{10}Cl_4MoO_2$	$C_4H_{10}Cl_4WO_2$
Formula weight	385.98	327.86	415.77
Temperature	298.1(5) K	100.00(10) K	100.00(10) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	Cc	Cc
*a, b, c (*Å)	7.5956(2), 11.4732(4), 9.0193(3)	8.0686(5), 11.3057(6), 11.6997(6)	8.0766(2), 11.3089(2), 11.7413(3)
α, β, γ (°)	90, 106.347(3), 90	90, 90.519(5), 90	90, 90.687(2), 90
Volume (Å^3)	754.22(4)	1067.22(10)	1072.34(4)
Z	2	4	4
Density (calculated) (mg/m^3)	1.700	2.041	2.575
Absorption coefficient (mm^{-1})	1.560	2.185	11.724
R(int)	0.0199	0.0389	0.0358
Absorption correction method	Analytical	Gaussian	Gaussian
Data/restraints/parameters	2234/0/73	2068/2/102	3809/2/102
Goodness-of-Fit on F^2	1.067	1.166	1.052
R_1 ($I > 2\sigma(I)$)	0.0212	0.0372	0.0224
wR_2 (all data)	0.0516	0.1093	0.0558
Largest diff. peak and hole (e.Å^{-3})	0.44 and -0.42	0.486 and -0.815	2.322 and -0.760

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mo1	5000	5000	5000	27.36(7)
Cl2	4992.3(7)	3729.4(4)	7057.4(5)	46.66(12)
Cl1	1872.4(6)	4626.5(5)	3796.2(6)	48.42(12)
O1	5717.4(15)	3624.5(10)	3799.6(13)	34.6(3)
C3	4791(2)	2483.9(15)	3613(2)	42.1(4)
C1	7190(2)	3718.0(16)	3026(2)	41.6(4)
C2	6481(3)	3603(2)	1311(2)	60.4(6)
C4	6032(3)	1525.7(18)	4386(3)	61.9(6)

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Mo1	5719.8(7)	2344.4(5)	5022.4(6)	13.4(2)
Cl1	5453(3)	1448.8(19)	3234.5(16)	20.3(5)
Cl2	7216(4)	799(2)	5799(2)	32.9(6)
Cl3	8044(3)	3422(2)	4555(2)	26.7(5)
Cl4	5359(3)	3306.7(17)	6765.1(16)	18.5(5)
O1	3313(9)	1597(5)	5383(5)	19.7(13)
O2	4030(7)	3647(5)	4344(5)	14.5(12)
C1	3029(17)	877(8)	6387(9)	32(3)
C2	1975(15)	2455(8)	5218(10)	24(2)
C3	2375(12)	3172(7)	4172(8)	20.3(19)
C4	4444(11)	4502(8)	3471(7)	18.8(18)

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	**y**	**z**	**U(eq)**
W1	1332.5(5)	7363.7(2)	4805.1(4)	15.76(6)
Cl1	1620.6(18)	8327.1(13)	3055.7(12)	20.8(3)
Cl2	-172(2)	5811.1(17)	4023.1(15)	34.9(4)
Cl3	-998.5(19)	8443.9(18)	5285.3(15)	29.2(3)
Cl4	1569.4(19)	6455.0(14)	6588.2(12)	23.4(3)
O1	3726(6)	6631(4)	4434(4)	22.4(9)
O2	3021(5)	8653(4)	5477(4)	18.1(8)
C1	4000(11)	5894(7)	3433(6)	36.0(17)
C2	5082(10)	7481(6)	4606(8)	25.8(14)
C3	4695(7)	8195(6)	5638(6)	23.2(12)
C4	2630(8)	9509(6)	6354(6)	25.5(12)

Table S5. Bond lengths [Å] and angles [°] for **1**.

Mo(1)- Cl(2)[1]	2	Cl(2)-Mo(1)-Cl(2)[1]	180.0
Mo(1)-Cl(2)	2	Cl(1)-Mo(1)-Cl(2)[1]	88.588(18)
Mo(1)-Cl(1)	2	Cl(1)[1]-Mo(1)-Cl(2)	88.589(18)
Mo(1)-Cl(1)[1]	2	Cl(1)[1]-Mo(1)-Cl(2)[1]	91.411(18)
Mo(1)-O(1)	2	Cl(1)-Mo(1)-Cl(2)	91.412(18)
Mo(1)-O(1)[1]	2	Cl(1)[1]-Mo(1)-Cl(1)	180.0
O(1)-C(3)	1	O(1)[1]-Mo(1)-Cl(2)[1]	89.98(3)
O(1)-C(1)	1	O(1)-Mo(1)-Cl(2)	89.98(3)
C(3)-C(4)	1	O(1)[1]-Mo(1)-Cl(2)	90.02(3)
C(1)-C(2)	1	O(1)-Mo(1)-Cl(2)[1]	90.02(3)
		O(1)-Mo(1)-Cl(1)[1]	90.00(3)
		O(1)[1]-Mo(1)-Cl(1)	90.00(3)
		O(1)-Mo(1)-Cl(1)	90.00(3)
		O(1)[1]-Mo(1)-Cl(1)[1]	90.00(3)
		O(1)-Mo(1)-O(1)[1]	180.00(5)
		C(3)-O(1)-Mo(1)	123.31(9)
		C(3)-O(1)-C(1)	114.25(12)
		C(1)-O(1)-Mo(1)	122.43(10)
		O(1)-C(3)-C(4)	112.58(15)
		O(1)-C(3)-C(4)	112.46(15)

Symmetry transformations used to generate equivalent atoms: (1) [1]1-X,1-Y,1-Z

Table S6. Bond lengths [Å] and angles [°] for **2**.

Mo(1)- Cl(1)	2	Cl(2)-Mo(1)-Cl(1)	93.90(8)
Mo(1)-Cl(2)	2	Cl(2)-Mo(1)-Cl(3)	94.01(10)
Mo(1)-Cl(3)	2	Cl(2)-Mo(1)-Cl(4)	94.48(8)
Mo(1)-Cl(4)	2	Cl(3)-Mo(1)-Cl(1)	94.88(9)
Mo(1)-O(1)	2	Cl(3)-Mo(1)-Cl(4)	93.97(8)
Mo(1)-O(2)	2	Cl(4)-Mo(1)-Cl(1)	167.35(9)
O(1)-C(1)	1	O(1)-Mo(1)-Cl(1)	85.99(17)
O(1)-C(2)	1	O(1)-Mo(1)-Cl(2)	95.45(18)
O(2)-C(3)	1	O(1)-Mo(1)-Cl(3)	170.42(17)
O(2)-C(4)	1	O(1)-Mo(1)-Cl(4)	83.80(17)
C(2)-C(3)	1	O(2)-Mo(1)-Cl(1)	85.02(16)
		O(2)-Mo(1)-Cl(2)	172.28(18)
		O(2)-Mo(1)-Cl(3)	93.70(16)
		O(2)-Mo(1)-Cl(4)	85.41(16)
		O(2)-Mo(1)-O(1)	76.9(2)
		C(1)-O(1)-Mo(1)	121.8(7)
		C(1)-O(1)-C(2)	111.0(8)
		C(2)-O(1)-Mo(1)	112.2(5)
		C(3)-O(2)-Mo(1)	112.1(5)
		C(4)-O(2)-Mo(1)	124.6(5)
		C(4)-O(2)-C(3)	111.6(7)
		O(1)-C(2)-C(3)	107.5(9)

O(2)-C(3)-C(2)	106.9(8)

Table S7. Bond lengths [Å] and angles [°] for **4**.

