Electronic Supplementary Information for Dalton Transactions

Amidinate-Carboxylate Complexes of Dimolybdenum and Ditungsten: $M_2(O_2CR)_2((N^iPr)_2CR')_2$. Preparations, Molecular and Electronic Structures and Reactions.

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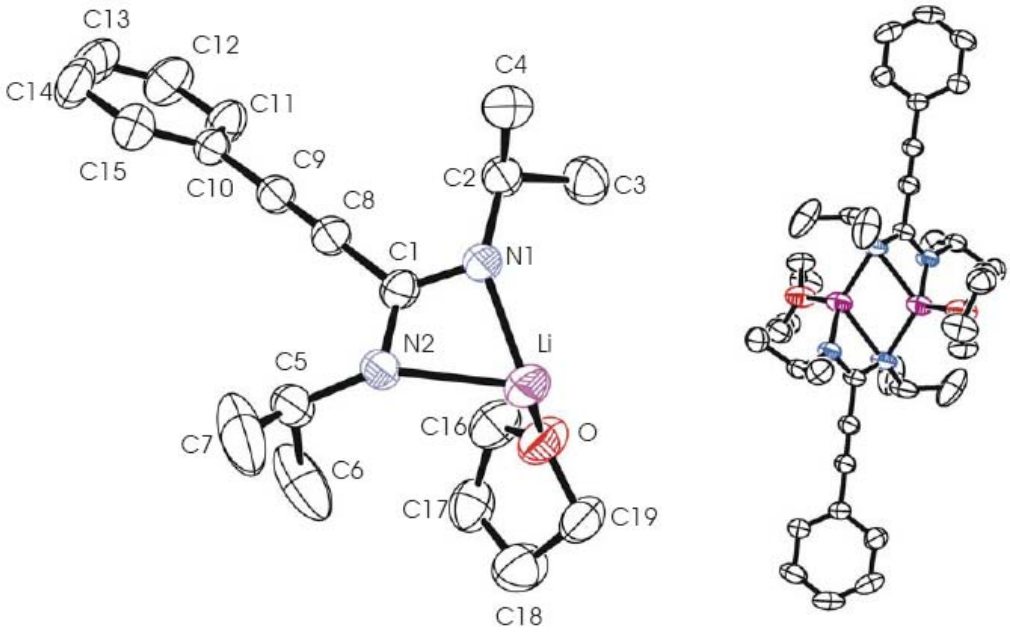

Figure S1. ORTEP diagram of asymmetric unit (left) and centrosymmetric dimer (right) of Li[(N^{i}Pr)$_2$CC≡CPh] with coordinating THF drawn with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

