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Evidence for Photodisproportionation of d^1–d^1 Dimers $[(MO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (M = Mo, W) Containing Linear Oxo Bridges and for Oxygen Atom Transfer from $[WO_2\{S_2CN(CH_2Ph)_2\}_2]$ to PEt_3

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The d^1–d^1 dimer $[(MoO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (**4**), containing a linear oxo bridge, is photosensitive, and the equilibrium disproportion of **4** to $[MoO\{S_2CN(CH_2Ph)_2\}_2]$ (**8**) and $[MoO_2\{S_2CN(CH_2Ph)_2\}_2]$ (**9**) is displaced toward the disproportionation products under ambient lighting. Tungsten analogues of **4** and **9** have been prepared by controlled oxidation of $[W(CO)_3\{S_2CN(CH_2Ph)_2\}_2]$ (**10**) (prepared from $Na[S_2CN(CH_2Ph)_2]$ and $[W(CO)_4Cl_2]$ at −78 °C)—prolonged exposure of **10** to O_2 in THF gives $[WO_2\{S_2CN(CH_2Ph)_2\}_2]$ (**6**), while limited exposure to O_2 in CH_2Cl_2 followed by slow reduction in the polarity of the medium precipitates $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (**5**). The dimer **5** crystallizes in the monoclinic space group $P2_1/n$ with a = 11.738 (4) Å, b = 21.291 (7) Å, c = 13.819 (5) Å, β = 99.83 (3)°, D_{calc} = 1.635 g cm^{-3}, and Z = 2. Diffraction analysis (R_{wF} = 3.94%) establishes that the dimer contains a linear oxo bridge, and that the terminal oxo groups in the W_2O_3 core have an anti orientation. Prolonged oxidation (14 h in CH_2Cl_2) converts **5** to **6**, but the reaction is accelerated (1 h) by long-wavelength irradiation (λ > 515 nm). Electronic spectra show that the d^1–d^1 dimer **5** photodissociates under ambient lighting. The W(VI) dioxo complex can be reduced by PEt_3 to a W(IV) oxo complex, isolated as the PEt_3 adduct $[WO(PEt_3)\{S_2CN(CH_2Ph)_2\}_2]$ (**7**).

Introduction

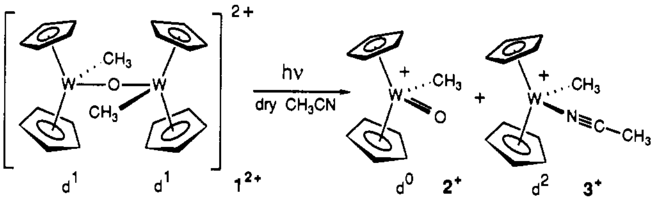
Bridging oxo groups are found in many complexes containing oxo metal functional groups,[1] and when there is a single bridging atom, M–O–M groups often have linear geometries indicative of strong π interactions. If the metal centers have odd electron centers, such π interactions can allow spin pairing, and in the case of d^1–d^1 complexes containing the common M_2O_3 functional group, for example, all except $Mo_2O_3(TPP)_2$[2] (TPP = tetraphenylporphyrin) are diamagnetic[1a] and most can be described by variations of the Dunitz–Orgel model of bridge bonding[3] first advanced to account for the diamagnetism of $[Cl_5RuORuCl_5]^{4-}$.

We have recently observed that the diamagnetic W(V) complex $[\{W(\eta\text{-}C_5H_5)_2(CH_3)\}_2O]^{2+}$ (1^{2+}), containing a linear d^1–d^1 oxo bridge, photodisproportionates in acetonitrile to the W(VI) oxo complex $[W(\eta\text{-}C_5H_5)_2(O)(CH_3)]^+$ (2^+) and the W(IV) acetonitrile complex $[W(\eta\text{-}C_5H_5)_2(NCCH_3)(CH_3)]^+$ (3^+) (Scheme I).[4] There is only one prior report of photodisproportionation of a linear oxo bridge—Richman observed[5] that irradiation of $[\{Fe(TPP)\}_2O]$, containing a d^5–d^5 linear oxo bridge, in the presence of PPh_3 gives $OPPh_3$ and (in benzene) $[Fe(TPP)(PPh_3)]$, with a low quantum yield (Φ_{410} for $[Fe(TPP)(PPh_3)]$ production is 1×10^{-4}).

