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Unexpected formation of *anti*-1,2-$W_2(SBu^t)_2(NMe_2)_4$ in the thiolysis of *gauche*-1,2-$W_2Cp_2(NMe_2)_4$ and $W_2COT(NMe_2)_4$ with Bu^tSH

Malcolm H. Chisholm *, Judith C. Gallucci, Carl B. Hollandsworth [1]

Newman and Wolfrom Laboratory of Chemistry, The Ohio State University, 100 W. 18th Avenue, Columbus, OH 43210, United States

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Abstract

Thiolysis of $W_2Cp_2(NMe_2)_4$ and $W_2COT(NMe_2)_4$ with excess Bu^tSH leads to cleavage of the respective carbocyclic rings from the ditungsten center and formation of the compound *anti*-1,2-$W_2(SBu^t)_2(NMe_2)_4$ which was characterized via a single-crystal X-ray diffraction study. This product was found to be isostructural with its dimolybdenum analogue. The compound is a prototypical ethane-like dimer having a W≡W bond distance of 2.3011(3) Å and thiolate ligands in an *anti* configuration about the W≡W bond. The thiolysis reactions for both dimethylamide precursors are contrasted with the results of their respective alcoholysis reactions.

Keywords: Ditungsten; Thiol; Thiolate; Thiolysis; Dimethylamide

1. Introduction

Dimolybdenum and ditungsten dimethylamido compounds typically undergo facile thiolysis to give the corresponding thiolate compounds and liberated dimethylamine [1]. $Mo_2(NMe_2)_6$ reacts with excess aryl thiol (ArSH) at room temperature to give incomplete thiolate for dimethylamide exchange product $Mo_2(NMe_2)_2(SAr)_4$ [2]. This compound was assumed to be a mixture of the 1,2-*anti* and 1,2-*gauche* rotamers based on solution NMR studies. Toluene solutions of $M_2(NMe_2)_6$ and mesitylenethiol (MesSH) react at 80 °C to give the complete thiolysis product, $M_2(SMes)_6$ (M = Mo, W) [3]. The same reactions also yielded some *anti*-1,2-$M_2(SR)_2(NMe_2)_4$ as a byproduct of incomplete thiolysis.

$W_2COT(NMe_2)_4$ undergoes alcoholysis with excess ROH (where R = Bu^t, Pr^i, and CH_2Bu^t) to give the corresponding alkoxides $W_2COT(OR)_4$ [4]. Alcoholysis of the same compound with less sterically demanding alcohols (MeOH, EtOH, and Pr^nOH) gives the tetranuclear species, $[W_2COT(OR)_4]_2$, wherein two μ_2-OR ligands span the $(W{\equiv}W)^{6+}$ units [5]. In these alcoholysis reactions, no compounds were observed in which the COT ligand was displaced from the W_2^{6+} center.

This finding is in contrast to the alcoholysis behavior of other 1,2-$W_2R_2(NMe_2)_4$ compounds (where R = Me, Et, Pr, Me_2CH, Me_2CHCH_2, CH_2CMe_3, CH_2SiMe_3, Ph, *p*-tolyl, CH_2Ph) wherein 1,2-$W_2R_2(OR')_4$ products are formed initially, followed by loss of the alkyl ligands to yield $W_2(OR')_6$ [6]. The formation of $W_2(OR')_6$ is rapid enough that in some cases that the intermediate compounds, $W_2R_2(OR')_4$ or $W_2R(OR')_5$, have not been isolable [6]. When the alkyl ligand, R, contains a β-hydrogen atom the hexa-alkoxides are formed as a result of the reductive elimination of one equivalent of alkane and one equivalent of alkene from the ditungsten center.

We have recently found that g*auche*-1,2-$W_2Cp_2(NMe_2)_4$ undergoes oxidative W≡W bond cleavage in neat MeOH,

* Corresponding author.
E-mail addresses: chisholm@chemistry.ohio-state.edu (M.H. Chisholm), hollandsworth@mail.chem.sc.edu (C.B. Hollandsworth).
[1] Present address: University of South Carolina, Chemistry and Biochemistry, 631 S. Sumter St., Columbia, SC 29208, United States. Tel.: +1 614 519 8751.

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EtOH, and Pr^nOH to form Cp_2WH_2 and $W(OR)_6$ [7]. It is this varied and rich substitution behavior of both $W_2COT(NMe_2)_4$ and $W_2Cp_2(NMe_2)_4$ that prompted the thiolysis studies reported herein.