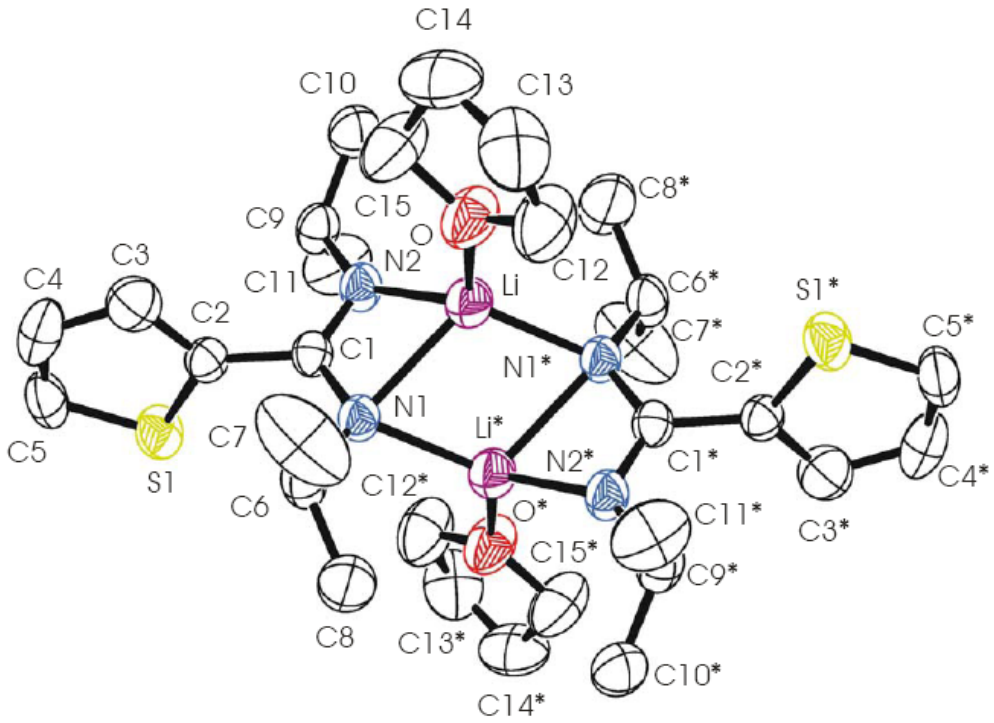

Figure S2. ORTEP diagram of centrosymmetric dimer of Li[(N^{i}Pr)$_2$C-2-C$_4$H$_4$S] with coordinating THF drawn with 50% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity. The starred atoms (*) are related to the unstarred atom by the crystallographic inversion center.

TABLE 1: CRYSTALLOGRAPHIC DETAILS

	Li[(N^{i}Pr)$_2$CC≡CPh]	Li[(N^{i}Pr)$_2$CC$_4$H$_4$S)]	Mo$_2$(O$_2$CCH$_3$)$_2$((N^{i}Pr)$_2$CMe)$_2$	Mo$_2$(O$_2$CCH$_3$)$_2$((N^{i}Pr)$_2$CC≡CPh)$_2$
Molecular formula	C38 H54 Li2 N4 O2	C15 H25 Li N2 O S	C20 H40 Mo2 N4 O4	C34 H44 Mo2 N4 O4 and 3 THFs
Formula weight	612.73	288.37	592.44	980.92
Temperature	200(2) K	200(2) K	150(2) K	200(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P$\bar{1}$	P2$_1$/c	P$\bar{1}$	P$\bar{1}$
Unit cell dimensions	a = 9.724(1) Å α = 93.575(5) ° b = 10.008(1) Å β = 91.225(5) ° c = 19.713(2) Å γ = 90.848(4) °	a = 9.173(1) Å b = 10.970(1) Å β = 95.953(7) ° c = 17.190(2) Å	a = 8.3023(10) Å α = 68.840(4) ° b = 9.0596(10) Å β = 77.080(4) ° c = 9.5252(10) Å γ = 65.805(5) °	a = 9.311(1) Å α = 66.083(3) ° b = 11.735(1) Å β = 74.895(3) ° c = 12.973(1) Å γ = 68.780(5) °
Volume	1914.0(3) Å^3	1720.5(3) Å^3	607.03(12) Å^3	1197.1(2) Å^3

Z	2	4	1	1
Density (calculated)	1.063 Mg/m^3	1.113 Mg/m^3	1.621 Mg/m^3	1.361 Mg/m^3
Absorption coefficient	0.065 mm^{-1}	0.185 mm^{-1}	1.065 mm^{-1}	0.574 mm^{-1}
F(000)	664	624	304	512
Crystal size	0.27 x 0.35 x 0.38 mm^3	0.15 x 0.23 x 0.31 mm^3	0.19 x 0.31 x 0.38 mm^3	0.15 x 0.31 x 0.38 mm^3
Theta range for data collection	2.04 to 25.05 °	2.21 to 25.04 °	2.99 to 27.46 °	2.74 to 27.44 °
Index ranges	-11≤h≤11, -11≤k≤11, -23≤l≤23	-10≤h≤10, -13≤k≤13, -20≤l≤20	-10≤h≤10, -11≤k≤11, -12≤l≤12	-12≤h≤11, -15≤k≤15, -16≤l≤16
Reflections collected	36676	27382	17872	32426
Independent reflections	6769 [R(int) = 0.028]	3031 [R(int) = 0.036]	2771 [R(int) = 0.027]	5452 [R(int) = 0.028]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6769 / 2 / 428	3031 / 9 / 221	2771 / 0 / 136	5452 / 4 / 273
Goodness-of-fit on F^2	1.007	1.040	1.084	1.036
Final R indices [I>2σ(I)]	R1 = 0.0518, wR2 = 0.1348	R1 = 0.0472, wR2 = 0.1249	R1 = 0.0169, wR2 = 0.0432	R1 = 0.0300, wR2 = 0.0797
R indices (all data)	R1 = 0.0676, wR2 = 0.1471	R1 = 0.0659, wR2 = 0.1361	R1 = 0.0180, wR2 = 0.0436	R1 = 0.0336, wR2 = 0.0818
Largest diff. peak and hole	0.184 and -0.248 $e/Å^3$	0.189 and -0.185 $e/Å^3$	0.345 and -0.436 $e/Å^3$	0.774 and -0.742 $e/Å^3$