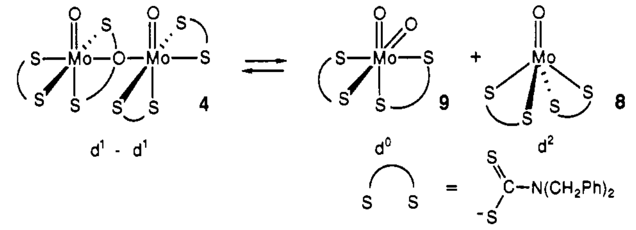
Like other d^1–d^1 complexes containing linear oxo bridges $\mathbf{1}^{2+}$ is an intense purple color, and photodisproportionation therefore results in marked photochromism. It is well established by studies of dithiocarbamato complexes containing the $Mo^V{}_2O_3$ core[6] that d^1–d^1 complexes containing linear oxo bridges can undergo equilibrium *thermal* disproportionation as shown in Scheme II, and it occurred to us that photodisproportionation of d^1–d^1 complexes containing linear oxo bridges might constitute a thermally reversible photochromic reaction with potential technical applications.

This has led us to explore the chemistry and photolysis of other systems containing d^1–d^1 linear oxo bridges, including classic molybdenum thiocarbamate complexes of the type shown in Scheme II and their tungsten analogues. We now wish to report that the molybdenum dithiocarbamate complex $[(MoO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (**4**) does indeed undergo thermally reversible photodisproportionation, that tungsten analogues of two of the three molybdenum oxo complexes shown in Scheme II can be prepared as shown in Scheme III, that the W(V) oxo-bridged dimer $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (**5**) has a linear oxo bridge and an anti geometry for the $(WO)_2O$ moiety, that **5** undergoes photoaccelerated oxidation to $[WO_2\{S_2CN(CH_2Ph)_2\}_2]$ (**6**), and that it has been possible for the first time to transfer an oxygen atom from a W(VI) dioxo complex (**6**) to an alkylphosphine to give a W(IV) oxo complex, trapped by excess phosphine as $[WO(PEt_3)\{S_2CN(CH_2Ph)_2\}_2]$ (**7**) (Scheme III).

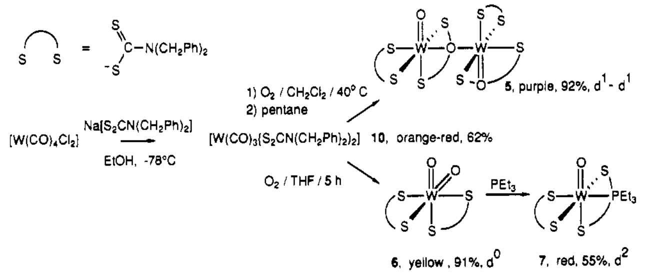
Scheme I



Scheme II



Scheme III



Experimental Section

General Data. All manipulations were carried out under a dry, oxygen-free nitrogen atmosphere. Solvents were freshly distilled under nitrogen from appropriate drying agents as follows: sodium benzophenone

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[†] University of Pittsburgh.

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(1) (a) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (b) Holm, R. H. *Coord. Chem. Rev.*, in press.

(2) Johnson, J. F.; Scheidt, W. R. *Inorg. Chem.* **1978**, *17*, 1280.

(3) Dunitz, J. D.; Orgel, L. E. *J. Chem. Soc.* **1953**, 2594.

(4) Jernakoff, P.; Fox, J. R.; Lee, S.; Cooper, N. J. in preparation for *J. Am. Chem. Soc.*

(5) (a) Richman, R. M.; Peterson, M. W. *J. Am. Chem. Soc.* **1982**, *104*, 5795. (b) Peterson, M. W.; Rivers, D. S.; Richman, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 2907.

(6) (a) Matsuda, T.; Tanaka, K.; Tanaka, T. *Inorg. Chem.* **1979**, *18*, 454. (b) Barral, R.; Bocard, C.; de Roch, I. S.; Sajus, L. *Tetrahedron Lett.* **1972**, 1693.

