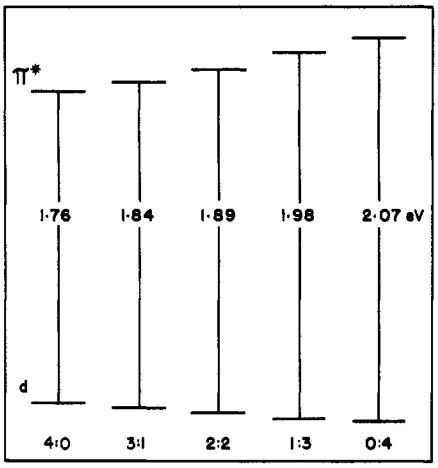

Figure 2. HOMO and LUMO levels for the $W(dcq)_n(mpic)_{4-n}$ series.

thylpicolinate ligands, the ligand π^* levels are high enough in energy that the MLCT transition energy values vary more than the $E^{\circ\prime}$ values. Smith and Schultz[12] had found only a small variation in the charge-transfer transitions of their S-donor complexes relative to the electrochemical potentials. However, their systems possess charge-transfer levels of the ligand-to-metal type rather than the metal-to-ligand variety; thus the LUMO and HOMO level changes appear to parallel each other in the S-donor species, unlike the present ones in which they move apart.

Acknowledgment. Partial support of this research by the Office of Naval Research is gratefully acknowledged. The help of Drs. Debra Rolison, David Venezky, and Marian Stankovich during various aspects of this study are also acknowledged with grateful appreciation.

Registry No. $W(mpic)_4$, 61805-72-9; $W(dcq)(mpic)_3$, 61805-73-0; $W(dcq)_2(mpic)_2$, 103301-97-9; $W(dcq)_3(mpic)$, 61880-51-1; $W(dcq)_4$, 33752-56-6; $W(mpic)_4^+$, 103202-97-7; $W(dcq)(mpic)_3^+$, 103202-98-8; $W(dcq)_2(mpic)_2^+$, 103202-99-9; $W(dcq)_3(mpic)^+$, 103203-00-5; $W(dcq)_4^+$, 47884-67-3.

Contribution from the Department of Chemistry,
University of Calgary, Calgary, Alberta, Canada T2N 1N4

An Oxotungsten(V) Dimer with Unusual Stereochemistry: Synthesis and Structure of *anti*-Bis(μ-2-methyl-1-propanethiolato)bis[oxodichloro(triphenylphosphine oxide)tungsten(V)]

Joanne M. Ball, P. Michael Boorman,* and John F. Richardson

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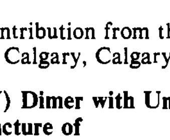
In contrast to the large variety of well-characterized oxomolybdenum(V) and -(VI) species of the types shown here (A–E), a more limited range of analogous compounds has been reported for tungsten.[1] Recent reports by Wieghardt and co-workers[2,3] described the first examples of compounds containing an anti M_2O_4 core (M = Mo, W), of type E. There are theoretical reasons[3] for speculating that the syn isomers of M_2O_4 systems, and those of related species such as M_2S_4, are more stable than the anti isomers. We are thus prompted to report the unexpected isolation and characterization of the title compound *anti*-$Cl_2O(Ph_3PO)W(\mu\text{-S-}i\text{-Bu})_2W(Ph_3PO)Cl_2O$ (**1**). This compound appears to be the first reported tungsten compound that contains the anti $OW(\mu\text{-X})_2WO$ moiety.