W(1)- Cl(1)	2	Cl(2)-W(1)-Cl(1)	93.57(6)
W(1)-Cl(2)	2	Cl(2)-W(1)-Cl(3)	94.13(8)
W(1)-Cl(3)	2	Cl(2)-W(1)-Cl(4)	93.36(6)
W(1)-Cl(4)	2	Cl(3)-W(1)-Cl(1)	93.31(6)
W(1)-O(1)	2	Cl(3)-W(1)-Cl(4)	94.11(6)
W(1)-O(2)	2	Cl(4)-W(1)-Cl(1)	169.45(6)
O(1)-C(1)	1	O(1)-W(1)-Cl(1)	84.40(13)
O(1)-C(2)	1	O(1)-W(1)-Cl(2)	95.51(14)
O(2)-C(3)	1	O(1)-W(1)-Cl(3)	170.20(13)
O(2)-C(4)	1	O(1)-W(1)-Cl(4)	87.03(13)
C(2)-C(3)	1	O(2)-W(1)-Cl(1)	86.36(12)
		O(2)-W(1)-Cl(2)	172.01(13)
		O(2)-W(1)-Cl(3)	93.85(12)
		O(2)-W(1)-Cl(4)	85.68(12)
		O(2)-W(1)-O(1)	76.52(17)
		C(1)-O(1)-W(1)	121.9(5)
		C(1)-O(1)-C(2)	111.3(6)
		C(2)-O(1)-W(1)	113.0(4)
		C(3)-O(2)-W(1)	113.0(4)
		C(4)-O(2)-W(1)	124.9(4)
		C(4)-O(2)-C(3)	110.8(5)
		O(1)-C(2)-C(3)	107.6(6)

O(2)-C(3)-C(2)	106.8(5)

Table S8. Anisotropic displacement parameters ($Å^2$ x 10^3) for **1**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	24.72(10)	28.86(11)	29.84(10)	1.48(7)	9.86(7)	-1.86(7)
Cl2	61.6(3)	41.8(2)	42.0(2)	10.94(18)	23.3(2)	1.8(2)
Cl1	27.25(19)	58.9(3)	55.8(3)	-8.3(2)	6.34(17)	-4.51(18)
O1	33.1(6)	32.3(6)	43.1(6)	-3.7(5)	18.2(5)	-3.9(5)
C3	42.5(9)	34.5(9)	49.2(10)	-5.5(7)	12.7(8)	-9.4(7)
C1	36.3(8)	43.6(10)	51.4(10)	-3.4(8)	23.0(8)	0.4(7)
C2	72.0(14)	69.2(15)	47.8(11)	-0.8(10)	29.7(10)	3.5(11)
C4	72.0(14)	37.9(11)	73.3(15)	5.1(10)	16.6(12)	0.6(10)

Table S9. Anisotropic displacement parameters ($Å^2$ x 10^3) for **2**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	14.2(4)	15.3(3)	10.8(3)	-1.5(3)	-1.2(2)	4.6(3)
Cl1	24.4(11)	22.7(11)	13.7(9)	-6.3(7)	-1.0(8)	6.1(8)
Cl2	51.5(17)	25.0(11)	22.0(11)	-2.6(8)	-10.0(11)	23.5(11)
Cl3	12.8(11)	41.8(13)	25.4(11)	-4.5(9)	1.5(8)	-3.0(9)
Cl4	27.9(12)	15.8(9)	11.8(9)	-3.0(7)	-0.7(8)	0.4(8)
O1	25(4)	15(3)	19(3)	1(2)	8(3)	0(2)

O2	8(3)	17(3)	18(3)	2(2)	-2(2)	1(2)
C1	55(8)	19(4)	23(5)	1(4)	12(5)	-7(5)
C2	20(6)	22(4)	29(6)	-1(3)	2(5)	-4(4)
C3	16(5)	20(4)	25(4)	-2(3)	-1(4)	-1(3)
C4	13(4)	25(4)	19(4)	9(3)	4(3)	3(4)

Table S10. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
W1	16.73(10)	16.94(9)	13.60(9)	1.18(18)	-0.95(6)	-4.26(18)
Cl1	30.3(7)	17.9(6)	14.2(5)	2.2(4)	0.1(5)	0.0(5)
Cl2	50.4(11)	28.8(8)	25.3(7)	2.0(6)	-10.5(7)	-20.1(7)
Cl3	15.8(6)	43.6(10)	28.1(7)	2.5(7)	1.0(5)	3.1(6)
Cl4	28.7(7)	25.4(7)	16.2(6)	5.5(5)	-0.1(5)	-6.4(5)
O1	29(2)	17(2)	22(2)	1.5(16)	4.4(17)	4.1(17)
O2	15.8(18)	20.4(19)	18.2(19)	-1.2(15)	-2.0(14)	-2.5(15)
C1	61(5)	23(3)	25(3)	-3(2)	10(3)	6(3)
C2	18(3)	25(3)	34(4)	1(2)	8(3)	3(2)
C3	13(2)	27(3)	31(3)	0(2)	-1(2)	1(2)
C4	24(3)	26(3)	27(3)	-9(2)	3(2)	-2(2)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **1**.

	x	y	z	U(eq)
H3A	4321.09	2309.38	2520.41	51
H3B	3755.49	2524.35	4041.01	51
H1A	8094.04	3113.99	3419.05	50
H1B	7795.59	4466.16	3274.96	50
H2A	7433.3	3804.25	847.63	91
H2B	5455.18	4117.28	933.06	91
H2C	6098.1	2813.68	1049.87	91
H4A	7013.31	1444.42	3915.92	93
H4B	5353.13	809.79	4277.06	93
H4C	6530.01	1704.37	5462.45	93

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **2**.

	x	y	z	U(eq)
H1A	3905.47	280.03	6454.99	48
H1B	1951.07	482.48	6315.54	48
H1C	3037.82	1379.67	7069.11	48
H2A	1890.14	2976.89	5894.23	28
H2B	903.64	2040.04	5110.94	28

H3A	2337.34	2666.16	3481.14	24
H3B	1563.78	3821.72	4073.64	24
H4A	5513.72	4868.62	3657.85	28
H4B	3584.11	5113.64	3435.55	28
H4C	4515.05	4104.18	2729.1	28

Table S13. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **4**.

	x	**y**	**z**	**U(eq)**
H1A	3189.63	5249.06	3416.85	54
H1B	5121.01	5563.42	3468.29	54
H1C	3873.37	6374.53	2743.18	54
H2A	5176.88	8003.08	3932.48	31
H2B	6144.57	7057.72	4715.46	31
H3A	4757.34	7694.5	6329.45	28
H3B	5493.74	8853.46	5725.19	28
H4A	1551.69	9869.68	6183.28	38
H4B	3483.9	10124.15	6376.29	38
H4C	2588.94	9110.84	7094.35	38

Table S14. Calculated raw and relative energetics for singlet and triplet states and *cis*– and *trans*–isomers of MCl_4(dme), $MCl_4(OEt_2)_2$, $MCl_4(OH_2)_2$, $MCl_4(OMeH)_2$, and $MCl_4(OMe_2)_2$ (M = Mo, W) using various model chemistries.