(7) Anker, M. W.; Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1967**, *20*, 9.

ketyl for diethyl ether, tetrahydrofuran (THF), and benzene; $LiAlH_4$ for pentane; CaH_2 for CH_2Cl_2. ^1H and ^{13}C NMR spectra were recorded on a Brucker AF 300 spectrometer. Irradiation with light of wavelength greater than 515 nm was achieved by means of a 200-W Oriel Mercury (Xenon) arc lamp in combination with a Swift 3-70 cutoff filter. Infrared spectra were recorded on a Perkin-Elmer 783 spectrometer or on an IBM IR/32 spectrometer. Electronic spectra were recorded under N_2 on a Perkin-Elmer Lambda 3B UV/vis spectrophotometer. Microanalyses were performed as indicated by Multichem Laboratories, Lowell, MA (Mul) or Dornis u. Kolbe, Mülheim a. d. Ruhr, FRG (DK).

Reagents. The thiocarbamate salt $Na[S_2CN(CH_2Ph)_2]$ was prepared according to a literature procedure.[8] A literature method[8] was adapted to prepare $[(MoO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ from Na_2MoO_4, and $[MoO_2\{S_2CN(CH_2Ph)_2\}_2]$ was prepared by an adaptation of a literature method.[9] Dimethylphenylphosphine and triethylphosphine were used as received from Aldrich. Tungsten hexacarbonyl was used as purchased from Pressure Chemical Co. Tetracarbonyltungsten dichloride was prepared by a modification of the literature method[7] in which $[W(CO)_6]$ was stirred with 1 equiv of Cl_2 for 2 h in CH_2Cl_2 at −78 °C and the resulting yellow solids were thoroughly washed with cold CH_2Cl_2. Oxygen used was "extra dry" grade from Linde.

Preparation of $[W(CO)_3\{S_2CN(CH_2Ph)_2\}_2]$. A yellow solution of $[W(CO)_4Cl_2]$ (7.20 g, 19.42 mmol) in ethanol (100 mL) chilled to −78 °C was added to a stirred yellow solution of $Na[S_2CN(CH_2Ph)_2]$ (11.47 g, 38.83 mmol) in ethanol (100 mL) at −78 °C to give an orange precipitate and a dark red solution. After 2 h, the stirred solution was warmed to room temperature and stirred for a further 0.5 h. The orange solids were collected on a 5-cm pad of Celite 545 on a 5-cm filter frit, and the pad was washed with ethanol (3 × 100 mL). The orange material was dried under vacuum for 12 h and then extracted into CH_2Cl_2 (3 × 100 mL) to give a dark red solution. The solution was concentrated under reduced pressure to ca. 50 mL and then stirred under a carbon monoxide atmosphere for 30 min. Pentane (150 mL) was added and the solution cooled under CO to −78 °C over 24 h to yield orange-red crystalline $[W(CO)_3\{S_2CN(CH_2Ph)_2\}_2]$, which was collected by decantation, washed with pentane (2 × 20 mL), and dried in vacuo (9.80 g, 12.06 mmol = 62%). Anal. Calcd for $C_{33}H_{28}N_2O_3S_4W$: C, 48.77; H, 3.47; N, 3.45. Found (Mul): C, 48.28; H, 3.52; N, 3.42. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.35–7.26 (c, 20 H, 4 C_6H_5), 4.85 (s, 8 H, 4 CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.45 MHz): δ 232.34 (s, CO), 211.38 (s, CS_2), 134.02, 129.05, 128.33, 128.2 (all s, C_6H_5), 50.86 (s, CH_2). IR (Nujol mull, CsI): 2016 (s), 1929 (s), 1898 (s), 1887 (m), 1603 (vw sh), 1483 (vs sh), 1460 (vs), 1439 (vs), 1217 (s sh), 1148 (mw sh), 1080 (mw), 1028 (w), 1003 (mw sh), 934 (mw sh), 885 (w sh), 749 (s sh), 698 (vs), 631 (mw), 569 (mw sh), 515 (ms), 484 (m), 424 (vw) cm^{-1}.