A



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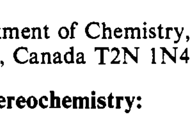
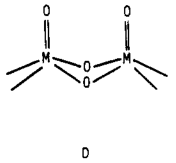
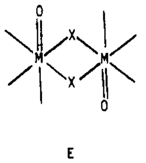


C



D



E

Table I. Crystallographic Parameters

formula	$C_{44}H_{48}Cl_4O_4P_2S_2W\cdot 1.6CH_2Cl_2$
fw	1412.4
space group	$P2_1/n$ (alt $P2_1/c$, No. 14)
a, Å	11.303 (3)
b, Å	14.229 (2)
c, Å	16.952 (4)
β, deg	98.67 (1)
vol, Å^3	2695 (1)
Z	2
D_c, g cm^{-3}	1.95
cryst descn	red, irregular blocks
cryst dimens, mm	0.24 × 0.35 × 0.40
radiation	Mo Kα (λ = 0.71069 Å, graphite monochromator)
temp, °C	21 (1)
scan range ($\Delta\omega$), deg	$1.5(0.80 + 0.347 \tan \theta)$
scan speed, deg min^{-1}	3.4–0.7
max Θ, deg	25
octants collected	$+h,-k,\pm l$
no. of unique data collected	4734
no. of obsd data ($I > 3\sigma(I)$)	3556
μ(Mo Kα), cm^{-1}	50.8
min, max abs cor	0.67, 1.37
no. of variables in final cycle	285
GOF	1.17
weighting formula	$[\sigma^2(F_o) + 0.00001(F_o^2)]^{-1}$
isotropic ext parameter	1.4 (4) × 10^{-5}
R, R_w[a]	0.048, 0.051

[a] $R = \sum(\|F_o\| - \|F_c\|)/\sum\|F_o\|$; $R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$.

Experimental Section

Synthesis. In an attempt to prepare a heterobimetallic μ-thiolato complex containing a $W^{IV}(\mu\text{-SR})_2Cu^I$ moiety, a stirred solution of $WCl_4(Me_2S)_2$ (1 g) in CH_2Cl_2 (30 mL) was reacted with 2 molar equiv of $Pb(S\text{-}i\text{-Bu})_2$ under an atmosphere of dry nitrogen. After the heterogeneous mixture was stirred for 15 min, 1 molar equiv of Cu(I) was added, in the form of the complex $[CuCl(Ph_3P)]_4$. After the $PbCl_2$ (produced in the initial metathesis reaction between $WCl_4(Me_2S)_2$ and $Pb(S\text{-}i\text{-Bu})_2$) was filtered off, the solution was reduced in volume to ~10 mL and allowed to stand at room temperature for 48 h. Red crystals were formed that appeared from the infrared spectrum to contain terminal oxo groups, W–Cl bonds, and probably Ph_3P. In view of the small quantities of the product and the inferred incorporation of Cu–PPh_3 entities, we undertook an X-ray crystal structure determination which showed that the crystals were, in fact, the unexpected compound **1**, rather than a compound containing the target moiety, $W(\mu\text{-S-}i\text{-Bu})_2Cu$.

IR spectrum of **1** (Nujol mull between CsI plates) (cm^{-1}): 1590 (w), 1270 (m), 1245 (w), 1160 (w), 1120 (s) (ν(P=O)), 1100 (sh), 1060 (s), 1030 (w), 1000 (w), 970 (s) (ν(W=O)), 940 (sh), 750 (s), 730 (s), 690 (s), 535 (s), 520 (m, sh), 450 (w), 405 (w), 330 (w) [308 (m), 290 (sh), 280 (m) (ν(W–Cl))].

X-ray Analysis. The crystal data and experimental details are given in Table I. The crystal chosen for data collection was an irregular block cut from a larger sample and sealed in a glass capillary under nitrogen. Cell constants and orientation matrices were determined by least-squares refinement of the diffraction geometry for 25 accurately centered reflections ($15 < \theta < 19°$). The choice of space group $P2_1/n$ is unam-

