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Preparation and Structure of Two Ditungsten Compounds Synthesized with the 3,5-Dichlorophenylformamidinate Ligand

Kathryn M. Carlson-Day, Judith L. Eglin,* and Laura T. Smith

Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762

Richard J. Staples

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

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The structure, preparation, and spectroscopy of a W_2(II, II) paddlewheel complex with four formamidinate ligands is reported. Upon exposure to air and moisture in solution, the W_2(II, II) core undergoes an oxidative addition reaction to form a W_2(III, III) edge-sharing bioctahedral (ESBO) complex with two bridging hydroxides. The products, $W_2(\mu\text{-DCPF})_4$ (**1**) and $W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$ (**2**) where DCPF is $[(3,5\text{-}Cl_2C_6H_3)NC(H)N\text{-}(3,5\text{-}Cl_2C_6H_3)^-]$, were characterized by UV−vis and ^{1}H NMR spectroscopy. Structural data are presented for $W_2(\mu\text{-DCPF})_4$ with four bridging formamidinate ligands and $W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$ with the formamidinate ligands in both chelating and bridging positions. Crystallographic data for $W_2(\mu\text{-DCPF})_4$ (**1**) and $W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$ (**2**) are as follows: (**1**), $C_{68}H_{60}Cl_{16}N_8O_4W_2$, $a = 12.6906(3)$ Å, $b = 12.7818(4)$ Å, $c = 13.0450(3)$ Å, $\alpha = 109.173(1)°$, $\beta = 93.865(1)°$, $\gamma = 103.746(1)°$, triclinic, $P\bar{1}$ (No. 2), and $Z = 1$ and (**2**), $C_{59}H_{35}Cl_{16}N_8O_2W_2$, $a = 17.1524(1)$ Å, $b = 20.6568(3)$ Å, $c = 19.3959(3)$ Å, $\beta = 102.791(1)°$, monoclinic, $C2/c$ (No. 15), and $Z = 4$.

Introduction

The ability of the formamidinate ligands to act as bridging bidentate ligands and form classic paddlewheel dinuclear group 6 transition metal species is well documented.[1−9] To date a single ditungsten complex, $W_2(\mu\text{-DFM})_4$ where HDFM is di-*p*-tolylformamidine,[3] has been synthesized using the more basic formamidinate ligand instead of a carboxylate ligand.[10−14] With the versatility of the formamidinate ligand to form systems with and without metal−metal bonds,[1−9,15−51] a recent focus area has become the systematic study of the tunability of the electronic and spectroscopic properties of complexes as a result of variations in the ligand periphery.[6−8]

One of the difficulties in the study of W_2(II, II) compounds is their susceptibility to oxidative addition.[14,52−57] The develop-

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* To whom all correspondence should be addressed.

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ment of a simpler synthetic route to multiply bonded ditungsten complexes has increased our ability to synthesize compounds containing the W_2(II, II) core and begin the systematic study of the reactivity and spectroscopy of $W_2(\mu\text{-form})_4$ derivatives where Hform is the formamidine ligand.[10,14,58] In addition to the development of a new synthetic route to $W_2(\mu\text{-form})_4$ complexes, $W_2(\mu\text{-DCPF})_4$ (**1**) where DCPF is [(3,5-$Cl_2C_6H_3$)NC(H)N(3,5-$Cl_2C_6H_3$)$^-$] and the oxidative addition product $W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$ were structurally and spectroscopically characterized.

Experimental Section

Materials and Methods. Standard vacuum line, drybox, and Schlenk techniques were employed under an argon atmosphere. Commercial grade tetrahydrofuran (THF), toluene, and hexanes were dried over potassium/sodium benzophenone ketyl and freshly distilled under argon prior to use. Commercial grade methanol was dried over magnesium turnings with freshly sublimed iodine and distilled prior to use. The 1.0 M solution of sodium triethylborohydride in toluene and 1.4 M solution of methyllithium in diethyl ether purchased from Aldrich Chemical Co. were packaged in Sure-Seal bottles and used without further purification. The starting materials WCl_4 and the formamidine ligand (3,5-$Cl_2C_6H_3$)NHC(H)N(3,5-$Cl_2C_6H_3$) were prepared according to literature methods.[59,60]