Preparation of $[WO_2\{S_2CN(CH_2Ph)_2\}_2]$. Oxygen saturated with THF was bubbled through a solution of $[W(CO)_3\{S_2CN(CH_2Ph)_2\}_2]$ (1.01 g, 1.24 mmol) in THF (150 mL) for 5 h in the absence of light. After the orange solution had turned purple and then yellow, the volatiles were removed under reduced pressures. The yellow residues was extracted into benzene (50 mL) and filtered. The resulting yellow solution was decreased in volume to ca. 15 mL under reduced pressure, and ether was added (50 mL). The solvent mixture was allowed to stand at ambient temperature for 24 h in the absence of light to yield yellow distorted cubes of analytically pure $[WO_2\{S_2CN(CH_2Ph)_2\}_2]$. The crystals were collected by decantation, washed with ether (3 × 10 mL), and dried in vacuo (0.86 g, 1.13 mmol = 91%). Anal. Calcd for $C_{30}H_{28}N_2O_2S_4W$: C, 47.37; H, 3.71; N, 3.68. Found (DK): C, 47.45; H, 3.76; N, 3.95. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.37–7.27 (c, 20 H, 4 C_6H_5), 4.87 (s, 8 H, 4 CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.45 MHz): δ 200.95 (s, CS_2), 133.15, 129.21, 128.75, 128.3, (all s, C_6H_5), 53.76 (s, CH_2). IR (Nujol mull, CsI): 1603 (vw sh), 1502 (vs), 1482 (vs), 1443 (vs), 1358 (m), 1318 (vw), 1254 (mw), 1221 (s sh), 1206 (ms), 1156 (mw), 1136 (m), 1080 (m), 1030 (vw), 984 (s), 939 (vs), 893 (vs), 824 (vw), 741 (vs sh), 698 (vs), 629 (ms), 610 (vw), 548 (ms sh), 521 (s), 444 (vw), 413 (m) cm^{-1}.

Preparation of $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]\cdot 2CH_2Cl_2$. An orange solution of $[W(CO)_3\{S_2CN(CH_2Ph)_2\}_2]$ (6.00 g, 7.38 mmol) in CH_2Cl_2 (300 mL) was allowed to stir in oxygen at 40 °C for 90 min. Slow addition of pentane (850 mL) to the resulting deep red solution over 3 h yielded black/purple microcrystalline solids and a purple solution. The solids were collected by filtration, washed with CH_2Cl_2 (3 × 50 mL), and dried in vacuo (5.12 g, 3.40 mmol = 92%). Analytically pure materials could be obtained as black distorted cubes (ca. 80% recovery) from a saturated CH_2Cl_2 solution by addition of pentane (v/v = 1:3) in a darkened room. Anal. Calcd for $C_{62}H_{60}Cl_4N_4O_3S_8W_2$: C, 44.44; H, 3.61; N, 3.34. Found (DK): C, 44.61; H, 3.52; N, 3.78. ^1H NMR ($CDCl_3$ 300 MHz): δ 7.36–7.26 (c, 40 H, C_6H_5), 5.30 (s, 4 H, 2 CH_2Cl_2), 4.90 (br s, 16 H, CH_2). IR (Nujol mull, CsI): 1603 (vw sh) 1584 (vw), 1493 (vs), 1466 (vs), 1354 (m), 1259 (s sh), 1213 (s), 1145 (mw), 1080 (m), 1028 (w), 984 (m), 885 (w), 803 (vw), 752 (m), 730 (m), 699 (s), 628 (w), 554 (vw), 517 (m), 409 (m) cm^{-1}.

Table I. Summary of Crystal Data for $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]\cdot 2CH_2Cl_2$

formula	$C_{60}H_{56}N_4O_3S_8W_2\cdot 2CH_2Cl_2$	Z	2
fw	1675.33	μ(Mo Kα), cm^{-1}	40.09
space group	$P2_1/n$	D_{calc}, g cm^{-3}	1.635
		T, K	296
a, Å	11.738 (4)	λ(Mo Kα), Å	0.71073
b, Å	21.291 (7)	T_{max}/T_{min}	1.262
c, Å	13.819 (5)	R_F, R_{wF}, %	3.78, 3.94
β, deg	99.83 (3)		
V, Å^3	3403 (2)		

Oxidation of $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]$. Oxygen saturated with CH_2Cl_2 was bubbled through a solution of $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (0.054 g, 0.036 mmol) in CH_2Cl_2 (100 mL) for 14 h in the absence of light, while the mixture changed color from purple to light green-yellow. Addition of ether (30 mL) to the concentrated (7 mL) CH_2Cl_2 solution yielded 0.044 g (0.058 mmol = 81%) of $[WO_2\{S_2CN(CH_2Ph)_2\}_2]$, which was collected by filtration, washed with ether (3 × 5 mL), dried under vacuum, and identified by comparison of IR, ^1H NMR, and ^{13}C NMR spectra with those of an authentic sample.