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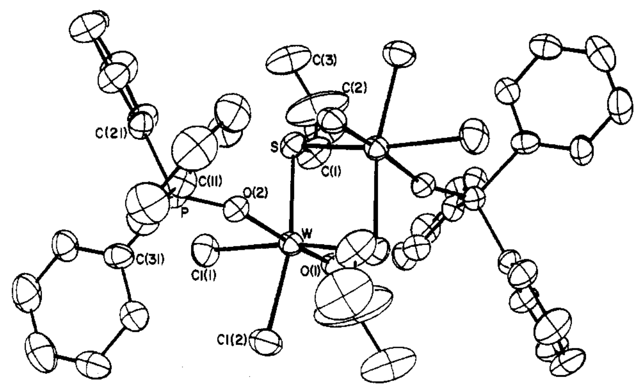

Figure 1. ORTEP view of the structure of *anti*-$Cl_2O(Ph_3PO)W(\mu$-S-*i*-Bu$)_2W(Ph_3PO)Cl_2O$ (**1**), showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

biguous. Data were collected on an Enraf-Nonius CAD4F automated diffractometer by using the ω-2θ scan technique. The data were corrected for background, Lorentz, and polarization effects as well as crystal decay (average drop in intensity of 23% for three standard reflections, probably due to solvent loss).[4] The data were corrected for absorption by using an empirical method (DIFABS)[5] to account for irregular crystal shape, grease, and capillary. Details concerning data collection and reduction can be found in ref 6.

Atomic scattering factors for non-hydrogen atoms were those of Cromer and Mann,[7] the H scattering factors were taken from ref 8, and real and anomalous dispersion corrections were applied to all non-hydrogen atoms.[9] The structure was solved by using the Patterson method to find the W atom, followed by difference Fourier syntheses. Refinement was carried out by block-diagonal least-squares techniques based on F, minimizing the function $\sum w(|F_o| - |F_c|)^2$. All H atoms, with the exception of those on the CH_3 groups, were readily located on a difference Fourier map. These were included in calculated positions with isotropic thermal parameters set to 1.1 × B_{equiv} of the bonded atom, but not refined. In the final cycles the occupancy factor for the CH_2Cl_2 solvate was set to 0.8 (average refined value for C(5), Cl(3), and Cl(4)) and all non-H atoms, with the exception of C(5) of the solvate, were refined anisotropically. The model converged with maximum shift/error of 0.3 (U_{22} of C(2)) and an average shift/error of 0.02.

Results and Discussion

Structure of 1. The edge-sharing bioctahedral structure of **1** is shown in Figure 1. The positional parameters for all non-hydrogen atoms are given in Table II, with selected bond length and bond angle data in Table III. The structure is centrosymmetric, as crystallographically required, and therefore possesses the very unusual feature of the terminal oxo ligands lying in an anti disposition to one another. Of necessity, the μ-S-*i*-Bu groups also have the *i*-Bu groups in an anti configuration. The selected bond lengths and angles in Table III indicate that there is a weak W–W bond. The W–W bond length (2.979 (1) Å) compares with a W–W distance of 2.791 (1) Å for $W_2S_2(S_2CNEt_2)_2(OMe)_4$[10] (regarded as "bonding") and 3.814 (1) Å for W_2Cl_{10} in which a metal–metal repulsion has been shown.[11] The acute W–S–W bond angle in **1** (75.3 (1)°) is a good indicator for an attractive interaction. A concomitant increase in the S–W–S′ bond angle (104.7 (1)°) is observed. In a "pure" bioctahedral structure both W–S–W′ and S–W–S′ angles would be 90°. However, the O(1)–W–O(2) bond angle (175.7 (3)°) is certainly not indicative of a very strong metal–metal attraction, since under these circumstances the axial ligands are normally pushed away from the metal–metal vector.[12] The W=O$_t$ bond distance is sensitive to, and influences, the ligand trans to it. In this case Ph_3PO is the