	UM06LGD3	UM06LGD3	UM06LGD3	UBLYPGD3	UPBEPBEGD3
	def2SVP				
	ZPE	def2SVP	def2TZVP	def2TZVP	def2TZVP
cis-MoCl4(OEt2)2 singlet	0.283088	-2375.605890	-2376.723854		
trans-MoCl4(OEt2)2 singlet	0.282835	-2375.614719	-2376.729782		
trans-cis		**-23.8**	**-16.2**		
cis-MoCl4(OEt2)2 triplet	0.282907	-2375.634708	-2376.752406	-2376.582072	-2375.475688
trans-MoCl4(OEt2)2 triplet	0.282905	-2375.636427	-2376.751935	-2376.583381	-2375.477317
trans-cis		**-4.5**	**1.2**	**-3.4**	**-4.3**
cis-MoCl4(OEt2)2 triplet-singlet		**-76.1**	**-75.4**		
trans-MoCl4(OEt2)2 triplet-singlet		**-56.8**	**-58.0**		
cis-WCl4(OEt2)2 singlet	0.282911	-2374.503687	-2375.620340		
trans-WCl4(OEt2)2 singlet	0.282730	-2374.513238	-2375.628490		
trans-cis		**-25.6**	**-21.9**		
cis-WCl4(OEt2)2 triplet	0.282496	-2374.532100	-2375.647992	-2375.480577	-2374.378452
trans-WCl4(OEt2)2 triplet	0.282801	-2374.533949	-2375.650845	-2375.485574	-2374.382820
trans-cis		**-4.1**	**-6.7**	**-12.3**	**-10.7**
cis-WCl4(OEt2)2 triplet-singlet		**-75.7**	**-73.7**		
trans-WCl4(OEt2)2 triplet-singlet		**-54.2**	**-58.5**		
cis-MoCl4(OH2)2 triplet	0.055744	-2061.440122	-2062.218194	-2062.182345	-2061.355467
trans-MoCl4(OH2)2 triplet	0.055913	-2061.426606	-2062.202040	-2062.168078	-2061.342290
trans-cis		**35.9**	**42.9**	**37.9**	**35.0**
cis-MoCl4(OMeH)2 triplet	0.113127	-2139.969970	-2140.834850	-2140.766433	-2139.866828
trans-MoCl4(OMeH)2 triplet	0.113094	-2139.958971	-2140.821034	-2140.756115	-2139.856581
trans-cis		**28.8**	**36.2**	**27.0**	**26.8**
cis-MoCl4(OMe2)2 triplet	0.168829	-2218.490765	-2219.444000	-2219.345869	-2218.372938
trans-MoCl4(OMe2)2 triplet	0.169374	-2218.493268	-2219.443174	-2219.343831	-2218.370612
trans-cis		**-5.1**	**3.6**	**6.8**	**7.5**
cis-WCl4(OH2)2 triplet	0.055653	-2060.335790	-2061.112305	-2061.076134	-2060.255309
trans-WCl4(OH2)2 triplet	0.055950	-2060.324663	-2061.100009	-2061.063436	-2060.244512
trans-cis		**30.0**	**33.1**	**34.1**	**29.1**
cis-WCl4(OMeH)2 triplet	0.112867	-2138.865911	-2139.729295	-2139.661744	-2138.767539
trans-WCl4(OMeH)2 triplet	0.113305	-2138.856876	-2139.718928	-2139.653587	-2138.759484
trans-cis		**24.9**	**28.4**	**22.6**	**22.3**
cis-WCl4(OMe2)2 triplet	0.168913	-2217.387307	-2218.338798	-2218.241509	-2217.273527
trans-WCl4(OMe2)2 triplet	0.168371	-2217.391206	-2218.341125	-2218.243501	-2217.274676
trans-cis		**-11.7**	**-7.5**	**-6.7**	**-4.4**
cis-MoCl4(dme) singlet	0.149374	-2217.267752	-2218.214865	-2218.124509	-2217.155175
cis-MoCl4(dme) triplet	0.149304	-2217.298296	-2218.245647	-2218.152852	-2217.184918
cis-MoCl4(dme) triplet-singlet		**-80.4**	**-81.0**	**-74.6**	**-78.3**
cis-WCl4(dme) singlet	0.149314	-2216.164160	-2217.109986	-2217.023224	-2216.058726
cis-WCl4(dme) triplet	0.149121	-2216.193821	-2217.139654	-2217.048318	-2216.085523
cis-WCl4(dme) triplet-singlet		**-78.4**	**-78.4**	**-66.4**	**-70.9**

Table S14 (continued)

	UM06LGD3	UDLPNO-CCSD	UDLPNO-CCSD(T)	UDLPNO-CCSD	UDLPNO-CCSD(T)
	def2SVP	//UM06LGD3	//UM06LGD3	//UPBEPBEGD3	//UPBEPBEGD3
	ZPE	def2TZVP	def2TZVP	def2TZVP	def2TZVP
cis-MoCl4(OEt2)2 singlet	0.283088				
trans-MoCl4(OEt2)2 singlet	0.282835				
trans-cis					
cis-MoCl4(OEt2)2 triplet	0.282907	-2373.407334		-2373.380993	
trans-MoCl4(OEt2)2 triplet	0.282905	-2373.411236		-2373.385339	
trans-cis		**-10.2**		**-11.4**	
cis-WCl4(OEt2)2 singlet	0.282911				
trans-WCl4(OEt2)2 singlet	0.282730				
trans-cis					
cis-WCl4(OEt2)2 triplet	0.282496	-2372.235362	-2372.375267	-2372.209300	-2372.356153
trans-WCl4(OEt2)2 triplet	0.282801	-2372.243178	-2372.381900	-2372.217104	-2372.362674
trans-cis		**-19.7**	**-16.6**	**-19.7**	**-16.3**
cis-MoCl4(OH2)2 triplet	0.055744	-2059.641611	-2059.726590	-2059.620087	-2059.709191
trans-MoCl4(OH2)2 triplet	0.055913	-2059.625615	-2059.710986	-2059.603365	-2059.692904
trans-cis		**42.4**	**41.4**	**44.3**	**43.2**
cis-MoCl4(OMeH)2 triplet	0.113127			-2138.042633	-2138.148556
trans-MoCl4(OMeH)2 triplet	0.113094			-2138.030995	-2138.136830
trans-cis				**30.5**	**30.7**
cis-MoCl4(OMe2)2 triplet	0.168829	-2216.479684	-2216.597744	-2216.459132	-2216.583015
trans-MoCl4(OMe2)2 triplet	0.169374	-2216.484570	-2216.602154	-2216.460840	-2216.583915
trans-cis		**-11.4**	**-10.1**	**-3.1**	**-0.9**
cis-WCl4(OH2)2 triplet	0.055653	-2058.466505	-2058.542497	-2058.444322	-2058.524486
trans-WCl4(OH2)2 triplet	0.055950	-2058.455058	-2058.531321	-2058.433621	-2058.513963
trans-cis		**30.8**	**30.1**	**28.9**	**28.4**
cis-WCl4(OMeH)2 triplet	0.112867			-2136.868855	-2136.965294
trans-WCl4(OMeH)2 triplet	0.113305			-2136.861332	-2136.957732
trans-cis				**20.9**	**21.0**
cis-WCl4(OMe2)2 triplet	0.168913	-2215.306710	-2215.415517	-2215.284855	-2215.399674
trans-WCl4(OMe2)2 triplet	0.168371	-2215.315144	-2215.423420	-2215.291670	-2215.405340
trans-cis		**-23.6**	**-22.2**	**-19.3**	**-16.3**
		UPBEPBEGD3			
		def2TZVP	**UPBEPBEGD3**		
		ZPE	**def2TZVP**		
cis-MoCl4(OH2)2 triplet flat H2O		0.052009	-2061.347649		
trans-MoCl4(OH2)2 triplet flat H2O		0.052412	-2061.336255		
trans-cis		**1.1**	**31.0**		
cis-WCl4(OH2)2 triplet flat H2O		0.051850	-2060.247263		
trans-WCl4(OH2)2 triplet flat H2O		0.051409	-2060.234592		
trans-cis		**-1.2**	**32.1**		

Table S15. Experimental and calculated bond distances (pm) for MCl_4(dme) and *cis*– and *trans*-$MCl_4(ORR')_2$ (M = Mo, W; R, R' = H, Me, Et) using various DFT models and the def2-TZVP basis set. The ether ligands are considered to be in the equatorial plane, so Cl_{eq} atoms are *trans* to ether O atoms, while Cl_{ax} atoms are *cis* to ether O atoms. Values are averaged for bonds of the same type.