The oxidation of $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ in CH_2Cl_2 with oxygen can be accelerated by irradiation at wavelengths longer than 515 nm. Thus oxygenation of an irradiated solution of $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (0.089 g, 0.059 mmol) in 150 mL of CH_2Cl_2 at room temperature for 1 h resulted in a color change from deep purple to light green-yellow, and addition of pentane (30 mL) to the concentrated (10 mL) CH_2Cl_2 solution yielded 0.076 g (0.099 mmol = 85%) of $[WO_2\{S_2CN(CH_2Ph)_2\}_2]$ as yellow irregular rectangular cubes. These were collected by filtration, washed with pentane (3 × 5 mL), dried under vacuum, and identified by comparison of IR, ^1H NMR, and ^{13}C NMR spectra with those of an authentic sample.

Preparation of $[WO(PEt_3)\{S_2CN(CH_2Ph)_2\}_2]$. Addition of PEt_3 (0.52 mL, 3.52 mmol) to a yellow solution of $[WO_2\{S_2CN(CH_2Ph)_2\}_2]$ (0.89 g, 1.174 mmol) in THF (80 mL) resulted in an immediate color change to red. After 7 h at 67 °C there was a deep red solution over white insoluble solids. The volatiles were removed under vacuum and the resulting red oil was extracted into 100 mL of ether. The red solution was passed through a 3-cm bed of Celite 545 on a 5-cm filter frit and the pad washed with ether (2 × 20 mL). Concentration of the solution to ca. 50 mL under vacuum, followed by addition of pentane (100 mL), gave red distorted cubic crystals. The crystals were collected by decantation, washed with pentane (3 × 30 mL), and dried under vacuum (0.56 g, 0.65 mmol = 55%). Anal. Calcd for $C_{36}H_{43}N_2PS_4W$: C, 50.11; H, 5.02. Found (Mul): C, 50.19; H, 4.86. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.46–7.26 (c, 20 H, 4 C_6H_5), 5.77–4.75 (c, 8 H, 4 CH_2), 3.6 (c, 6 H, excellent PANIC[11] simulation based on $\Delta\delta_{H_a,H_b} = 0.0833$, $J_{PH_a} = 15.7$ Hz, $J_{PH_b} = 9.8$ Hz, $J_{H_aH_b} = 16$ Hz, $J_{H_aH} = J_{H_bH} = 7.5$ Hz, PCH_aH_b), 1.06 (dt, $J_{PH} = 16$ Hz, $J_{HH} = 8$ Hz, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.45 MHz): δ 269.21 (s, CS_2 trans to PEt_3), 226.76 (s, CS_2 trans to O), 138.17–127.61 (c, C_6H_5), 59.59, 56.97, 52.02, 51.64 (all s, CH_2Ph) 18.59, (d, $J_{PC} = 26$ Hz, PCH_2), 8.10 (s, CH_3). IR (Nujol mull, CsI): 1603 (mw), 1585 (vw), 1493 (vs), 1480 (vs), 1441 (vs), 1425 (s), 1416 (s), 1365 (s), 1338 (vs), 1331 (vs), 1302 (vw), 1279 (m), 1233 (vs), 1178 (vw sh), 1147 (mw), 1138 (w), 1082 (m), 1040 (m), 1031 (m), 1011 (w), 995 (m), 970 (vw sh), 937 (vs sh), 911 (ms), 888 (vw sh), 845 (ms), 825 (vw), 816 (vw), 795 (vw), 769 (m), 754 (ms), 737 (s), 726 (m), 705 (s), 693 (ms sh), 666 (vw), 642 (vw), 619 (w), 606 (vw), 566 (vw), 552 (vw sh), 517 (m), 507 (m), 459 (vw), 430 (vw sh), 399 (w sh).