TABLE 2: CRYSTALLOGRAPHIC DETAILS

	$W_2(O_2CCH_3)_2((N^iPr)_2CC{\equiv}CPh)_2$	$Mo_2(O_2CCH_3)_2((N^iPr)_2CC{\equiv}CFc)_2$	$W_2(O_2CCH_3)_2((N^iPr)_2CC{\equiv}CFc)_2$	Mo_2(*cis*-μ-O_2C-9-anthracene)$_2$(η^2-$(N^iPr)_2CMe)_2$
Molecular formula	C34 H44 N4 O4 W2	C42 H52 Fe2 Mo2 N4 O4 and 4 THFs	C42 H52 Fe2 N4 O4 W2 and 4 THFs	C46 H52 Mo2 N4 O4 and THF
Formula weight	940.43	1268.87	1444.69	988.90
Temperature	150(2) K	200(2) K	150(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_{1/}n$
Unit cell dimensions	a = 8.279(1) Å	a = 11.135(1) Å	a = 11.051(1) Å α =	a = 21.482(2) Å

	α = 75.741(6) ° b = 9.371(1) Å β = 71.498(6) ° c = 12.082(1) Å γ = 78.558(5) °	α= 67.157(1) ° b = 11.862(1) Å β= 78.161(1) ° c = 12.321(1) Å γ= 85.503(1) °	67.331(4) ° b = 11.816(1) Å β = 77.860(4) ° c = 12.251(1) Å γ= 85.531(4) °	b = 9.609(1) Å β= 97.633(4) ° c = 22.527(3) Å
Volume	854.1(2) $Å^3$	1468.0(2) $Å^3$	1443.1(2) $Å^3$	4608.65(9) $Å^3$
Z	1	1	1	4
Density (calculated)	1.828 Mg/m^3	1.435 Mg/m^3	1.662 Mg/m^3	1.425 Mg/m^3
Absorption coefficient	6.770 mm^{-1}	0.956 mm^{-1}	4.521 mm^{-1}	0.595 mm^{-1}
F(000)	456	660	724	2048
Crystal size	0.12 x 0.19 x 0.27 mm^3	0.12 x 0.27 x 0.27 mm^3	0.15 x 0.38 x 0.38 mm^3	0.08 x 0.15 x 0.23 mm^3
Theta range for data collection	2.62 to 27.51°	2.35 to 27.51°	2.55 to 27.48 °	2.33 to 27.47 °
Index ranges	-10≤h≤10, -12≤k≤12, -15≤l≤15	-14≤h≤14, -15≤k≤15, -15≤l≤16	-14≤h≤14, -15≤k≤15, -15≤l≤15	-27≤h≤27, -12≤k≤12, -29≤l≤29
Reflections collected	26489	40640	40553	82643
Independent reflections	3913 [R(int) = 0.042]	6736 [R(int) = 0.033]	6607 [R(int) = 0.051]	10574 [R(int) = 0.083]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3913 / 0 / 199	6736 / 16 / 314	6607 / 4 / 284	10574 / 0 / 560
Goodness-of-fit on F^2	1.065	1.042	1.039	1.035
Final R indices [I>2σ(I)]	R1 = 0.0169, wR2 = 0.0398	R1 = 0.0422, wR2 = 0.1174	R1 = 0.0331, wR2 = 0.0841	R1 = 0.0528, wR2 = 0.1141
R indices (all data)	R1 = 0.0190, wR2 = 0.0404	R1 = 0.0540, wR2 = 0.1248	R1 = 0.0413, wR2 = 0.0876	R1 = 0.0968, wR2 = 0.1287
Largest diff. peak and hole	1.152 and -1.393 $e/Å^3$	1.232 and -0.738 $e/Å^3$	2.022 and -1.251 $e/Å^3$	2.085 and -0.598 $e/Å^3$

Attempted preparation of $[\text{-}Mo_2((N^iPr)_2CC{\equiv}CC_6H_4)_2(O_2CPhCO_2)\text{-}]_n$. 230 mg of **3A** and 50 mg of terephthalic acid were mixed at room temperature in approximately 25 mL of ethanol. The solution was red in color and showed suspended white terephthalic acid. After 20 days, the solution remained red

but no terephthalic acid was visible. The mixture was centrifuged; the solvent was cannulared off, and the remaining solid was dried under vacuum. Analysis by MALDI-MS indicated low molecular weight oligimers with one, two, or three M_2 repeating units.
Microanalysis found: C 50.94; H 4.88; N 6.55%. $C_{38}H_{42}N_4O_4Mo_2$ requires: C 56.30; H 5.22; N 6.91%.