		Expt	UM06L+GD3	UBLYP+GD3	UPBEPBE+GD3
$MoCl_4$(dme)	Mo–Cl_{eq}	230.6	228.5	231.2	228.5
	Mo–Cl_{ax}	233.2	233.4	236.1	233.4
	Mo–O	215.9	232.4	236.0	232.6
WCl_4(dme)	W–Cl_{eq}	231.9	230.3	233.1	230.5
	W–Cl_{ax}	233.9	234.8	237.7	234.9
	W–O	214.7	231.1	233.0	230.3
***cis*–$MoCl_4(OEt_2)_2$**	Mo–Cl_{eq}		229.2	231.8	229.1
	Mo–Cl_{ax}		233.7	236.4	233.7
	Mo–O		233.3	237.4	233.9
***trans*–$MoCl_4(OEt_2)_2$**	Mo–Cl	235.5	237.7	240.5	237.5
	Mo–O	206.7	210.0	212.7	210.3
***cis*–$WCl_4(OEt_2)_2$**	W–Cl_{eq}		231.0	233.8	231.1
	W–Cl_{ax}		235.7	238.6	235.9
	W–O		230.6	232.8	229.9
***trans*–$WCl_4(OEt_2)_2$**	W–Cl	235.7	236.8	239.5	236.8
	W–O	207.0	218.3	220.5	218.0
***cis*–$MoCl_4(OH_2)_2$**	Mo–Cl_{eq}				229.1
	Mo–Cl_{ax}				232.1
	Mo–O				231.2
***trans*–$MoCl_4(OH_2)_2$**	Mo–Cl				234.6
	Mo–O				219.2
***cis*–$WCl_4(OH_2)_2$**	W–Cl_{eq}				230.9
	W–Cl_{ax}				233.6
	W–O				231.5
***trans*–$WCl_4(OH_2)_2$**	W–Cl				235.8
	W–O				219.7
***cis*–$MoCl_4(OMeH)_2$**	Mo–Cl_{eq}				229.0
	Mo–Cl_{ax}				233.2
	Mo–O				230.2
***trans*–$MoCl_4(OMeH)_2$**	Mo–Cl				235.0
	Mo–O				217.4
***cis*–$WCl_4(OMeH)_2$**	W–Cl_{eq}				230.8
	W–Cl_{ax}				234.6
	W–O				229.6
***trans*–$WCl_4(OMeH)_2$**	W–Cl				236.3
	W–O				217.8
***cis*–$MoCl_4(OMe_2)_2$**	Mo–Cl_{eq}				228.5
	Mo–Cl_{ax}				232.2
	Mo–O				239.5
***trans*–$MoCl_4(OMe_2)_2$**	Mo–Cl				235.3
	Mo–O				218.5
***cis*–$WCl_4(OMe_2)_2$**	W–Cl_{eq}				230.4
	W–Cl_{ax}				234.0
	W–O				236.9
***trans*–$WCl_4(OMe_2)_2$**	W–Cl				236.5
	W–O				218.7

Table S16. Calculated (TD, nm) electronic transition energies for MCl_4(dme) and *trans*-$MCl_4(OEt_2)_2$ (M = Mo, W) using various model chemistries. Band positions are generally approximated within 10 nm, owing to a choice of a peak width at half height = 30 nm.

	Exp	**UCAM-B3LYP**	**UωB97XD**	**UM06LHF**	**ULC-BLYP**	**ULC-M06L**
$MoCl_4$(dme)	410 (sh)	490	510	460	480	430
	360 (sh)	390 (sh)	400 (sh)	325	390	370
	310	360	360		310 (sh)	310 (sh)
$MoCl_4$(dme)					460	410
toluene					380 (sh)	365 (sh)
					320	320 (sh)
WCl_4(dme)	400 (sh) ?	450	460	600	440	405
	320 (sh)	380	390	420	370	355
WCl_4(dme)					425	390
toluene					360	350
trans-$MoCl_4(OEt_2)_2$	550 (sh) ?	440 (sh)	450 (sh)	380	360 (sh)	350 (sh)
	365	400	410	320	310 (sh)	
		325	330			
trans-$MoCl_4(OEt_2)_2$					360 (sh)	340 (sh)
toluene					310 (sh)	305 (sh)
trans-$WCl_4(OEt_2)_2$	660					
	480 (sh)					
	380 (sh)	340	340	310	< 300	<300
trans-$WCl_4(OEt_2)_2$					< 300	< 300
toluene						

Table S17. Calculated (TD–ULC-M06L/def2TZVP, SCRF=toluene, nm) electronic transition wavelengths for $MCl_4(dme)$ and *trans*-$MCl_4(OEt_2)_2$ (M = Mo, W).

***trans*-$MoCl_4(OEt_2)_2$ C_{2h}**				***trans*-$WCl_4(OEt_2)_2$ C_{2h}**		
Sym	**λ**	**Intensity**		**Sym**	**λ**	**Intensity**
BG	7311.97	0.00000				
AG	1797.09	0.00000		BG	2974.58	0.00000
AG	375.27	0.00000		BG	393.78	0.00000
AG	367.65	0.00000		BG	361.36	0.00000
BG	366.30	0.00000		BG	327.65	0.00000
BG	363.55	0.00000		AG	317.79	0.00000
AU	341.43	0.00460		BG	306.85	0.00000
AU	337.37	0.00180		BU	290.03	0.02410
BG	313.72	0.00000		BU	288.99	0.02770
BG	309.76	0.00000		AU	256.08	0.00000
BU	305.05	0.00930		AG	254.31	0.00000
AG	304.48	0.00000		BG	247.61	0.00000
BG	294.51	0.00000		BU	240.46	0.02010
AU	291.07	0.00020		AU	239.61	0.00000
AU	284.91	0.00200		BU	238.55	0.03940
BU	284.49	0.00190		BG	238.24	0.00000
AU	278.28	0.01330		BU	234.99	0.03150
AG	274.90	0.00000		AU	232.50	0.00000
AU	272.90	0.00120		BU	229.87	0.01690
AG	271.37	0.00000		BG	229.41	0.00000
AU	270.96	0.02720		BG	225.34	0.00000
AU	266.58	0.00000		AU	222.59	0.00000
BU	264.91	0.02160		AU	220.21	0.00440
BU	256.41	0.00760		BG	216.61	0.00000
BU	252.22	0.07580		AU	215.76	0.00010
$MoCl_4(dme)$ C_2				***W*$Cl_4(dme)$ C_2**		
Sym	**λ**	**Intensity**		**Sym**	**λ**	**Intensity**
B	2995.65	0.00060		B	4665.44	0.00040
B	2252.77	0.00020		B	2465.61	0.00010
A	434.34	0.00000		A	408.85	0.00000
B	428.99	0.00030		B	393.91	0.00130
B	411.13	0.00240		B	385.20	0.00240
A	365.57	0.00290		A	344.52	0.00340
A	327.22	0.00510		A	268.81	0.00550
B	318.60	0.00280		B	264.89	0.00260
B	302.97	0.02410		A	254.52	0.00010
A	301.63	0.00000		B	249.82	0.02490
A	289.52	0.00000		A	240.24	0.00170
A	282.40	0.00000		A	238.65	0.00030
B	277.50	0.00870		A	238.02	0.00030
A	277.42	0.00030		B	237.23	0.00550
A	271.76	0.02280		A	230.19	0.03070
A	254.39	0.00000		B	224.02	0.05640
B	254.19	0.03870		A	223.57	0.00000
A	250.84	0.00010		B	216.93	0.00280
B	247.99	0.02930		A	216.30	0.00020
B	246.52	0.00120		B	214.85	0.00140
A	242.48	0.00210		A	210.58	0.00740
B	242.47	0.03060		B	210.47	0.06920
A	240.39	0.00020		B	208.27	0.00890
B	239.67	0.00200		A	207.88	0.00090
B	237.06	0.01740		B	205.03	0.01330

Table S18. Optimized Cartesian coordinates (UM06L+GD3/def2-TZVP) for all triplet MCl_4L_2 complex molecules examined (M = Mo, W).