UV−vis spectra were recorded on a Hewlett-Packard 8452 model diode array spectrophotometer from 300 to 820 nm. ^1H (400 MHz) NMR spectra were recorded on a General Electric Omega NMR spectrometer and referenced to residual CH_3CN for **1** and $CHCl_3$ for **2** in the deuterated solvents CD_3CN and $CDCl_3$, respectively. Calibration of the temperature for the GE spectrometer was performed using a methanol sample and the set point did not vary from the actual temperature by more than 1 K over the temperature range from 178 to 295.5 K.[61] When the set point for each of the two temperatures was reached during data collection, the sample was allowed to equilibrate for 20 min in the spectrometer before data were collected.

W_2 (μ-DCPF)$_4$ (1). A gray slurry of 1.0 g of WCl_4 (3.07 mmol) in 15 mL of THF was cooled to −70 °C and 6.14 mL (6.14 mmol) of $NaBEt_3H$ was added dropwise. The reaction mixture was allowed to warm to −20 °C to result in a green solution. In a separate flask, 2.025 g (6.10 mmol) of (3,5-$Cl_2C_6H_3$)NHC(H)N(3,5-$Cl_2C_6H_3$) in 15 mL of THF was cooled in an ice bath and 4.4 mL (6.16 mmol) of methyllithium added. The lithium formamidinate salt [LiDCPF] that formed upon warming the solution to room temperature was transferred via cannula to the flask containing the reduced ditungsten solution. After the reaction mixture warmed to room temperature, the mixture was refluxed for 6 h. The viscous dark orange-brown solution was filtered through Celite, all solvents were removed under vacuum, and the residual oil was gently heated under vacuum for 1 h to remove any remaining solvent. To the deep brown-orange oil was added 30 mL of methanol and the solution refluxed for 2 h. After cooling of the methanol solution, a fine orange powder precipitated from the brown solution. All the methanol was removed by cannula and the orange powder washed two times with 30 mL aliquots of methanol and dried under dynamic vacuum (0.880 g, 34%). UV−vis (THF): 398 and 462 nm (sh). ^1H NMR spectroscopy ($CDCl_3$): δ 8.46 (s, 2H), 6.73 (s, 2H), 6.55 (s, 4H).

$W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$ (2). In the synthesis of $W_2(\mu\text{-DCPF})_4$ using WCl_4 (0.500 g, 1.53 mmol) as described above, the reaction mixture was filtered through Celite and dried under dynamic vacuum. After dissolving the orange-brown product in toluene, hexanes were added to precipitate an orange powder from an orange-brown solution. The supernatant solution was transferred via cannula to a volumetric flask, and deep red crystals were observed on the sides of the flask after 24 h, collected, and dried (0.136 g, 9.9%). The use of toluene and hexanes in the synthesis does not provide the optimal yield of $W_2(\mu\text{-DCPF})_4$, but solutions of the compound exposed to air and moisture undergo oxidative addition to yield the ESBO compound, $W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$. The yield for $W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$ was not optimized since the compound is obtained as a side product. UV−vis (CH_2Cl_2): 374 and 522 nm. ^1H NMR spectroscopy ($CDCl_3$): δ 9.08 (s, 2H), 8.54 (s, 2H), 7.89 (s, 4H), 7.29 (s, 2H), 7.10 (s, 2H), 6.54 (s, 4H), 2.05 (s, 2H, J_{H-W} 168 Hz).

Structure Determination. Orange crystals of **1** were grown from a toluene solution of the compound layered with hexanes. The deep red crystals of **2** were grown from slow solvent evaporation of the supernatant toluene/hexanes solvent mixture of $W_2(\mu\text{-DCPF})_4$ in an open volumetric flask exposed to air and moisture. Data for **1** and **2** were collected using a Siemens SMART CCD (charge coupled device) based diffractometer equipped with an LT-2 low-temperature apparatus operating at 213 K. Suitable crystals of **1** and **2** were chosen and mounted on glass fibers using grease. Data for **1** and **2** were measured using omega scans of 0.3° per frame for 30 s such that a hemisphere was collected. A total of 1271 frames were collected with a final resolution of 0.75 Å. The first 50 frames were recollected at the end of data collection for **1** and **2** to monitor for decay, but the crystals used for the diffraction study showed no decomposition during data collection. Cell parameters were retrieved using SMART[62] software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software,[63] which corrects for Lorentz and polarization effects and decay. Absorption corrections were applied using SADABS,[64] supplied by George Sheldrick. The structures were solved by the direct method using the SHELXS-90[65] program and refined by least-squares method on F^2, SHELXL-93[66] incorporated in SHELXTL-PC V 5.03.[67]