Solvent 1: 230 mg of *trans*-$Mo_2(O_2CCH_3)_2((N^iPr)_2CC{\equiv}CPh)_2$ (0.3 mmol) and 50 mg of terephthalic acid (0.3 mmol) were mixed at room temperature in approximately 25 mL of THF. The solution was red in color with a white suspension of terephthalic acid. After 20 days, the solution remained red but no terephthalic acid was visible. The mixture was centrifuged; the solvent was cannulared off, and the remaining solid was dried under vacuum. ^{1}H NMR spectrum indicated a mixture of products with overlapping resonances. Analysis by MALDI-TOF indicated low molecular weight oligomers with mono-, di-, tri- or tetra-Mo_2 units.

Solvent 2: This reaction was carried out under similar conditions outlined for the initial reaction using 230 mg of *trans*-$Mo_2(O_2CCH_3)_2((N^iPr)_2CC{\equiv}CPh)_2$ (0.3 mmol) and 50 mg of terephthalic acid (0.3 mmol) in approximately 25 mL of ethanol. A red solid was isolated by centrifugation. ^{1}H NMR spectrum indicated a mixture of products with overlapping resonances. Analysis by MALDI-TOF indicated low molecular weight oligomers with mono-, di, and tri-Mo_2 units. No elemental analysis was conducted.

Solvent 3: This reaction was carried out under similar conditions outlined for the initial reaction using 230 mg of *trans*-$Mo_2(O_2CCH_3)_2((N^iPr)_2CC{\equiv}CPh)_2$ (0.3 mmol) and 50 mg of terephthalic acid in approximately 25 mL of hexanes. A red solid was isolated by centrifugation. ^{1}H NMR spectrum indicated a mixture of products with overlapping resonances. Analysis by MALDI-TOF indicated low molecular weight oligomers with mono- and di-Mo_2 units.

Microanalysis found: C 55.25; H 5.51; N 6.59%. $C_{72}H_{86}N_8O_8Mo_4$ (simple pairs of dimers) requires: C 54.90; H 5.50; N 7.11%.

Attempted preparation of [*trans*-$Mo_2((N^iPr)_2CC{\equiv}CPh)_2]^{2+}$.

Method A: To a solution of 380 mg of *trans*-$Mo_2(O_2CCH_3)_2((N^iPr)_2CC{\equiv}CPh)_2$ (0.5 mmol) in 10 mL of CH_2Cl_2 and 2.5 mL of MeCN was added 330 mg of Me_3OBF_4 (2.25 mmol). Within 1h all of the solid material had dissolved and the solution was bright red. After stirring overnight, the reaction mixture was concentrated and cooled to -20 ºC. After several days, red crystals formed. The product was isolated by removal of the mother liquor under a dynamic vacuum; the residue was washed with diethyl ether, and dried under vacuum. ^{1}H NMR characterized the product as a $[Mo_2(O_2CCH_3)((N^iPr)_2CC{\equiv}CPh)(CH_3CN)_4](BF_4^-)_2$ species. Full characterization of this product was deferred since it was not the target complex.

Method B: 0.16 mL of N,N′-di-*iso*-propylcarbodiimide (1.0 mmol) was dissolved in approximately 25 mL of THF and cooled to 0 ºC. 5 mL of 1.0 M lithium phenylacetylide (1.0 mmol) in THF was added to the mixture. The solution was allowed to warm slowly to room temperature. After stirring overnight, it was used *in situ* for the next reaction. A solution of 0.475 g of $[Mo_2(CH_3CN)_{10}]^{4+}(BF_4^-)_4$, (0.5 mmol) in approximately 25 mL of CH_3CN was made and cooled to 0 ºC. The in situ solution was cooled again to 0 ºC. The *in-situ* solution was slowly added to the solution. The initial color change was gray-black. After stirring at room temperature overnight, the solvent was evaporated under a dynamic vacuum and the residue extracted with approximately 25 mL of hexanes. The solution was filtered over Celite. The filtrate was near colorless with no apparent soluble product.