2. Experimental

2.1. General considerations

$W_2COT(NMe_2)_4$ [8] and 1,2-$W_2Cp_2(NMe_2)_4$ [9] were prepared as previously reported. A single-crystal X-ray diffraction experiment was undertaken on 1,2-$W_2Cp_2(NMe_2)_4$ crystals grown by slow evaporation from dimethoxyethane (DME) solution in the drybox. Reactions were carried out under an atmosphere of Ar. Bu^tSH (Aldrich), was used as received. A fume hood with adequate ventilation should be employed when using Bu^tSH as its odor is pervasive even at small concentrations.

2.2. Thiolysis reactions

In these experiments, $W_2COT(NMe_2)_4$ (0.250 g, 0.386 mmol) or *gauche*-1,2-$W_2Cp_2(NMe_2)_4$ (0.250 g, 0.370 mmol) was dissolved in Bu^tSH (ca. 5 mL) in a 25 mL Schlenk flask in the dry box. In the former case, the reaction solution rapidly turned from forest green to olive green in color. For the Cp compound, the reaction mixture turned from yellow/orange to olive green. A PTFE-coated magnetic stir bar was added and the reactions were allowed to stir overnight (12 h). The excess Bu^tSH and other volatile components were subsequently removed under reduced pressure into a cold trap. Toluene (5 mL) was added to the crude, green products and these solutions were refrigerated at ca. −20 °C overnight. Yellow-green crystals of *anti*-1,2-$W_2(SBu^t)_2(NMe_2)_4$ (0.188 g, 66% for the COT reaction; 0.097 g, 34% for the Cp reaction) were isolated by filtration. The identity of the crystalline product was confirmed by ^1H NMR spectra, which matched the previously reported spectral data for this compound [10] and also via a single-crystal X-ray diffraction experiment.

2.3. X-ray crystallographic studies

2.3.1. General considerations

All work was done at 200 K using an Oxford Cryostreams Cooler [11] on a Nonius Kappa CCD diffractometer. A combination of φ and ω scans with a frame width of 1.0° was used. Data integration was done with the program Denzo [12]. Scaling and merging of the data was done with Scalepack [12].

2.3.2. X-ray experiment on gauche-$(\eta^3$-Cp$)_2W_2(NMe_2)_4$

The data collection crystal was an orange chunk. Examination of the diffraction indicated an orthorhombic crystal system. The data collection strategy was set up to measure a quadrant of reciprocal space with a redundancy factor of 4.1. An absorption correction is inherent in this procedure and is reflected in the scale factor range for the frames of 7.69–10.04. Merging the data and averaging the symmetry equivalent reflections (but not the Friedel pairs) resulting in an R_{int} value of 0.044. The structure was solved by the Patterson method in SHELXS-97 [13]. The space group is Iba2. Full-matrix, least-squares refinements based on F^2 were performed in SHELXS-93 [14].

For each methyl group, the hydrogen atoms were added at calculated positions using a riding model with $U(H) = 1.5 \times U_{eq}$ for the bonded C atom. The torsion angle, which defines the orientation of the methyl group about the N–C bond, was refined. The other hydrogen atoms were included in the model at calculated positions using a riding model with $U(H) - 1.2 \times U_{eq}$ for the bonded C atom. The final refinement cycle was based on 4576 intensities and 226 variables and resulted in agreement factors of $R_1(F) = 0.020$ and $wR_2(F^2) = 0.037$. For the subset of data with $I > 2\sigma(I)$, the $R_1(F)$ value is 0.017 for 4313 reflections. The final difference electron density map contains maximum and minimum peak heights of 0.94 and -0.81 e A^{-3}. Neutral atom scattering factors were used and include terms for anomalous dispersion [15].

2.3.3. X-ray experiment on anti-$W_2(SBu^t)_2(NMe_2)_4$

The data collection crystal was a yellow-green block. Examination of the diffraction on a Nonius Kappa CCD diffractometer indicated a monoclinic crystal system. The data collection strategy was set up to measure a quadrant of reciprocal space with a redundancy factor of 4.3. A combination of φ and ω scans with a frame width of 1.0° was used. Merging the data and averaging the symmetry equivalent reflections resulted in an R_{int} value of 0.042. The structure was solved by the Patterson method in SHELXS-86 [16] for the two W atoms. All of the non-hydrogen atoms were located by standard Fourier methods. Full-matrix, least-squares refinements based on F^2 were performed in SHELXL-93 [14].