The structures of **1** and **2** were solved in the space groups $P\bar{1}$ (No. 2) and $C2/c$ (No. 15), respectively, by successful solution and refinement

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Table 1. Crystal Data and Structure Refinement for $W_2(\mu\text{-DCPF})_4 \cdot 4THF$ (**1**) and $W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$ (**2**)

compound	**1**	**2**
chemical formula	$C_{68}H_{60}Cl_{16}N_8O_4W_2$	$C_{59}H_{35}Cl_{16}N_8O_2W_2$
formula weight	1988.14	1822.85
space group	$P\bar{1}$	$C2/c$
a (Å)	12.6906(3)	17.1524(1)
b (Å)	12.7818(4)	20.6568(3)
c (Å)	13.0450(3)	19.3959(3)
α (deg)	109.173(1)	
β (deg)	93.865(1)	102.791(1)
γ (deg)	103.746(1)	
volume (Å^3)	1916.85(9)	6701.7(2)
Z	1	4
ρ_{calc} (g/cm^3)	1.722	1.807
absorption coefficient (mm^{-1})	3.608	4.117
wavelength (Å)	0.71073	0.71073
temperature (K)	213(2)	213(2)
final *R* indices [$I > 2\sigma(I)$]	$^aR_1 = 0.0365$, $^bwR_2 = 0.0660$	$^aR_1 = 0.0348$, $^bwR_2 = 0.0595$

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^b wR_2 = \sqrt{(\sum[(F_o{}^2 - F_c{}^2)^2/\sum[wF_o{}^4])}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $W_2(\mu\text{-DCPF})_4 \cdot 4THF$

W(1)−W(1)#1	2.1920(3)	N(1)−C(1)	1.326(5)
W(1)−N(1)	2.141(4)	N(2)−C(1)#1	1.343(5)
W(1)−N(2)	2.138(4)	N(3)−C(2)	1.334(5)
W(1)−N(3)	2.142(3)	N(4)−C(2)	1.337(5)
W(1)−N(4)#1	2.144(3)		
N(1)−W(1)−N(3)	90.55(13)	N(1)−C(1)−N(2)#1	119.7(4)
N(1)−W(1)−N(4)#1	89.14(14)	N(3)−C(2)−N(4)	120.0(4)
N(2)−W(1)−N(4)#1	90.58(14)	C(1)−N(1)−W(1)	118.7(3)
N(3)−W(1)−N(4)#1	176.75(13)	C(1)#1−N(2)−W(1)	118.3(3)
N(2)−W(1)−W(1)#1	91.64(9)	C(2)−N(3)−W(1)	118.5(3)
N(1)−W(1)−W(1)#1	91.48(9)	C(2)−N(4)−W(1)#1	118.2(3)
N(3)−W(1)−W(1)#1	91.56(9)	C(3)−N(1)−W(1)	122.4(3)
N(4)#1−W(1)−W(1)#1	91.68(9)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$

