Supporting Information
for

Remarkable Regioselectivity in the Preparation of the First Heterotrimetallic Mo≡W···Cr Chain

Michael Nippe, George H. Timmer, and John F. Berry*

Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wisconsin 53706, USA

Experimental.

General. All reactions were carried out under a dry N_2 atmosphere using Schlenck techniques and glovebox methods. Solvents tetrahydrofuran (THF) and hexanes were purified using a Vacuum Atmospheres solvent purification system. Dichloromethane was freshly distilled under an N_2 atmosphere over CaH_2 prior to use. Naphthalene, 1,2-dichlorobenzene (anhydrous), and benzene (anhydrous) were purchased from Sigma-Aldrich. MeLi solution in diethyl ether (Sigma Aldrich), CD_2Cl_2 (Sigma-Aldrich) , pivalic acid (Sigma Aldrich), $Mo(CO)_6$ (STREM), $W(CO)_6$ (STREM), anhydrous $CrCl_2$ (STREM), and I_2 (Sigma-Aldrich) were purchased. The ligand dpaH (2,2′-dipyridylamine, Sigma-Aldrich) was recrystallized from hot hexanes prior to use. $MoW(piv)_4$ was prepared using a modified literature procedure.[1]

Modified Preparation of $MoW(piv)_4$.

$Mo(CO)_6$ (2.50 g, 9.47 mmol), $W(CO)_6$ (10.00 g, 28.42 mmol) and pivalic acid (7.74 g, 75. 8 mmol) were suspended in 1,2-dichlorobenzene (100 mL) and placed in a preheated sandbath (T ~ 190 °C) and stirred under heavy reflux for about 5 hours, during which time the solution turned black. The reaction mixture was cooled down to room temperature and kept at -20°C for 10 hours. The bright yellow crystalline precipitate was collected by filtration and washed with 1,2-dichlorobenzene (30mL). The ratio of $Mo_2(piv)_4$ to $MoW(piv)_4$ in this initial precipitate was similiar to the reported one,[1] as determined by MALDI-TOF MS. The mixture (2.28 g) was dissolved in benzene (100 mL) and solid I_2 (0.22 g, 0.87 mmol) was added to the stirred solution which resulted in precipation of a fine greyish powder. This solid was collected by filtration, washed with benzene (100 mL) and combined with Zn powder (5.00 g, 76.5 mmol) in benzene (100 mL) and stirred for 24 h at room temperature. The now yellow solution was filtered and the pure product $MoW(piv)_4$ was obtained after removal of the solvent under vacuum. Yield: 0.67 g (56 % based on added I_2), MALDI-Mass spectrum (100% peak): m/z = 684 $[M]^+$.

Preparation of $MoW(dpa)_4$ (2).

The ligand dpaH (602 mg, 3.52 mmol) was dissolved in THF (40 mL) and cooled down to -78 °C. Upon addition of one equivalent of MeLi (1.6 M solution in diethyl ether) a white suspension resulted which was allowed to warm to room temperature. The white suspension was added via cannula to solid bright yellow $MoW(piv)_4$ (520 mg, 0.762 mmol) resulting in the immediate formation of a dark purple solution and a fine dark precipitate. The mixture was stirred at room temperature for 40 min and subsequently heated to reflux for at least 3 h. After removal of half of the solvent under reduced pressure, the solid was collected by filtration and washed with hexanes (30 mL). Yield: 420 mg (57 %). Anal. Calcd for $C_{40}H_{32}MoWN_{12}$ (**2**): C, 50.02 %; H, 3.36 %; N, 17.50 %. Found: C, 49.91 %; H, 3.75 %; N, 16.46 %. MALDI-Mass spectrum (100% peak): m/z = 962 $[M]^+$. IR (KBr, cm^{-1}): 1597 m, 1578 s, 1559 w, 1477 s, 1456 s, 1428 s, 1374 m, 1362 m, 1301 w, 1280 w, 1264 w, 1246 m, 1149 m, 1016 m, 987 w, 909 w, 769 m, 755 m, 731 m.