For each methyl group, the hydrogen atoms were added at calculated positions using a riding model with $U(H) = 1.5 \times U_{eq}$ for the bonded C atom. The torsion angle, which defines the orientation of the methyl group about the C–C or N–C bond, was refined. The final refinement cycle was based on 5664 intensities and 231 variables and resulted in agreement factors of $R_1(F) = 0.032$ and $wR_2(F^2) = 0.036$. For the subset of data with $I > 2\sigma(I)$, the $R_1(F)$ value is 0.020 for 4685 reflections. The final difference electron density map contains maximum and minimum peak heights of 1.07 and −0.80 electrons per A^3. Neutral atom scattering factors were used and include terms for anomalous dispersion [15].

3. Results and discussion

An X-ray diffraction experiment was carried out on the 1,2-$W_2Cp_2(NMe_2)_4$ starting reagent. The cyclopentadienyl rings are found in a *gauche* orientation and they bind to tung-

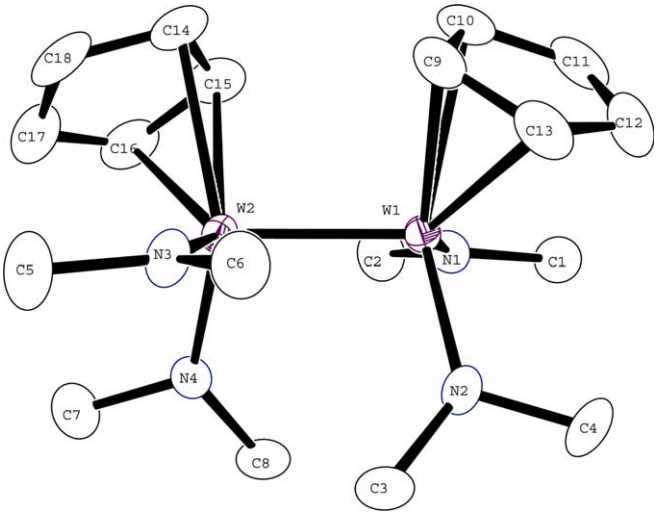

Fig. 1. ORTEP-style diagram of *gauche*-1,2-(η^3-Cp)$_2$W$_2$(NMe$_2$)$_4$. Thermal ellipsoid probabilities are drawn at the 50% level. The hydrogen atoms are omitted for clarity. Pertinent bond distances (Å): W(1)–W(2), 2.3405(2); W(1)–N(1), 1.966(3); W(1)–N(2), 1.960(4); W(1)–N(3), 1.958(3); W(1)–N(4), 1.969(3); W(1)–C(9), 2.379(4); W(1)–C(10), 2.445(4); W(1)–C(13), 2.528(4); W(2)–C(14), 2.449(4); W(2)–C(15), 2.379(5); W(2)–C(16), 2.532(4). Pertinent bond angles (°) W2–W1–N1, 101.7(1); W2–W1–N2, 102.0(1); W1–W2–N3, 102.3(1); W1–W2–N4, 101.5(1).

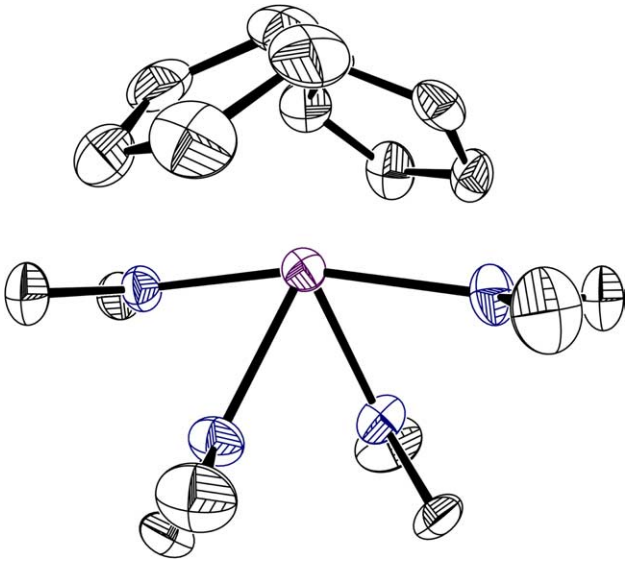

Fig. 2. ORTEP-style diagram of 1,2-(η^3-Cp)$_2$W$_2$(NMe$_2$)$_4$ looking down the W≡W bond. The *gauche* relationship of the Cp rings can be seen from this view.

sten in an η^3-fashion in a manner similar to that found for the MeCp and indenyl analogues [17]. The structure of this molecule was otherwise unremarkable and is not considered further. The refined geometry is represented in Figs. 1 and 2 and the X-ray experimental details are given in Table 1.