W(1)−W(1)#1	2.3508(3)	W(1)−O(1)#1	1.972(3)
W(1)−N(1)	2.182(3)	N(1)−C(1)	1.335(5)
W(1)−N(2)	2.178(3)	N(2)−C(1)	1.322(5)
W(1)−N(3)	2.116(4)	N(3)−C(14)	1.344(5)
W(1)−N(4)	2.124(4)	N(4)−C(14)#1	1.312(5)
W(1)−O(1)	1.963(3)		
N(2)−W(1)−N(1)	60.72(12)	N(4)−W(1)−W(1)#1	88.86(10)
N(3)−W(1)−N(1)	90.16(13)	N(2)−C(1)−N(1)	112.1(4)
N(3)−W(1)−N(2)	93.08(13)	N(4)#1−C(14)−N(3)	121.1(4)
N(3)−W(1)−N(4)	178.82(12)	C(1)−N(1)−W(1)	93.3(3)
N(4)−W(1)−N(1)	90.40(13)	C(1)−N(2)−W(1)	93.9(3)
N(4)−W(1)−N(2)	88.10(13)	C(14)−N(3)−W(1)	119.1(3)
N(1)−W(1)−W(1)#1	150.24(9)	C(14)#1−N(4)−W(1)	120.8(3)
N(2)−W(1)−W(1)#1	148.93(9)	O(1)−W(1)−O(1)#1	106.64(9)
N(3)−W(1)−W(1)#1	90.13(10)	W(1)−O(1)−W(1)#1	73.36(9)

of structure **1** or analysis of systematic absences for structure **2**. All non-hydrogen atoms are refined anisotropically. Hydrogen atoms for both structures were calculated by geometrical methods and refined as a riding model. In the structure of **2**, the hydrogen atoms of the disordered interstitial solvent toluene were not modeled. The toluene was disordered over the inversion symmetry site and resulted in the correct position of the solvent molecule with respect to hydrogen bonding.

Table 1 provides data collection information for **1** and **2**. Tables 2 and 3 include selected bond distances and angles for **1** and **2**, respectively.

Results and Discussion

Synthesis. The use of $NaBEt_3H$ in the reduction of WCl_4 is analogous to the use of Na/Hg in the preparation of the *p*-tolylformamidinate compound, $W_2(\mu\text{-DFM})_4$.[3] The primary difference in the synthetic route is the use of the alternative reducing agent, $NaBEt_3H$,[14,58,68,69] with subsequent steps in the synthesis following the established literature procedure.[3] The orange quadruply-bonded product is very soluble in THF and slightly soluble in toluene, acetone, acetonitrile, and methanol. When $W_2(\mu\text{-DCPF})_4$ is dissolved in a toluene/hexanes solution and exposed to moisture and oxygen, oxidative addition occurs to result in **2**. Compound **2** is an ESBO W_2(III, III) compound with two bridging hydroxide ligands, two bridging formamidinate ligands, and two chelating formamidinate ligands. In studies of $W_2(\mu\text{-DFM})_4$, oxidative addition does not take place in deoxygenated water, even under reflux conditions; therefore, the decomposition of $W_2(\mu\text{-DCPF})_4$ is due to the combination of moisture and oxygen.[3]

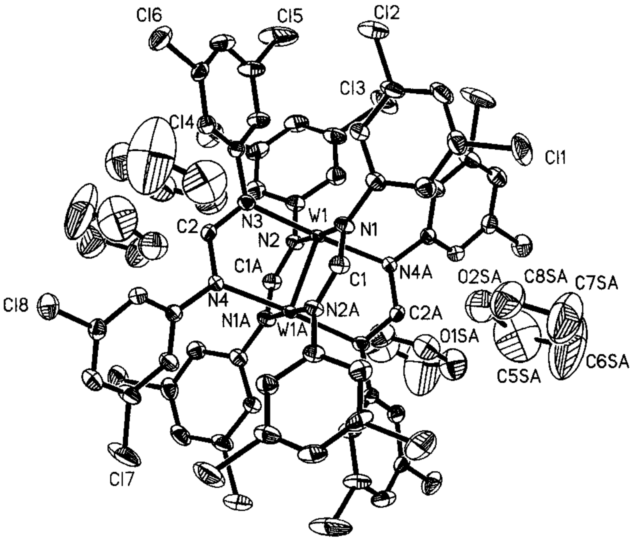

Figure 1. A thermal ellipsoid plot of $W_2(\mu\text{-DCPF})_4$ (**1**) viewed at approximately 90° to the W−W axis. Thermal ellipsoids for W, C, and N atoms are shown at 50% probability. H atoms are omitted for clarity.