Table II. Positional (×10^4) and B_{equiv} (×10) Parameters for Non-Hydrogen Atoms of *anti*-$Cl_2O(Ph_3PO)W(\mu$-S-*i*-Bu$)_2W(Ph_3PO)Cl_2O$

atom	*x*	*y*	*z*	B_{equiv}
W	4500.2 (5)	4610.44 (3)	4203.7 (3)	25.5 (2)
Cl(1)	2708 (3)	3817 (2)	3608 (2)	40 (2)
Cl(2)	5275 (3)	4120 (2)	3019 (2)	42 (2)
S	3486 (3)	4783 (2)	5364 (2)	30 (1)
P	4995 (3)	2225 (2)	4805 (2)	24 (1)
O(1)	4084 (7)	5713 (5)	3864 (4)	32 (4)
O(2)	5037 (7)	3285 (5)	4714 (4)	26 (4)
C(1)	2386 (13)	5713 (9)	5102 (8)	50 (8)
C(2)	1565 (21)	5924 (16)	5617 (13)	129 (10)
C(3)	1289 (15)	5354 (13)	6258 (9)	79 (10)
C(4)	621 (14)	6670 (12)	5250 (10)	71 (10)
C(11)	3960 (11)	1870 (8)	5439 (6)	26 (6)
C(12)	4246 (12)	1203 (9)	6026 (7)	35 (7)
C(13)	3426 (14)	925 (10)	6503 (8)	44 (8)
C(14)	2317 (14)	1312 (11)	6402 (8)	52 (9)
C(15)	2001 (12)	1994 (11)	5823 (9)	51 (9)
C(16)	2825 (12)	2275 (9)	5344 (7)	35 (7)
C(21)	6423 (10)	1784 (8)	5247 (6)	24 (6)
C(22)	6988 (12)	1080 (9)	4898 (7)	32 (6)
C(23)	8069 (14)	719 (10)	5281 (8)	49 (8)
C(24)	8576 (13)	1073 (11)	6025 (8)	47 (8)
C(25)	7974 (13)	1772 (10)	6367 (7)	39 (7)
C(26)	6910 (12)	2128 (9)	5990 (7)	35 (7)
C(31)	4570 (12)	1643 (8)	3861 (6)	30 (6)
C(32)	5274 (12)	1803 (9)	3277 (7)	36 (7)
C(33)	4973 (13)	1382 (10)	2533 (7)	42 (7)
C(34)	4007 (15)	806 (10)	2402 (8)	48 (8)
C(35)	3303 (13)	631 (10)	2989 (9)	48 (8)
C(36)	3598 (12)	1058 (9)	3719 (7)	33 (6)
C(5)	9312 (19)	1618 (14)	2502 (11)	80 (6)
Cl(3)	10574 (6)	2153 (6)	2909 (4)	116 (5)
Cl(4)	8329 (7)	1361 (5)	3026 (5)	141 (6)

Table III. Selected Bond Distances (Å) and Angles (deg) for *anti*-$Cl_2O(Ph_3PO)W(\mu$-S-*i*-Bu$)_2W(Ph_3PO)Cl_2O$

	Distances		
W–W	2.979 (1)		
W–Cl(1)	2.404 (3)	W–Cl(2)	2.412 (3)
W–S	2.434 (3)	W–S′	2.442 (3)
W–O(1)	1.712 (7)	W–O(2)	2.124 (7)
P–O(2)	1.518 (7)	P–C(11)	1.778 (13)
P–C(21)	1.788 (11)	P–C(31)	1.802 (11)
S–C(1)	1.824 (14)	C(1)–C(2)	1.40 (3)
C(2)–C(3)	1.43 (3)	C(2)–C(4)	1.57 (3)
	Angles		
W–S–W	75.3 (1)	Cl(1)–W–Cl(2)	84.4 (1)
Cl(1)–W–S	85.2 (1)	Cl(1)–W–S′	168.7 (1)
Cl(2)–W–S	167.6 (1)	Cl(2)–W–S′	85.0 (1)
Cl(1)–W–O(1)	96.7 (3)	Cl(1)–W–O(2)	85.7 (2)
Cl(2)–W–O(1)	95.8 (3)	Cl(2)–W–O(2)	88.0 (2)
O(1)–W–S	92.3 (3)	O(1)–W–S′	88.5 (3)
O(2)–W–S	84.3 (2)	O(2)–W–S′	89.7 (2)
O(1)–W–O(2)	175.7 (3)	S–W–S′	104.7 (1)
W–S–C(1)	105.2 (5)	W′–S–C(1)	112.8 (5)
W–O(2)–P	155.8 (4)	O(2)–P–C(11)	112.2 (5)
O(2)–P–C(21)	110.6 (5)	O(2)–P–C(31)	112.0 (5)
S–C(1)–C(2)	120 (1)	C(1)–C(2)–C(3)	127 (2)
C(1)–C(2)–C(4)	112 (2)	C(3)–C(2)–C(4)	118 (2)