When excess Bu^{t}SH is added to W$_2$COT(NMe)$_4$ or 1,2-W$_2$Cp$_2$(NMe$_2$)$_4$ the resulting solutions immediately turn olive green. The reaction is not noticeably exothermic, as is often the case with alcoholysis or thiolysis of W$_2$(NMe$_2$)$_6$. Furthermore, no gas evolution is observed. Upon cooling the reaction solutions at ca. −20 °C overnight, green

Table 1
Experimental crystallographic details for *gauche*-1,2-(η^3-Cp)W$_2$(NMe$_2$)$_4$ and *anti*-1,2-W$_2$(SBu^t)$_2$(NMe$_2$)$_4$

Compound	*gauche*-1,2-(η^3-Cp)$_2$W$_2$-(NMe$_2$)$_4$	*anti*-1,2-W$_2$-(SBu^t)$_2$(NMe$_2$)$_4$
Empirical formula	$W_2C_{18}H_{34}N_4$	$W_2S_2N_4C_{16}H_{42}$
Formula weight (g mol^{-1})	674.19	722.36
Temperature (K)	200(2)	200(2)
Wavelength (Å)	0.711	0.711
Crystal system	Orthorhombic	Monoclinic
Space group	*Iba*2	$P2_1/n$
a (Å)	13.393(1)	9.954(1)
b (Å)	20.030(2)	17.567(2)
c (Å)	15.400(1)	14.426(1)
α (°)	90	90
β (°)	90	101.638(1)
γ (°)	90	90
Volume (Å^3)	4131.2(6)	2470.7(4)
Z	8	4
Density (g/cm^3)	2.168	1.942
Absorption coefficient (mm^{-1})	11.136	9.480
F(000)	2544	1384
Crystal size (mm)	0.15 × 0.23 × 0.23	0.12 × 0.12 × 0.15
Theta range for data (°)	2.65–27.48	2.56–27.49
Index ranges	$17 \geqslant h \geqslant -17$ $26 \geqslant k \geqslant -25$ $19 \geqslant l \geqslant -19$	$12 \geqslant h \geqslant -12$ $22 \geqslant k \geqslant -22$ $18 \geqslant l \geqslant -18$
Reflections	44017	49047
Independent reflections [*R*(int)]	4576 [0.044]	5664 [0.042]
Data/restraints/parameters	4576/1/226	5664/0/231
Goodness of fit on F^2	1.042	1.028
Final *R* indices	$R_1 = 0.0171$ $wR_2 = 0.0361$	$R_1 = 0.0198$ $wR_2 = 0.0345$
R indices (all data)	$R_1 = 0.0200$ $wR_2 = 0.0369$	$R_1 = 0.0315$ $wR_2 = 0.0364$
Largest difference in peak and hole (e$^-$/Å^3)	0.942 and −0.808	1.070 and −0.804

crystals are obtained. Single-crystal X-ray diffraction studies revealed this product to be the same for both reactions: *anti*-1,2-W$_2$(SBu^t)$_2$(NMe$_2$)$_4$ (Fig. 3). This compound is isostructural with the known molybdenum analogue [10] wherein the thiolate ligands are found *anti* to each other with respect to the W–W bond and the dimethylamide ligands are oriented in a perfectly proximal/distal orientation. This ligand orientation maximizes the dimethylamide to tungsten π-bonding, thus relieving some of the electron deficiency of the formally 12 e$^-$ tungsten atoms. In the solid state, the Bu^t groups of the thiolate ligand are both distally oriented relative to the W–W bond. This is likely the best orientation of the Bu^t groups for minimizing Bu^t-to-dimethylamide methyl group interactions across the W–W bond.

The selective removal of the carbocyclic ligands (Eqs. (1) and (2)) in these reactions is somewhat of a surprise. Dimethylamide for thiolate or alkoxide exchange is a typically rapid and facile process. It is likely that the increased acidity of the thiol, as compared to Bu^{t}OH for instance, leads to selective carbocycle protonation and formation of *anti*-1,2-W$_2$(SBu^t)$_2$(NMe$_2$)$_4$.