Molecular Structure. The W−W bond distance for $W_2(\mu\text{-DCPF})_4$ shown in Figure 1 of 2.1920(3) Å is similar to the bond distances of 2.196(1) Å for $W_2(\mu\text{-}O_2CC_6H_5)_4(C_4H_8O)_2$[70] and 2.187(1) Å for $W_2(\mu\text{-DFM})_4$[3] with formal shortness ratios (FSR) of 0.842 and 0.838, respectively.[3,71] To compare the W−W bond distance of $W_2(\mu\text{-DCPF})_4$ to the analogous Cr−Cr and Mo−Mo tetraformamidinate compounds, the FSR was calculated [0.840]. The W−W bond distance is 0.10 Å longer than the corresponding Mo−Mo bond length, as expected for a homologous Mo_2 and W_2 series.[72] As in the case of the $M_2(\mu\text{-DFM})_4$ series,[3] the FSR of the ditungsten compound is larger than either the dimolybdenum analogue (FSR = 0.809, Mo−Mo 2.0965(5) Å)[6,72] or the dichromium analogue (FSR = 0.808, Cr−Cr 1.9162(10) Å).[73] The significant increase in the value of FSR cannot be attributed to loss of orbital overlap due to an increase

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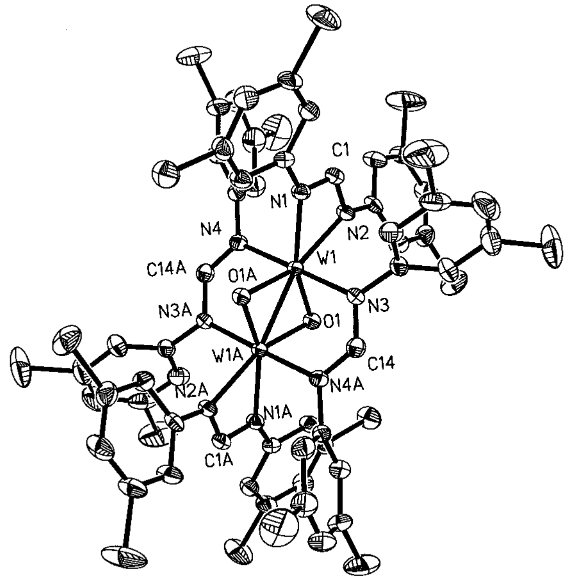

Figure 2. A thermal ellipsoid plot of $W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$ (**2**) viewed at approximately 90° to the W−W axis. Thermal ellipsoids for W, C, O, and N atoms are shown at 50% probability. H atoms are omitted for clarity.

in the torsion angles, N1−W1−W1A−N2A (0.2°) and N3−W1−W1A−N4 (0.2°).

The W−N bond distances are 2.138(4), 2.142(3), 2.141(4), and 2.144(3) Å. The bond distances are similar to the W−N bond distances of 2.13(1) and 2.14(1) Å observed for $W_2(\mu\text{-DFM})_4$[3] but longer than the W−O bond distance of 2.077(4) Å observed for $W_2(\mu\text{-}O_2CC_6H_5)_4(C_4H_8O)_2$.[70] The Mo_2 analogue $Mo_2(\mu\text{-DCPF})_4$[6] with a shorter metal−metal bond has longer metal to nitrogen bond lengths, 2.157(2), 2.163(2), 2.174(2), and 2.170(2) Å. The trend, shorter metal−metal bond distances and longer metal−ligand bond distances for the dimolybdenum compound in comparison to the ditungsten compounds, is also observed for the *p*-tolylformamidinate derivatives, but the structural characterization of additional W_2(II, II) complexes in the series is required for a complete comparison.[2,3]