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trans ligand, and the $W{=}O_t$ distance is longer (1.712 (7) Å) than those observed (1.66 (1) Å) in structures with weakly bound μ-Cl ligands in the trans position, as found[13] in the ions $[Cl_2OW(\mu\text{-}Cl)(\mu\text{-}SR)_2WCl_2O]^-$. The oxo ligand nevertheless causes an apparent weakening of the $W\text{-}O(PPh_3)$ bond, which is longer (2.124 (7) Å) than that observed in $WOCl_3(Ph_3PO)_2$ (2.088 (11) Å)[14] and in $WSCl_3(Ph_3PO)_2$ (2.06 (1) Å).[15] The variation of $Mo{=}O$ bond lengths found in $MoOCl_3(Ph_3PO)_2$ is compatible with an interpretation of a trans influence of the oxo ligand in **1**, since $Mo{-}O(PPh_3)$ trans to $Mo{=}O$ is 2.136 (11) Å, while that trans to a terminal Cl is much shorter (2.065 (10) Å).[16] The geometry of the Ph_3PO ligand is normal and has dimensions P–O = 1.518 (7) Å, P–C = 1.79 Å (mean), and O–P–C = 107–112°. The W–O–P angle is 155.8 (4)°, and the complete set of data is consistant with those previously reported by Mabbs and co-workers[14] and by Garner and co-workers.[16]

The Cl_2S_2 unit is planar to within 0.03 Å, with the W atom lying 0.13 Å out of this plane, toward O(1). In the triply bridged anionic complexes $[Cl_2OW(\mu\text{-}Cl)(\mu\text{-}SR)_2WOCl_2]^-$ we observed a much greater deviation (0.38 Å),[13] which is indicative of weaker $W{=}O_t$ bonding in **1** and consistent with the comparative $W{=}O$ bond lengths described above.

Origin of 1. The isolation of **1** in the reaction described above is in itself of some interest, since the Ph_3PO must have originated from Ph_3P coordinated to a Cu^I center. The abstraction of oxygen from metal centers by Ph_3P is well documented,[17] and it seems likely that the Ph_3PO arose in this way. It requires only very minute quantities of adventitious oxygen to yield oxotungsten complexes, and these tend to crystallize from solution much more quickly than the target complexes. Hence, the likely pathway here was the oxidation of W^{IV} to a W^{VI} dioxo species, followed by reaction with free Ph_3P (derived from the dissociation of $[CuCl(Ph_3P)]_4$). The catalytic oxidation of Ph_3P at the copper center cannot be excluded as another possible mechanism. The dimerization of $W(SR)_n$ complexes is a facile reaction, and indeed isolation of terminal thiolato–tungsten complexes has been shown to be very difficult, unless hindered thiols are used.