Compound **2** was crystallized by heating ~50 mg of **2** in naphthalene (4 g) to 200 °C for 15 min in a 50 mL Schlenck tube. The dark purple solution was kept at 130°C for 10 h after which small needle shaped crystals, suitable for X-ray crystallography, had formed.

Preparation of CrWMo(dpa)$_4$Cl$_2$ (1).

Solid dark purple MoW(dpa)$_4$ (100 mg, 0.104 mmol) and grey anhydrous CrCl$_2$ (40 mg, 0.33 mmol) were combined in napthalene (4 g) in a Schlenck flask equipped with a reflux condenser. The flask was set under stirring into a preheated 180 °C sand bath and stirred for 60 min, after which the reaction temperature was increased to ~220°C for 10 min. The mixture remained purple and was allowed to cool to room temperature. Hexanes (90 mL) were added and the mixture was again heated to reflux. The hot hexanes were then filtered off, and the last 3 steps were repeated. The solid residue was extracted with CH$_2$Cl$_2$ (30 mL). The resulting pinkish-purple solution was layered with hexanes and crystals of **1·2CH$_2$Cl$_2$** were obtained after 1 day. Yield: 49 mg, (37 %). Anal. Calcd for $C_{41}H_{34}Cl_4CrWMoN_{12}$: C, 42.15 %; H, 2.93 %; N, 14.39 %. Found: C, 42.21 %; H, 2.61 %; N, 14.37 %. MALDI-Mass spectrum (100% peak): m/z = 1084 $[M]^+$, 1049 $[M\text{-}Cl]^+$. IR (KBr, cm^{-1}): 1602 s, 1589 m, 1559 w, 1541 w, 1473 s, 1463 vs, 1416 vs, 1343 s, 1312 s, 1282 m, 1257 m, 1236 w, 1166 w, 1153 m, 1110 w, 1055 w, 1045 w, 1015 m, 964 w, 908 w, 762 s, 748 m, 739 m, 688 w, 642 w.

Physical Measurements. Cyclic voltammograms (CVs) were taken on a BAS Epsilon-EC instrument using CH$_2$Cl$_2$ solutions with 0.1 M NBu$_4$PF$_6$ and <1 mM substrate. The electrodes were as follows: Glassy carbon (working), Pt wire (auxiliary) and Ag/AgCl in CH$_3$CN (reference). The potentials were referenced versus the ferrocene/ferrocenium redox couple, by externally added ferrocene. Elemental analysis was carried out by Columbia Analytical Services (formerly Desert Analytics) in Arizona, USA. Mass spectrometry data were recorded at the Mass Spectrometry Facility of the Chemistry Instrument Center of the University of

Wisconsin-Madison. Matrix-assisted laser desorption/ionization (MALDI) mass spectra were obtained using a Bruker REFLEX II™ (Billerica, MA) equipped with a 337 nm laser, a reflectron, delayed extraction, and a time-of-flight (TOF) analyzer. In the positive ion mode, the acceleration voltage was 25 kV. The IR spectra were taken on a BRUKER TENSOR 27 using KBr techniques. The UV-Vis spectra were recorded under an atmosphere of Argon on a VARIAN CARY 50 Scan UV-Visible Spectrophotometer using quartz cells (path length 0.5 cm). The room temperature magnetic susceptibility of **1** in CD_2Cl_2 was determined using the Evans method[2] on a Bruker AC+ 300 NMR spectrometer. Experimental susceptibility data were corrected for the underlying diamagnetism using Pascal's constants.[3]

Computational Methods.