$MoCl_4$(dme)

Mo	0.061797	-0.000277	0.000035
Cl	-0.431910	-0.789709	2.140184
Cl	1.591360	1.587289	0.602646
Cl	1.577774	-1.601476	-0.600832
Cl	-0.422372	0.793533	-2.140673
O	-1.792102	1.316101	0.482544
C	-1.715276	2.732059	0.296727
H	-0.818157	3.068799	0.806657
H	-2.597444	3.200086	0.735880
H	-1.647581	2.971757	-0.766526
C	-2.963659	0.754058	-0.118079
H	-2.966479	0.986970	-1.187649
H	-3.847878	1.201474	0.344555
C	-2.970425	-0.727493	0.114683
O	-1.803259	-1.300006	-0.484602
C	-1.739327	-2.716594	-0.298704
H	-0.844675	-3.061355	-0.807609
H	-2.625146	-3.176706	-0.738870
H	-1.674997	-2.956883	0.764625
H	-2.976555	-0.960366	1.184247
H	-3.858083	-1.166978	-0.348966

WCl_4(dme)

W	0.050215	-0.000226	0.000030
Cl	-0.438216	-0.790246	2.156657
Cl	1.609406	1.586766	0.596664
Cl	1.595792	-1.601163	-0.594766
Cl	-0.428546	0.794139	-2.157170
O	-1.791981	1.312649	0.474083
C	-1.711724	2.732101	0.296000
H	-0.808097	3.060767	0.799797
H	-2.588430	3.198663	0.746556
H	-1.652138	2.975157	-0.766671
C	-2.972087	0.754336	-0.118486
H	-2.979801	0.988289	-1.187629
H	-3.850227	1.204413	0.352053
C	-2.978882	-0.727605	0.114964
O	-1.803138	-1.296501	-0.476211
C	-1.735847	-2.716616	-0.298041
H	-0.834613	-3.053388	-0.800770
H	-2.616174	-3.175285	-0.749637
H	-1.679705	-2.960191	0.764699
H	-2.989963	-0.961474	1.184095
H	-3.860472	-1.169778	-0.356618

***cis*-$MoCl_4(OEt_2)_2$**

Mo	0.000855	-0.024742	0.043954
O	1.300491	1.946623	0.024944
C	1.956523	2.366967	1.248771
C	1.310129	3.612186	1.787338
H	1.811518	3.933436	2.699388
H	1.363495	4.433423	1.072240
H	0.263855	3.425052	2.023671
H	3.015838	2.516022	1.029638
H	1.884521	1.535157	1.944768
C	1.947477	2.511087	-1.138727
C	3.171759	1.739036	-1.546267
H	2.911269	0.716159	-1.809802
H	3.632371	2.210855	-2.413438
H	3.915611	1.706777	-0.751174
H	2.179427	3.554082	-0.904159
H	1.203206	2.510327	-1.932221
O	-1.922934	1.165321	-0.393355
C	-1.877659	2.412693	-1.102471
C	-2.810065	2.443777	-2.282920
H	-2.614736	1.603656	-2.947212
H	-3.856989	2.412754	-1.983671
H	-2.659798	3.364939	-2.843776
H	-2.076074	3.226225	-0.398212
H	-0.842778	2.511223	-1.422878
C	-3.193090	0.833140	0.211019
C	-3.745396	1.921537	1.091183
H	-4.618744	1.539501	1.617279
H	-3.013555	2.228851	1.836682
H	-4.065884	2.799104	0.530582
H	-2.991373	-0.068918	0.783022
H	-3.887120	0.563975	-0.589884
Cl	-1.245803	-1.951857	0.050798

***cis*-$WCl_4(OEt_2)_2$**

W	0.046336	-0.661191	-0.106524
O	1.909015	0.546950	0.621993
C	2.602555	0.140159	1.831971
C	2.334338	1.121941	2.936941
H	2.858467	0.822864	3.843626
H	2.671631	2.124501	2.672663
H	1.268761	1.160011	3.158869
H	3.666098	0.062103	1.597926
H	2.248521	-0.858590	2.074866
C	2.760424	1.346221	-0.235777
C	3.674859	0.502052	-1.078216
H	3.100690	-0.139138	-1.743804
H	4.311771	1.144396	-1.685226
H	4.321099	-0.129374	-0.469697
H	3.311802	2.033321	0.412096
H	2.094078	1.939300	-0.858442
O	-1.299269	1.117534	0.337762
C	-0.845448	2.475863	0.189773
C	-1.684512	3.264679	-0.777316
H	-1.744440	2.752937	-1.736380
H	-2.695066	3.432544	-0.407406
H	-1.231470	4.241481	-0.939101
H	-0.807333	2.938707	1.179714
H	0.178284	2.386635	-0.165725
C	-2.634138	0.959323	0.881208
C	-2.811662	1.641267	2.209452
H	-3.775130	1.354557	2.627495
H	-2.037444	1.330768	2.909855
H	-2.803599	2.728119	2.134135
H	-2.763121	-0.116020	0.968423
H	-3.345497	1.315820	0.132450
Cl	-1.809428	-1.838396	-0.852936

Table S18. *(continued)*

Cl	0.171163	0.124824	-2.277632
Cl	1.966542	-1.091130	0.527194
Cl	-0.568414	0.682423	2.201181

***trans*-$MoCl_4(OEt_2)_2$**

Mo	0.000000	0.000000	-0.000000
Cl	-0.788470	1.528795	1.653465
Cl	-2.004446	0.264926	-1.231559
O	-0.862822	-1.593158	1.061590
C	-0.230995	-2.906240	1.154668
H	-0.234905	-3.186121	2.209203
H	0.800064	-2.737812	0.853668
C	-0.923378	-3.908969	0.277562
H	-0.950089	-3.560404	-0.752985
H	-1.939219	-4.121249	0.606887
H	-0.368953	-4.845740	0.304386
C	-2.138637	-1.469169	1.760858
H	-2.748642	-2.322850	1.461664
H	-2.591497	-0.569979	1.350457
C	-1.940821	-1.379634	3.246463
H	-1.537150	-2.297694	3.670333
H	-2.903229	-1.196183	3.721610
H	-1.277679	-0.553060	3.493965
Cl	0.788470	-1.528795	-1.653465
Cl	2.004446	-0.264926	1.231559
O	0.862822	1.593158	-1.061590
C	0.230995	2.906240	-1.154668
H	0.234905	3.186121	-2.209203
H	-0.800064	2.737812	-0.853668
C	0.923378	3.908969	-0.277562
H	0.950089	3.560404	0.752985
H	1.939219	4.121249	-0.606887
H	0.368953	4.845740	-0.304386
C	2.138637	1.469169	-1.760858
H	2.748642	2.322850	-1.461664
H	2.591497	0.569979	-1.350457
C	1.940821	1.379634	-3.246463
H	1.537150	2.297694	-3.670333
H	2.903229	1.196183	-3.721610
H	1.277679	0.553060	-3.493965

***cis*-$MoCl_4(OH_2)_2$**

Mo	0.000009	0.000006	0.012964
Cl	0.261666	-1.677108	1.551462
Cl	2.194401	0.340608	-0.662591
Cl	-0.259425	1.678464	1.550371
Cl	-2.195356	-0.341186	-0.659121
O	-0.259717	1.663800	-1.569404
H	-1.112612	2.097871	-1.437600
H	0.420869	2.336729	-1.438325
O	0.257450	-1.665172	-1.568322
H	1.110534	-2.099129	-1.437371
H	-0.422945	-2.337986	-1.435671

***trans*-$MoCl_4(OH_2)_2$**

Mo	-0.000000	0.000000	0.000000
Cl	0.323489	0.480025	-2.145298
Cl	1.512471	-2.402792	-0.430396
Cl	-0.364600	-1.011609	2.190971

***trans*-$WCl_4(OEt_2)_2$**

W	0.000000	0.000000	-0.000000
Cl	0.852708	1.527254	-1.602440
Cl	-1.985693	-0.227891	-1.261898
O	0.892513	-1.657770	-1.105054
C	0.274472	-2.968635	-1.180724
H	0.310839	-3.287445	-2.224475
H	-0.769673	-2.804707	-0.922117
C	0.937781	-3.948995	-0.255293
H	1.975249	-4.137740	-0.527351
H	0.410618	-4.901016	-0.298815
H	0.904924	-3.588663	0.770940
C	2.149189	-1.533118	-1.820103
H	2.754922	-2.406956	-1.571360
H	2.635479	-0.660877	-1.388009
C	1.933295	-1.383793	-3.299494
H	2.893359	-1.235853	-3.791964
H	1.306694	-0.519237	-3.509228
H	1.472425	-2.266032	-3.741345
Cl	-0.852708	-1.527254	1.602440
Cl	1.985693	0.227891	1.261898
O	-0.892513	1.657770	1.105054
C	-0.274472	2.968635	1.180724
H	-0.310839	3.287445	2.224475
H	0.769673	2.804707	0.922117
C	-0.937781	3.948995	0.255293
H	-1.975249	4.137740	0.527351
H	-0.410618	4.901016	0.298815
H	-0.904924	3.588663	-0.770940
C	-2.149189	1.533118	1.820103
H	-2.754922	2.406956	1.571360
H	-2.635479	0.660877	1.388009
C	-1.933295	1.383793	3.299494
H	-2.893359	1.235853	3.791964
H	-1.306694	0.519237	3.509228
H	-1.472425	2.266032	3.741345