The W−W bond distance for $W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$ (**2**) shown in Figure 2 is rather short (2.3508(3) Å), indicating a strong W−W interaction, $\sigma^2\pi^2\delta^2$, for the W_2(III, III) core. The W−W bond distance is similar to the triply bonded complexes $W_2(\mu\text{-H})_2Cl_2(PPh_3)_2(\mu\text{-}O_2CC_6H_5)_2$ (2.3500(12) Å)[74] and $W_2(\mu\text{-H})_2Cl_4(\mu\text{-dppm})_2$ (2.3918(7) Å)[75] with two bridging hydrides. The W−W bond distance of **2** is over 0.10 Å longer than either the related W_2(III, III) compound with two bridging hydroxides $[W_2L_2(\mu\text{-OH})_2Br_2]Br_2\cdot 2H_2O$[76] (2.477(3) Å), where L is the 1,4,7-triazacyclononane ligand or $W_2(\mu\text{-CO})_2(\mu$-di-3,5-xylylformamidinato$)_2(\eta^2$-di-3,5-xylylformamidinato$)(\eta^1$-methylene-3,5-xylylformamidinato) (2.464(2) Å) with two bridging formamidinate ligands, one chelating formamidinate ligand, and a chelating formamidinate ligand that has undergone insertion of a CH_2 group between the metal and formamidinate ligand.[77] In comparison to ESBO complexes with bridging chlorides, such as $W_2(\mu\text{-Cl})_2Cl_4(\mu\text{-dppm})_2$ and $W_2(\mu\text{-Cl})_2Cl_4(\mu\text{-dmpm})_2$, the bond distance of **2** is over 0.2 Å shorter.[55] As in the case of the dimolybdenum series $Mo_2(\mu\text{-X})_2X_4(\text{dppm})_2$, where X is Cl (2.789(1) Å),[78] Br (2.879(2) Å),[79] or I (3.061(1) Å),[79,80] the W−W bond distance increases with an increase in the principal quantum number of the bridging ligand.

The W−OH bond distances of **2** are slightly shorter than either the M−OH bond distances of the dinuclear complex $[W_2L_2(\mu\text{-OH})_2Br_2]Br_2\cdot 2H_2O$ (2.095(20) Å)[76] or the tetranuclear complex $[Mo_2(\text{DTolF})_3]_2(\mu\text{-OH})_2$ (2.123(3) and 2.118(3) Å with a Mo−O−Mo angle of 147.7(2)°).[51] The W−OH bond distance of **2** is also shorter than other bridging W−OR bond distances such as the $OSiMe_2Bu^t$ group in $HW_2(OSiMe_2Bu^t)_6(\mu\text{-CCH=CHMe})$ (2.05(1) Å),[81] the bridging OMe group in $W_2Cl_4(OMe)_4(MeOH)_2$ (2.034(6) Å), or the OEt group in $W_2Cl_4(OEt)_4(EtOH)_2$ (2.022(8) Å).[82] Surprisingly, the W−OH bond distances are shorter than the bridging W=O bond distances of $K_3H[W_2O_4F_6]$ (1.99(2) and 1.98(1) Å) with a W−W bond distance of 2.620(1) Å and W−O−W bond angle of 82.5(5)°.[83]

The structure of $W_2(\mu\text{-CO})_2(\mu$-di-3,5-xylylformamidinato$)_2(\eta^2$-di-3,5-xylylformamidinato$)(\eta^1$-methylene-3,5-xylylformamidinato) contains two short W−N bond distances to the bridging formamidinate ligands (2.12(3) and 2.11(3) Å) and two longer W−N bond distances to the chelating formamidinate ligand (2.26(3) and 2.31(3) Å), as in the case of $W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$.[77] The W−N−C bond angles of **2** for the chelating formamidinates 93.3(3) and 93.9(3)° are more acute in comparison to the angles for the bridging ligands, 119.1(3) and 120.8(3)°. The N−C−N bond angles in **2** deviate from the predicted sp^2 hybridization to form a more acute angle for the chelating formamidinate ligand (112.1(4)°) in comparison to the bridging formamidinate ligand (121.1(4)°).[77] A similar trend in bond angles is observed for the dichromium system $Cr_2(\text{DTolF})_4Cl_2$, where HDTolF is di-*p*-tolylformamidine, but all of the Cr−N bond distances are similar with no significant change between the bridging and chelating geometry of the ligand.[23] In contrast to $W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$, where a triple bond is proposed, $Cr_2(\text{DTolF})_4Cl_2$ has no Cr−Cr bond.[23]