All calculations were performed with the ORCA program.[4] Initial geometry optimizations and frequency calculations were performed at the BP86 level[5, 6] of density functional theory, including all electron scalar relativistic effects within the ZORA approximation.[7] All electron Gaussian basis sets from the Ahlrichs group were used and recontracted for use with ZORA.[8, 9] The triple-ξ quality for the valence electron basis set, TZV, was applied to the transition metals. The double-ξ quality for the valence electron basis set, SV, was applied to the ligands. The Ahlrichs auxiliary basis sets used to fit the electron density in the resolution of identity (RI) [10-12] approximation were obtained from the TurboMole basis set library under ftp.chemie.uni-karlsruhe.de/pub/jbasen.[13, 14] The integration grid was modified by increasing the number of radial shells for molybdenum and tungsten (75 and 99, respectively) within a grid that used 302 angular points per shell. This was necessary to prevent wild imaginary frequencies.[15] Following the frequency calculations, geometries were further optimized by increasing the basis sets of nitrogen and chlorine to TZV and by including two sets of polarization functions[16] on all metal and nitrogen atoms and one set on all other atoms. The final integration grid increased the number of radial shells on all atoms (except for molybdenum and tungsten which were already augmented) and provided 434 angular points per shell. Single point calculations at the final geometry were carried out at the B3LYP [17, 18] level with the RI approximation applied to the coulomb term. Surface plots were generated using the program Molekel.[19] Several low energy imaginary frequencies ($< 100i$ cm^{-1}) were observed that arise due to limitations inherent in the numerical integration procedures of currently available DFT methods. The genuine energy minimum (with no imaginary frequencies) is likely identical to or very close to the stationary point reported in this work.[19]

X-Ray Crystallography.

MoW(dpa)$_4$ (**2**): A purple needle-shaped crystal of **2** with approximate dimensions 0.04 x 0.02 x 0.02 mm was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam by using a video camera. The crystal evaluation and data collection were performed on a Bruker SMART APEXII diffractometer with Cu Kα (λ = 1.54178 Å) radiation and the diffractometer to crystal distance of 4.03 cm.

The initial cell constants were determined through an auto-indexing routine built in the APEXII program, but were also read into CELLNOW. The crystal was a two-component twin woth domains related to each other by a 180° rotation around b.

A full sphere of data was collected to a resolution of 0.82 Å. Using the TWINABS routine an hkl4 file was created using reflections from both domains. The centrosymmetric space group *C*2/*c* (and not *Cc*) was choosen because of the mean |E*E-1| value of 0.902 and the lower CFOM for *C*2/*c* (1.01) as compared to *Cc* (3.48). The structure was solved using the Patterson method and refined by least squares refinement on F^2 followed by difference Fourier synthesis. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The metal atoms occupy positions on a crystallographic two-fold axis. Disorder of the metal atoms was modeled by initially assuming 50 % occupancy for Mo and W while constraining their coordinates and displacement parameters to be the same. The occupancy was then refined to be 52 %. Using the hkl5 file for all reflections and refining the batch scale factor (final value 0.42) decreased the R_1 further.

$CrWMo(dpa)_4Cl_2$ (**1**): Crystals were selected under oil under ambient conditions. A purple block-shaped single crystal of **1** was attached to the tip of a nylon loop. The crystal was mounted in a stream of cold nitrogen at 100(2) K and centered in the X-ray beam of a Bruker CCD-1000 diffractometer (Mo K_α) using a video camera. The data were successfully indexed by an auto-indexing routine built into the SMART program.[20] The structure of **1** was solved using the Patterson method and refined by least squares refinement on F^2 followed by difference Fourier synthesis. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The centrosymmetric space group *C*2/*c* (and not *Cc*) was choosen because of the mean |E*E-1| value of 0.862 and the lower CFOM for *C*2/*c* (1.57) as compared to *Cc* (2.18). The metal axis lies on a crystallographic twofold axis. Crystallographic details and important bond distances are given in Tables S1 and S2.

Additional Acknowledgments.

Bruker AC 300 NMR spectrometer: NSF CHE-9208463 & NIH 1 S10 RR0 8389-01; UW Chemistry Computer Center (Dr. Hieu Tran).

References.