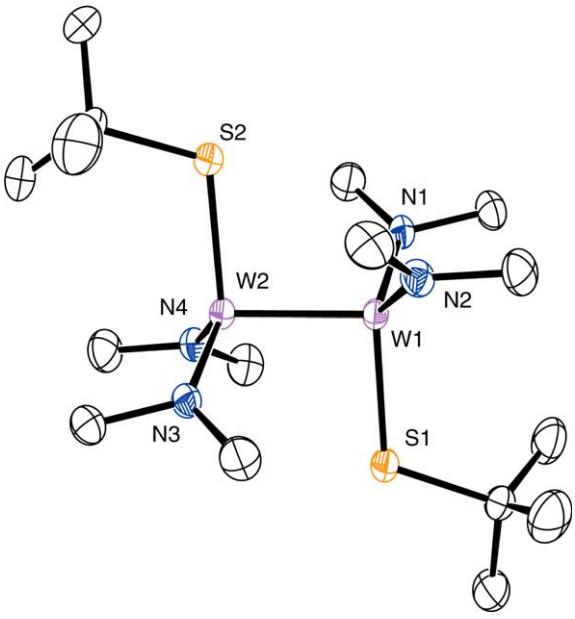

Fig. 3. ORTEP-style diagram of *anti*-1,2-$W_2(SBu^t)_2(NMe_2)_4$. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 45% probability level. Pertinent bond distances (Å): W1–W2, 2.3011(3); W1–S1, 2.3473(8); W2–S2, 2.3456(8); W1–N1, 1.957(2); W1–N2, 1.941(2); W2–N3, 1.950(2); W2–N4, 1.948(2). Pertinent bond angles (°): W1–W2–S2, 95.09(2); W2–W1–S1, 94.32(2); W1–W2–N3, 104.51(7); W1–W2–N4, 103.84(7); W2–W1–N1, 103.95(7); W2–W1–N2, 105.07(7), N1–W1–N2, 115.2(1); N1–W1–S1, 118.55(7); N2–W1–S1, 115.43(7); N3–W2–N4, 117.20(9); N3–W2–S2, 116.18(7); N4–W2–S3, 115.57(7).

$$W_2COT(NMe_2)_4 + \text{excess } Bu^tSH \rightarrow \textit{anti}\text{-}1,2\text{-}W_2(SBu^t)_2(NMe_2)_4 + COT\text{-}H_2 \quad (1)$$

$$1,2\text{-}W_2Cp_2(NMe_2)_4 + \text{excess } Bu^tSH \rightarrow \textit{anti}\text{-}1,2\text{-}W_2(SBu^t)_2(NMe_2)_4 + 2CpH \quad (2)$$

The selective removal of COT from $W_2COT(NMe_2)_4$ has not been observed during alcoholysis reactions with MeOH, EtOH, Pr^nOH, Bu^tCH_2OH, Pr^iOH, or Bu^tOH [4,5]. However, preliminary studies of alcoholysis of this precursor with 2,4,6-$Me_3C_6H_2OH$ or *p*-Bu^t-calix[4]arene have indicated the incomplete removal of NMe_2 ligands [18]. It is likely that the more acidic phenolic compounds, and also thiols, tend to attack the weaker M–C bonds first, and only further replace the dimethylamide ligands if the ditungsten unit in the initial product is sterically accessible to incoming alcohol or thiol. For instance, *anti*-1,2-$W_2(SBu^t)_2(NMe_2)_4$ undergoes no further thiolysis despite the presence of a large excess of Bu^tSH. The resulting dithiolate is quite sterically crowded, as can be seen in Fig. 3. Perhaps no good mechanism exists by which another thiol molecule can coordinate to the ditungsten center and transfer a proton to the remaining dimethylamide ligands.

4. Conclusions

Thiolysis of dimethylamido compounds does not give ditungsten Cp and COT compounds supported by thiolate ligands. Instead, these reactions give products resulting from loss of the carbocyclic ligands. The elimination of COT-H_2 (or COT) in the thiolysis of $W_2COT(NMe_2)_4$ contrasts with the results of alcoholysis of this precursor, but can be rationalized based on the relative acidity of the alcohols used in relation to Bu^tSH.

Supporting information

Structural data for *gauche*-1,2-(η^3-Cp)$_2$W$_2$(NMe$_2$)$_4$ and *anti*-1,2-$W_2(SBu^t)_2(NMe_2)_4$ have been deposited with the Cambridge Crystallographic Data Centre (CCDC), numbers 278721 and 280871, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, or by e-mailing deposit@ccdc.cam.ac.uk, or on the CCDC website at http://www.ccdc.cam.ac.uk.

Acknowledgment

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[18] M.H. Chisholm, C.B. Hollandsworth. In the reactions of $W_2COT(NMe_2)_4$ with four equivalents of 2,4,6-$Me_3C_6H_2OH$ or one equivalent of *p*-Bu^t-calix[4]arene no crystalline products have been obtained. However, ^{1}H NMR data for the crude product mixtures indicate incomplete alcoholysis due to the persistence of dimethylamide resonances (unpublished results).