***cis*-$WCl_4(OH_2)_2$**

W	-0.000001	-0.000001	-0.001469
Cl	0.170387	-1.702900	1.546492
Cl	2.220150	0.241963	-0.681629
Cl	-0.168035	1.704247	1.545264
Cl	-2.221184	-0.242556	-0.678039
O	-0.213938	1.693690	-1.561886
H	-1.137589	1.981657	-1.551604
H	0.318798	2.456174	-1.300454
O	0.211562	-1.695051	-1.560732
H	1.135228	-1.983010	-1.551605
H	-0.320775	-2.457307	-1.297825

***trans*-$WCl_4(OH_2)_2$**

W	0.000000	0.000000	-0.000000

Table S18. *(continued)*

Cl	1.669063	1.643038	0.086306
Cl	1.607871	-1.673618	0.350330
O	0.447792	-0.005151	-2.145618
H	0.584053	-0.902886	-2.476384
H	1.284201	0.472500	-2.257257
Cl	-1.616445	-1.665598	-0.349091
Cl	-1.660603	1.651523	-0.087529
O	-0.447808	-0.001258	2.145620
H	-0.588677	-0.898036	2.477052
H	-1.281753	0.480765	2.256903

***cis*-$MoCl_4(OMeH)_2$**

Mo	-0.070356	-0.039546	0.104333
Cl	-0.475217	1.557147	1.695598
Cl	-2.219360	-0.398861	-0.724718
Cl	0.117575	-1.760075	1.605069
Cl	2.171164	0.370503	-0.388582
O	0.258165	-1.612009	-1.544486
C	1.196943	-2.690949	-1.451080
H	2.161964	-2.245426	-1.231834
H	0.926470	-3.377031	-0.648975
H	1.243711	-3.215376	-2.404457
H	-0.627687	-1.958001	-1.723477
O	-0.176761	1.658070	-1.444964
C	-1.121444	2.734708	-1.390956
H	-1.054153	3.323355	-2.304803
H	-2.105310	2.281975	-1.319991
H	-0.950048	3.362416	-0.516999
H	0.724347	2.009099	-1.479975

***trans*-$MoCl_4(OMeH)_2$**

Mo	-0.015286	-0.016395	0.517325
Cl	0.184664	1.534556	2.238299
Cl	0.632808	1.648081	-1.051575
O	-2.141491	0.431499	0.338996
H	-2.437750	-0.105586	-0.412500
C	-2.626772	1.781801	0.204098
H	-2.253480	2.236373	-0.712536
H	-3.714680	1.767618	0.217535
H	-2.250321	2.328986	1.062069
Cl	-0.456061	-1.452056	-1.323433
Cl	-0.407584	-1.774783	1.986708
O	2.120067	-0.454615	0.533329
H	2.495617	0.170550	-0.106376
C	2.629797	-1.780008	0.287858
H	3.709734	-1.771642	0.420406
H	2.168732	-2.426913	1.026809
H	2.362007	-2.117466	-0.712455

***cis*-$MoCl_4(OMe_2)_2$**

Mo	0.203466	0.365025	-0.405228
Cl	1.914057	1.800644	0.081403
Cl	1.089069	-0.765825	-2.232654
Cl	-1.024360	1.937098	-1.526862
Cl	-0.942265	0.481484	1.610843
O	-1.504960	-1.193147	-0.900464
Cl	-1.736283	1.276872	-0.950492
Cl	1.519116	1.770520	-0.358538
O	-0.564484	0.545988	2.055443
H	0.040592	0.052745	2.634187
H	-1.456249	0.229295	2.258144
Cl	1.688425	-1.224333	1.105094
Cl	-1.476664	-1.823980	0.202677
O	0.577212	-0.543821	-2.052481
H	-0.190069	-0.509634	-2.641326
H	1.183006	0.155611	-2.349395

***cis*-$WCl_4(OMeH)_2$**

W	-0.057229	-0.042046	0.032738
Cl	-0.558850	1.532830	1.642812
Cl	-2.192675	-0.560587	-0.784447
Cl	0.257357	-1.754857	1.547006
Cl	2.157587	0.534119	-0.475152
O	0.366976	-1.593675	-1.608842
C	1.383575	-2.603353	-1.520133
H	2.314437	-2.088231	-1.305880
H	1.165972	-3.306136	-0.716764
H	1.462457	-3.121076	-2.474655
H	-0.491920	-2.000725	-1.792795
O	-0.290987	1.649869	-1.506315
C	-1.323427	2.646202	-1.459863
H	-1.275933	3.257290	-2.359662
H	-2.268020	2.112710	-1.429892
H	-1.228321	3.264636	-0.568141
H	0.579003	2.073030	-1.541613

***trans*-$WCl_4(OMeH)_2$**

W	0.000142	0.013184	0.000098
Cl	-1.033360	-1.591384	1.352704
Cl	-0.801939	1.738352	1.437256
O	-1.745501	0.077742	-1.315317
H	-1.545432	0.758317	-1.977080
C	-3.080718	0.263625	-0.800218
H	-3.175644	1.236365	-0.319790
H	-3.790226	0.160541	-1.618279
H	-3.236769	-0.522383	-0.068702
Cl	0.803115	1.712232	-1.467314
Cl	1.032462	-1.615834	-1.323804
O	1.745649	0.100484	1.314342
H	1.546326	0.793960	1.962825
C	3.081353	0.274271	0.796331
H	3.790235	0.187869	1.616860
H	3.237216	-0.527145	0.081698
H	3.177473	1.236575	0.295546

***cis*-$WCl_4(OMe_2)_2$**

W	0.000075	0.013727	0.000533
Cl	-1.712249	-1.435269	0.506919
Cl	0.093202	-0.216326	-2.326943
Cl	1.663995	-1.490866	0.546495
Cl	0.071466	1.195714	2.018344
O	1.684666	1.532207	-0.568059

Table S18. *(continued)*

C	-2.218515	-1.945595	0.070491	C	1.767151	2.860161	-0.066375
H	-1.533686	-2.188034	0.876645	H	0.755755	3.217262	0.099782
H	-3.059143	-1.376365	0.473348	H	2.318633	2.890944	0.875485
H	-2.582128	-2.867974	-0.386736	H	2.259548	3.492684	-0.807047
C	-2.261112	-1.023081	-2.098948	C	2.948500	1.052741	-1.032940
H	-1.611406	-0.560302	-2.834100	H	2.775678	0.102956	-1.527549
H	-2.588957	-2.000384	-2.458063	H	3.363357	1.771327	-1.741544
H	-3.127421	-0.383343	-1.917857	H	3.634375	0.913349	-0.195209
O	1.517069	-1.279423	0.728149	O	-1.734388	1.532920	-0.583322
C	2.922247	-1.263678	0.452098	C	-2.814594	1.000547	-1.363429
H	3.430114	-0.561192	1.115587	H	-3.560163	0.543425	-0.710694
H	3.323826	-2.268181	0.597170	H	-3.267129	1.810721	-1.937305
H	3.056831	-0.956376	-0.578464	H	-2.404986	0.254153	-2.033938
C	1.294685	-1.682881	2.077359	C	-2.233517	2.528666	0.311175
H	1.848120	-2.604078	2.268830	H	-2.836218	3.241213	-0.254232
H	1.620977	-0.906184	2.773058	H	-2.840863	2.071331	1.095584
H	0.233492	-1.856799	2.214393	H	-1.390822	3.035473	0.766984