1. V. Katovic, J. L. Templeton, R. J. Hoxmeier and R. E. McCarley, *J. Am. Chem. Soc.*, 1975, **97**, 5300.
2. E. M. Schubert, *J. Chem. Educ.*, 1992, **69**, 62.
3. G. A. Bain and J. F. Berry, *J. Chem. Educ.*, 2008, **85**, 532.
4. F. Neese, *ORCA – an ab initio, Density Functional and Semiempirical program package*, (2006), University of Bonn.
5. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
6. J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.
7. C. van Wullen, *J. Chem. Phys.*, 1998, **109**, 392.
8. A. Schafer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571.
9. A. Schafer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829.
10. E. J. Baerends, D. E. Ellis and P. Ros, *Chem. Phys.*, 1973, **2**, 41.
11. B. I. Dunlap, J. W. D. Connolly and J. R. Sabin, *J. Chem. Phys.*, 1979, **71**, 3396.
12. O. Vahtras, J. Almlof and M. W. Feyereisen, *Chem. Phys. Lett.*, 1993, **213**, 514.
13. K. Eichkorn, O. Treutler, H. O¨hm, M. Häser and R. Ahlrichs, *Chem. Phys. Lett.*, 1995, **240**, 283.
14. K. Eichkorn, F. Weigend, O. Treutler and R. Ahlrichs, *Theor. Chem. Acc.*, 1997, **97**, 119.
15. M. Buhl, C. Reimann, D. A. Pantazis, T. Bredow and F. Neese, *J. Chem. Theory Comput.*, 2008, **4**, 1449.
16. R. Ahlrichs and co-workers, Universität Karlsruhe, Karlsruhe, 2006 ftp.chemie.uni-karlsruhe.de/pub/basen
17. A. D. Becke, *J. Chem. Phys.*, 1996, **104**, 1040.
18. C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
19. H. P. L. P. Flukiger, S.Portmann and J.Weber, Swiss Center for Scientific Computing, *MOLEKEL*, (2000), Manno (Switzerland)
20. Y. M. Xie, H. F. Schaefer and R. B. King, *J. Am. Chem. Soc.*, 2000, **122**, 8746.
21. *SADABS V.2.05, SAINT V.6.22, SHELXTL V.6.10 & SMART 5.622*, (2000-2003) Bruker-AXS, Madison, Wisconsin.

Table S1. Selected experimental bond lengths in **1·2CH$_2$Cl$_2$** and **2** and calculated bond lengths in **2**.

	1·2CH$_2$Cl$_2$	**2**	**2** (calc.)
Mo≡W, Å	2.1548(4)	2.135(1)	2.155
W···Cr, Å	2.6742(5)	-	-
Cr−Cl, Å	2.5228(8)	-	-
Cr−N$_{av}$, Å	2.128[2]	-	-
W−N$_{av}$, Å	2.106[2]	2.147[4][a]	2.148
Mo−Cl, Å	2.7792(8)	-	-
Mo−N$_{av}$, Å	2.212[2]	2.147[4][a]	2.170

[a] Metal atoms are disordered

Table S2. Crystal Data.

Compound	**$1·2CH_2Cl_2$**	**2**
Formula	$CrWMo(C_{10}H_8N_3)_4Cl_2 \cdot 2\ CH_2Cl_2$	$MoW(C_{10}H_8N_3)_4$
Formula Weight, g/mol	1253.32	960.57
R(int)	0.026	0.0877
Number of reflections	37809	44391
Crystal system	Monoclinic	Monoclinic
Space group	*C* 2/*c*	*C* 2/*c*
a, Å	18.870(2)	18.1454(6)
b, Å	16.189(2)	11.5144(4)
c, Å	15.9337(19)	16.6938(5)
β, °	113.1020(10)	101.246(2)
V, Å^3	4477.3	3420.92(19)
Z	4	4
ρ, Mg m^{-3}	1.859	1.865
R1[a], *w*R2[b] ($I < 2\sigma(I)$)	0.0185, 0.0467	0.0401, 0.0865
R1[a], *w*R2[b] (all data)	0.0201, 0.0481	0.0620, 0.0949

[a] $R1 = 3||F_o| - |F_c||/3|F_o|$. [b] $wR2 = [3[w(F_o^2 - F_c^2)^2]/3[w(F_o^2)^2]]^{½}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table S3. Mulliken population analysis of important metal-metal bonding orbitals in **2** (calc.).

	π		σ	δ
% Mo	33.7	36.5	45.1	32
% W	33.5	37	40.4	25
% N_{py} on Mo	2.3	0.3	0	1.8
% N_{py} on W	0.2	2	0.2	1.9
% N_a on Mo	0.3	6.8	0.7	1.6
% N_a on W	8.6	0.6	0.7	1.6