Collection of Diffraction Data for $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]\cdot 2CH_2Cl_2$. An essentially black crystal (0.28 × 0.18 × 0.32 mm) of the title compound was mounted on a glass fiber with epoxy cement. Axial photographs confirmed both the crystal quality and the axial lengths. Unit-cell parameters were determined through a least-squares fit of 25

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(8) Colton, R.; Scollary, G. R. *Aust. J. Chem.* **1968**, *21*, 1427.

(9) Moore, F.; Larson, M. *Inorg. Chem.* **1967**, *6*, 998.

(10) (a) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2612. (b) Newton, W. E.; Watt, G. D.; McDonald, J. W. *Proceedings of Climax 3rd International Conference on the Chemistry and Uses of Molybdenum*; Barry, H. F., Mitchell, P. C. H., Eds.; Climax Molybdenum Co.: Ann Arbor, MI; 1980; p 259. (c) Pandeya, K. B.; Waraich, T. S.; Gaur, R. C.; Singh, R. P. *J. Ind. Chem. Soc.* **1982**, *59*, 213.

(11) *Aspect 3000 NMR Software Manual*; Bruker Instruments: Billerica, MA, 1985.

Table II. Fractional Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[(\mathrm{WO}\{S_2CN(CH_2Ph)_2\}_2)_2O]\cdot CH_2Cl_2$

	x	*y*	*z*	*U*[a]
W	3573.3 (3)	116.6 (2)	412.2 (3)	35.8 (1)
S(1)	3436 (2)	−989 (1)	960 (2)	42.0 (8)
S(2)	2782 (2)	−672 (1)	−1103 (2)	44.5 (8)
S(3)	3181 (2)	1024 (1)	−687 (2)	46.2 (8)
S(4)	1469 (2)	379 (1)	217 (2)	45.2 (8)
O(1)	5000	0	0	49 (3)
O(2)	3934 (6)	359 (3)	1603 (5)	65 (3)
N(1)	2679 (5)	−1851 (3)	−432 (5)	40 (3)
N(2)	885 (6)	1222 (3)	−1252 (5)	42 (3)
C(1)	2937 (6)	−1256 (4)	−231 (6)	35 (3)
C(2)	2825 (7)	−2339 (4)	345 (7)	46 (3)
C(3)	2236 (7)	−2073 (4)	−1436 (7)	48 (3)
C(4)	1718 (6)	919 (4)	−646 (6)	37 (3)
C(5)	1125 (7)	1662 (4)	−2034 (7)	50 (3)
C(6)	−368 (7)	1065 (4)	−1284 (7)	46 (3)
C(11)	5004 (5)	−2482 (3)	647 (5)	70 (4)
C(12)	5997	−2839	626	80 (5)
C(13)	5900	−3453	268	80 (5)
C(14)	4812	−3710	−69	82 (6)
C(15)	3819	−3353	−47	66 (4)
C(16)	3916	−2739	311	51 (4)
C(21)	550 (5)	−2840 (2)	−1697 (5)	61 (4)
C(22)	−631	−2970	−1837	71 (4)
C(23)	−1424	−2482	−1830	72 (5)
C(24)	−1035	−1865	−1683	77 (5)
C(25)	146	−1735	−1543	63 (4)
C(26)	939	−2222	−1550	47 (3)
C(31)	639 (6)	2605 (3)	−1014 (4)	66 (4)
C(32)	141	3197	−968	88 (6)
C(33)	−429	3483	−1823	87 (6)
C(34)	−499	3179	−2724	81 (5)
C(35)	−1	2587	−2771	58 (4)
C(36)	568	2300	−1916	45 (3)
C(41)	−353 (3)	72 (2)	−2293 (2)	60 (4)
C(42)	−821	−302	−3091	83 (5)
C(43)	−1763	−86	−3764	92 (5)
C(44)	−2236	503	−3639	79 (5)
C(45)	−1767	877	−2840	62 (4)
C(46)	−826	661	−2167	47 (3)
C(50)	3821	159	6941	109 (6)
Cl(1)	2282	223	6674	130 (2)
Cl(2)	4484	335	6019	139 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Lengths (Å) and Angles (deg) within $[(\mathrm{WO}\{S_2CN(CH_2Ph)_2\}_2)_2O]$