***trans*-$MoCl_4(OMe_2)_2$**

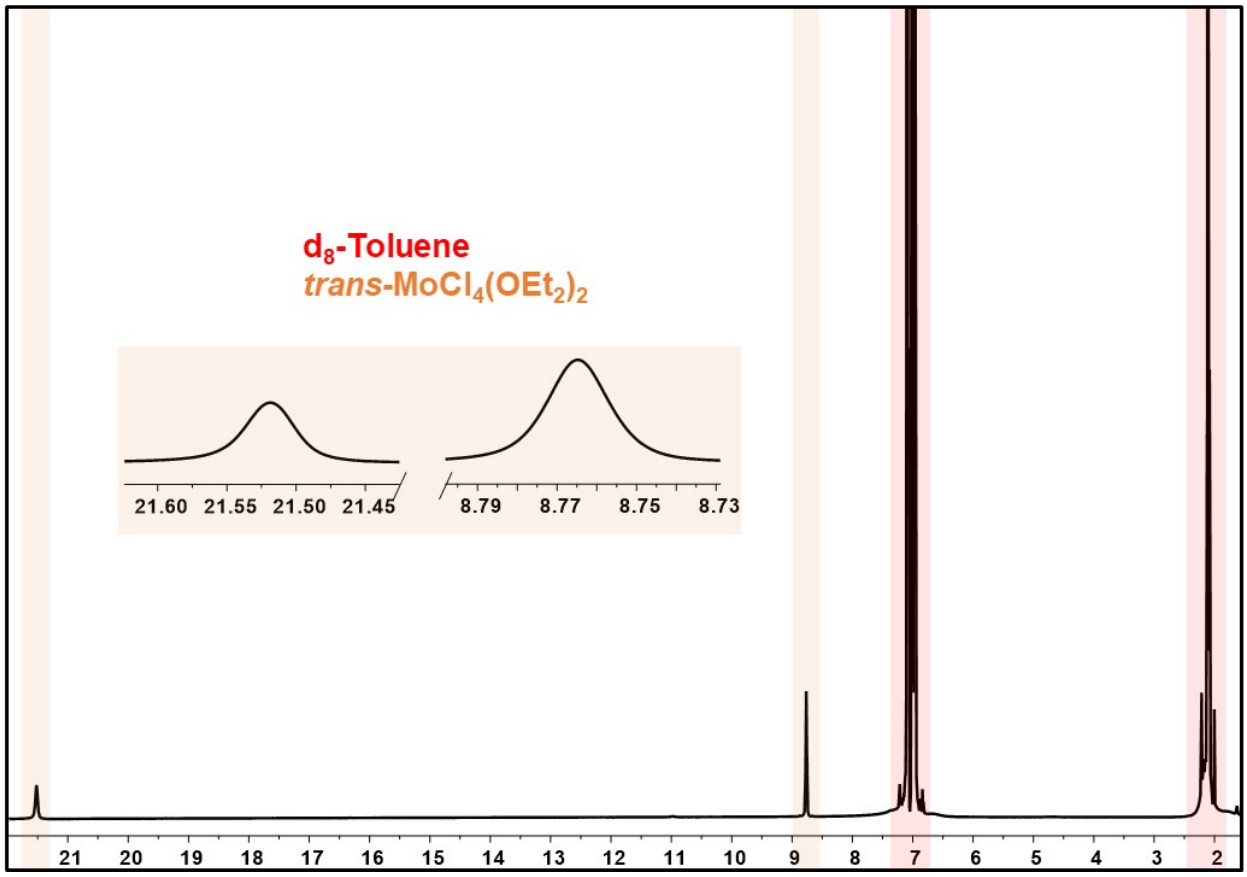
Mo	0.006581	-0.000034	0.015009
Cl	-0.162818	-1.664271	1.671734
Cl	-0.162639	1.665305	1.670679
O	2.164880	-0.000274	0.323133
C	2.922999	1.193683	0.090419
H	2.310969	2.030629	0.410899
H	3.836329	1.144300	0.683755
H	3.161837	1.289676	-0.969658
C	2.922996	-1.194036	0.089466
H	2.310914	-2.031200	0.409300
H	3.161728	-1.289191	-0.970714
H	3.836377	-1.145092	0.682758
Cl	0.175873	1.663993	-1.641958
Cl	0.175973	-1.665204	-1.640878
O	-2.151675	0.000159	-0.293062
C	-2.909773	-1.193768	-0.059800
H	-3.148140	-1.289533	1.000398
H	-3.823326	-1.144415	-0.652780
H	-2.297873	-2.030773	-0.380372
C	-2.909824	1.193994	-0.059613
H	-3.148340	1.289465	1.000580
H	-2.297832	2.031065	-0.379850
H	-3.823293	1.144763	-0.652738

***trans*-$WCl_4(OMe_2)_2$**

W	0.000384	0.000070	-0.000721
Cl	1.633640	0.352714	-1.673247
Cl	1.633395	0.352791	1.672028
O	-0.368034	2.162214	-0.000799
C	-0.828154	2.811235	1.193137
H	-0.336530	2.327657	2.031237
H	-0.546218	3.863065	1.144982
H	-1.910328	2.709734	1.285559
C	-0.828281	2.811136	-1.194739
H	-0.336747	2.327487	-2.032850
H	-1.910466	2.709626	-1.287035
H	-0.546340	3.862969	-1.146703
Cl	-1.632842	-0.353397	1.671977
Cl	-1.632598	-0.353466	-1.673642
O	0.367672	-2.162168	-0.000634
C	0.827900	-2.811096	-1.194582
H	1.910055	-2.709343	-1.287084
H	0.546278	-3.862985	-1.146426
H	0.336115	-2.327677	-2.032683
C	0.828059	-2.810983	1.193314
H	1.910223	-2.709198	1.285673
H	0.336365	-2.327504	2.031433
H	0.546453	-3.862882	1.145284

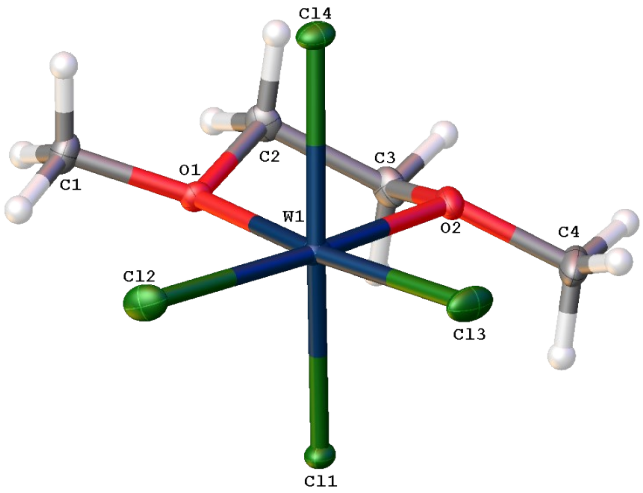
Nuclear Magnetic Resonance

Figure S1. ^{1}H NMR Spectrum of *trans*-$MoCl_4(Et_2O)_2$ in d_8-toluene.



X-ray Diffraction

Figure S2. Thermal ellipsoid plot (30%) and labelling scheme of **4**.