NMR Spectroscopy. The proton NMR spectra for **1** includes a singlet at 8.46 ppm for the methine proton shifted downfield due to diamagnetic anisotropy of the W−W quadruple bond. With the methine proton in a fixed position over the center of the W−W bond, the diamagnetic anisotropy of the quadruple bond can be estimated on the basis of the change of chemical shift. Using the McConnell equation[84] shown below, the diamagnetic anisotropy is calculated on the basis of the structural and ^1H NMR spectroscopic data. In eq 1

$$\Delta\delta = \Delta\chi[(1 - 3\cos^2\theta)/12\pi r^3] \tag{1}$$

$\Delta\delta$ is the change of chemical shift (ppm) of the methine proton of the ditungsten quadruply-bonded complex versus the non-bonded dinickel compound,[8] r is the length (Å) of the vector from the center of the W−W bond to the methine proton, θ is the angle between r and the W−W bond axis, and $\Delta\chi = \chi_1 -$

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$\chi_\perp$ is the diamagnetic anisotropy (in units of 10^{-36} m^3/molecule). Using the chemical shift of the methine proton for the Ni compound $Ni_2(\mu\text{-DCPF})_4$ as the zero point, the ring currents due to the phenyl substituents of the ligand are minimized. The value of $\Delta\chi$ based on the structural and spectroscopic data for $W_2(\mu\text{-DCPF})_4$ is 4067 × 10^{-36} m^3/molecule, which is significantly smaller than the value of $\Delta\chi$ for the related compound $W_2(\mu\text{-DFM})_4$ of 5480 × 10^{-36} m^3/molecule.[3] For the molybdenum and tungsten $M_2(\mu\text{-DFM})_4$ complexes, a lower diamagnetic anisotropy for the molybdenum compound in comparison to the tungsten analogue was observed. However, $Mo_2(\mu\text{-DCPF})_4$ has a $\Delta\chi$ value of 4730 × 10^{-36} m^3/molecule, higher than the $W_2(\mu\text{-DCPF})_4$ derivative.[6] The value of $\Delta\chi$ for $W_2(\mu\text{-DCPF})_4$ is significantly smaller than the average value for $\Delta\chi$ of 5728 × 10^{-36} m^3/molecule reported for three W−W quadruply-bonded complexes.[58] In a related series of dichromium tetraformamidinate complexes, the value of $\Delta\chi$ varies with the Hammett constant of the remote substituents of the formamidinate ligands. Smaller values of $\Delta\chi$ are obtained for electron withdrawing groups and the trend will be investigated in the ditungsten series as more compounds are structurally and spectroscopically characterized.[73,85]

The proton NMR spectra for **2** is complex due to the two types of formamidinate ligand environments. The methine proton of the chelating ligand which forms a four-membered ring system, WN_2C, has a larger downfield chemical shift of 9.08 ppm than the methine proton of the bridging formamidinate ligand, 8.54 ppm. The chemical shift of the bridging hydroxide protons occurs at 2.05 ppm with J_{W-H} of 168 Hz. The proton NMR spectra of **2** was recorded at 19.1 and 55 °C with a 2.8 Hz difference in the chemical shift of the protons of the bridging hydroxide. The small change in chemical shift upon an increase in temperature reflects a relatively large energy difference between the δ and δ^* orbitals.[74,75,86,87]

UV−Vis Spectroscopy. The UV−vis of the orange compound $W_2(\mu\text{-DCPF})_4$ contains the δ to δ^* transition at 398 nm, a 16 nm shift from the δ to δ^* transition at 414 nm for the $W_2(\mu\text{-DFM})_4$ analogue.[3] The difference in the δ to δ^* transition is larger than observed for the dimolybdenum analogues (δ 6 nm),[6] but more ditungsten tetraformamidinate compounds must be synthesized to determine if a correlation exists between the Hammett constant and the δ to δ^* transition.

Most ESBO complexes[75] have strong ligand-to-metal charge-transfer bands below 400 nm and an absorption in the 450−550 nm region that is dependent on the nature of the metal center, but the origin of the absorption band is unknown.[86,87] The UV−vis of the red compound $W_2(\mu\text{-OH})_2(\mu\text{-DCPF})_2(\eta^2\text{-DCPF})_2$ contains two peaks at 374 and 522 nm.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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