Anti (O)W(μ-SR)$_2$W(O) Stereochemistry. There seems to be general agreement in the literature that syn $[Mo_2O_4]^{2+}$ and $[Mo_2S_4]^{2+}$ cores are intrinsically more stable than their anti isomers.[3] Factors such as enhanced Mo–Mo bonding interactions[18,19] and diminished $O_t\cdots O_b$ interactions[20] have been cited to explain this apparent preference for the syn isomer. Hence, the anti geometry of **1**, which has a $OM(\mu\text{-}S)_2MO$ core, would not be expected to be stable. The most likely reason for the centrosymmetric anti structure being found for **1** would seem to be steric crowding, which the two Ph_3PO ligands would generate if they were mutually syn. The crowding is accentuated by the *i*-Bu groups of the bridging thiolates, and as Figure 1 shows, the anti configurations of these two groups interact minimally with the phenyl groups of the mutually anti Ph_3PO ligands. Steric factors of this type have been invoked previously to account for structural stabilities in $[L_2Mo_2O_4]^{2+}$ and related oxomolybdenum cores.[21,22]

Acknowledgment. Financial support of this work by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Registry No. 1, 102942-32-5; $WCl_4(SMe_2)_2$, 53922-82-0.

Supplementary Material Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, complete bond lengths and bond angles, and least-squares plane data (5 pages). Ordering information is given on any current masthead page.

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Contribution from RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama, 351-01 Japan

X-ray Crystal Structure of $Pd_2Cl_2(2,6\text{-}Me_2C_6H_3NC)_2(py)_2$. Unusual C-N-C Bond Angles and Infrared Spectrum in Bridging Isocyanide Groups[1]

Yasuhiro Yamamoto* and Hiroshi Yamazaki

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In the infrared spectrum of the transitional-metal complexes of isocyanides, the terminal NC stretching frequencies generally appear above 1900 cm^{-1}[1,2] but in some complexes the NC absorption occurs at ca. 1820 cm^{-1}, $Ru(t\text{-}BuNC)_5$ (1815 cm^{-1})[3] and $Fe(t\text{-}BuNC)_5$ (1830 cm^{-1}).[3] The low frequencies result from the bending of the NC bond, which is a reflection of a higher back-bonding. For example, the solid-state structure of $Fe(t\text{-}BuNC)_5$ shows substantial bending at the nitrogen atoms (mean value 134 (2)°). For a bridging isocyanide coordinated to two or more metals, the NC stretching frequencies of the M–M bridging ligand range from 1880 to 1580 cm^{-1}.[2]

We report the synthesis and X-ray crystal structure of $Pd_2Cl_2(2,6\text{-}Me_2C_6H_3NC)_2(py)_2$. As described below, this presents an interesting structural feature, including a unique linear bridging C–N–C bond.

The reaction of $Pd_2Cl_2(2,6\text{-}Me_2C_6H_3NC)_4$ (**1**)[4] with pyridine (py) gave orange crystals, formulated as $Pd_2Cl_2(2,6\text{-}Me_2C_6H_3NC)_2(py)_2$ (**2**). The infrared spectrum of **2** in KBr shows two absorption peaks at 2056 (s) and 1976 cm^{-1}, which are lower in energy by ca. 200–130 cm^{-1} from those for **1**. The ^1H NMR spectrum shows a peak at δ 2.52 due to *o*-methyl groups, compared with that (δ 2.53) of **1**.

Although the infrared and ^1H NMR spectroscopic data indicate the presence of terminal isocyanide groups, an X-ray analysis of **2** confirms the presence of two μ-bridging isocyanide ligands. A metal–metal bond joins the two palladium atoms and is bridged by two isocyanide ligands (Figure 1). The palladium geometry (ignoring the metal–metal bond) may be apparently described as square planar. A dihedral angle between the two planes consisting of the metal and two bridging carbons is ca. 129.7 (5)°, compared with the corresponding bridge plane–bridge plane angle (127.5°) in $Co_2(CO)_8$[5] and being smaller than that found in $Co_2(t\text{-}BuNC)_8$.[6] The Pd–Pd bond length is 2.662 (1) Å, longer than those found in the unbridging complexes $[Pd_2(MeNC)_6]^{2+}$ (2.5310 (9) Å),[7] $Pd_2Cl_2(t\text{-}BuNC)_4$ (2.532 (2) Å,[4] and $Pd_2I_2(MeNC)_4$ (2.533 (1) Å)[8] and shorter than the Pd–Pd bond distances (2.734 Å) found

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