Magnetic Susceptibility

Figure S3. Gouy Susceptibility Calculations

$MoCl_4(dme)$

First, the mass susceptibility was determined with the following equation:

$$\chi_g = \frac{(R - R_0)\ x\ C\ x\ L}{m\ x\ 10^9}$$

Where R is the reading of the sample and the tube, R_0 is the reading of the empty tube, C is the calibration standard of the balance, L is the length of the sample in the tube, and m is the mass of the sample in the tube.

$$\chi_g = \frac{(346 - (-36))\ x\ 1\ x\ 1.9\ cm}{0.122\ g\ x\ 10^9} = 5.95\ x\ 10^{-6}\ \frac{erg}{G^2\ x\ g}$$

From there, the molar susceptibility is determined by multiplying the mass susceptibility by the molar mass of the complex.

$$\left(5.95\ x\ 10^{-6}\ \frac{erg}{G^2\ x\ g}\right) x\ 327.88\ \frac{g}{mol} = 1.95\ x\ 10^{-3}\ \frac{erg}{G^2\ x\ mol}$$

The diamagnetic correction values and Pascal's constants for covalent species are then applied[4].

$$\chi_A = 1.95\ x\ 10^{-3}\ \frac{erg}{G^2\ x\ mol} + 1.731\ x\ 10^{-4}\ \frac{erg}{G^2\ x\ mol} = 2.12\ x\ 10^{-3}\ \frac{erg}{G^2\ x\ mol}$$

Finally, μ_{eff} is determined.

$$\mu_{eff} = 2.828(\chi_A T)^{\frac{1}{2}} = 2.828((2.12\ x\ 10^{-3}\ \frac{erg}{G^2\ x\ mol})(298.15K)^{\frac{1}{2}} = 2.25\ B.M.$$

$WCl_4(dme)$

First, the mass susceptibility was determined with the following equation:

$$\chi_g = \frac{(R - R_0)\ x\ C\ x\ L}{m\ x\ 10^9}$$

Where R is the reading of the sample and the tube, R_0 is the reading of the empty tube, C is the calibration standard of the balance, L is the length of the sample in the tube, and m is the mass of the sample in the tube.

$$\chi_g = \frac{(135 - (-36))\ x\ 1\ x\ 2.03\ cm}{0.181\ g\ x\ 10^9} = 1.92\ x\ 10^{-6}\ \frac{erg}{G^2\ x\ g}$$

From there, the molar susceptibility is determined by multiplying the mass susceptibility by the molar mass of the complex.

$$\left(1.92\ x\ 10^{-6}\ \frac{erg}{G^2\ x\ g}\right) x\ 415.78\ \frac{g}{mol} = 7.97\ x\ 10^{-4}\ \frac{erg}{G^2\ x\ mol}$$

The diamagnetic correction values and Pascal's constants for covalent species are then applied[4].

$$\chi_A = 7.97\ x\ 10^{-4}\ \frac{erg}{G^2\ x\ mol} + 1.791\ x\ 10^{-4}\ \frac{erg}{G^2\ x\ mol} = 9.77\ x\ 10^{-4}\ \frac{erg}{G^2\ x\ mol}$$

Finally, μ_{eff} is determined.

$$\mu_{eff} = 2.828(\chi_A T)^{\frac{1}{2}} = 2.828((9.77\ x\ 10^{-4}\ \frac{erg}{G^2\ x\ mol})(298.15K)^{\frac{1}{2}} = 1.53\ B.M.$$

Figure S3. SQUID Data Calculations

$MoCl_4(dme)$

Using the Curie Weiss calculations, the linear fit can be used to calculate the molar susceptibility at any given temperature. Slope = 1.8317, intercept = 146.885

$y = (1.8317)x + 146.885$

In this equation, y is the inverse molar susceptibility and x is the temperature. We are extracting the molar susceptibility at 298 K to compare to the benchtop Gouy measurements.

$$\frac{1}{\chi_{mol}} = (1.8317)(298) + 146.885$$

$$\chi_{mol} = 1.44\ x\ 10^{-3}$$

The diamagnetic correction values and Pascal's constants for covalent species are then applied[4].

$$\chi_A = 1.44\ x\ 10^{-3}\ \frac{erg}{G^2\ x\ mol} + 1.731\ x\ 10^{-4}\ \frac{erg}{G^2\ x\ mol} = 1.62\ x\ 10^{-3}\ \frac{erg}{G^2\ x\ mol}$$

Finally, μ_{eff} is determined.

$$\mu_{eff,\,298K} = 2.828(\chi_A T)^{\frac{1}{2}} = 2.828((1.62\ x\ 10^{-3}\ \frac{erg}{G^2\ x\ mol})(298K)^{\frac{1}{2}} = 1.97\ B.M.$$

$WCl_4(dme)$

Using the Curie Weiss calculations, the linear fit can be used to calculate the molar susceptibility at any given temperature. Slope = 4.9084, intercept = 402.3757

$y = (4.9084)x + 402.3757$

In this equation, y is the inverse molar susceptibility and x is the temperature. We are extracting the molar susceptibility at 298 K to compare to the benchtop Gouy measurements.

$$\frac{1}{\chi_{mol}} = (4.9084)(298) + 402.3757$$

$$\chi_{mol} = 5.36\ x\ 10^{-4}$$

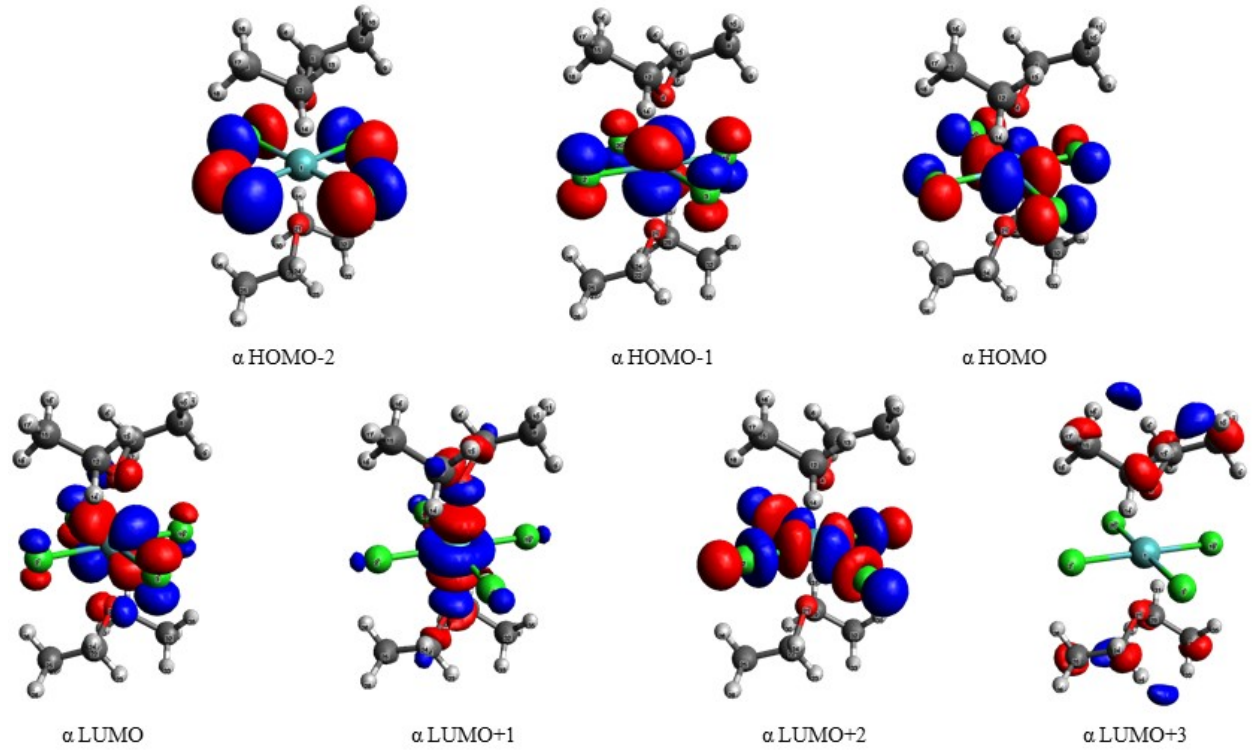
The diamagnetic correction values and Pascal's constants for covalent species are then applied[4].

$$\chi_A = 5.36\ x\ 10^{-4}\ \frac{erg}{G^2\ x\ mol} + 1.791\ x\ 10^{-4}\ \frac{erg}{G^2\ x\ mol} = 7.15\ x\ 10^{-4}\ \frac{erg}{G^2\ x\ mol}$$

Finally, μ_{eff} is determined.

$$\mu_{eff,\,298K} = 2.828(\chi_A T)^{\frac{1}{2}} = 2.828(\left(7.15\ x\ 10^{-4}\ \frac{erg}{G^2\ x\ mol}\right)(298K))^{\frac{1}{2}} = 1.31\ B.M.$$

Figure S4. Calculated frontier α molecular orbitals for triplet *trans*-$MoCl_4(OEt_2)_2$ (C_{2h} symmetry, UBLYP+GD3/def2-TZVP, isovalue = 0.04)



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