W–S(1)	2.487 (2)	N(1)–C(1)	1.320 (10)
W–S(2)	2.720 (2)	N(1)–C(2)	1.484 (11)
W–S(3)	2.452 (2)	N(1)–C(3)	1.474 (11)
W–S(4)	2.502 (2)	N(2)–C(4)	1.340 (10)
W–O(1)	1.875 (1)	N(2)–C(5)	1.492 (12)
W–O(2)	1.708 (6)	N(2)–C(6)	1.501 (10)
S(1)–C(1)	1.746 (8)	C(2)–C(16)	1.545 (11)
S(2)–C(1)	1.719 (8)	C(3)–C(26)	1.537 (10)
S(3)–C(4)	1.742 (8)	C(5)–C(36)	1.529 (11)
S(4)–C(4)	1.717 (9)	C(6)–C(46)	1.515 (9)

S(1)–W–S(2)	67.6 (1)	C(2)–N(1)–C(3)	115.8 (6)
S(1)–W–S(3)	156.9 (1)	C(4)–N(2)–C(5)	123.2 (7)
S(2)–W–S(3)	90.4 (1)	C(4)–N(2)–C(6)	121.2 (7)
S(1)–W–S(4)	97.5 (1)	C(5)–N(2)–C(6)	115.0 (6)
S(2)–W–S(4)	81.6 (1)	S(1)–C(1)–S(2)	113.8 (4)
S(3)–W–S(4)	71.3 (1)	S(1)–C(1)–N(1)	122.6 (6)
S(1)–S–O(1)	94.3 (1)	S(2)–C(1)–N(1)	123.6 (6)
S(2)–W–O(1)	83.7 (1)	N(1)–C(2)–C(16)	111.0 (7)
S(3)–W–O(1)	89.9 (1)	N(1)–C(3)–C(26)	110.3 (7)
S(4)–W–O(1)	156.0 (1)	S(3)–C(4)–S(4)	113.2 (4)
S(1)–W–O(2)	90.6 (2)	S(3)–C(4)–N(2)	122.4 (6)
S(2)–W–O(2)	157.5 (2)	S(4)–C(4)–N(2)	124.3 (6)
S(3)–W–O(2)	110.4 (2)	N(2)–C(5)–C(36)	110.1 (7)
S(4)–W–O(2)	96.6 (2)	N(2)–C(6)–C(46)	111.1 (7)
O(1)–W–O(2)	104.2 (2)	C(2)–C(16)–C(11)	119.3 (4)
W–S(1)–C(1)	92.8 (3)	C(2)–C(16)–C(15)	120.7 (4)
W–S(2)–C(1)	85.8 (3)	C(3)—C(26)–C(21)	120.2 (4)
W–S(3)–C(4)	87.7 (3)	C(3)–C(26)–C(25)	119.7 (4)
W–S(4)–C(4)	86.7 (3)	C(5)–C(36)–C(31)	123.2 (4)
W–O(1)–W(A)	180.0 (1)	C(5)–C(36)–C(35)	116.8 (4)
C(1)–N(1)–C(2)	121.7 (7)	C(6)–C(46)–C(41)	121.1 (3)
C(1)–N(1)–C(3)	122.5 (7)	C(6)–C(46)–C(45)	118.8 (3)

intense reflections ($20 \le 2\theta \le 25°$). Data were collected on a Nicolet R3m/μ diffractometer with graphite monochromator and Mo Kα radiation ($\lambda = 0.71073$ Å). An empirical absorption correction (six reflections, ψ scan, 216 data, $T_{max}/T_{min} = 1.262$) was applied to the data prior to reduction. Of the 5764 reflections collected, 5345 were independent ($R_{int} = 2.17\%$), and 3665 reflections with $F_o \ge 5\sigma$ were considered observed. Table I contains an abbreviated list of crystallographic data.

Structure Solution and Refinement. The structure of $[(\mathrm{WO}\{S_2CN(CH_2Ph)_2\}_2)_2O]\cdot 2CH_2Cl_2$ was solved via a Patterson map that located the W atom. All other non-hydrogen atoms were located through subsequent Fourier difference maps and least-squares refinement cycles. Systematic absences in the diffraction data uniquely determined the monoclinic space group $P2_1/n$. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated as idealized isotropic contributions (d(C–H) = 0.960 Å; $U = 1.2U$ of the attached carbon atom) except for those in the solvent, which were ignored. All phenyl rings were constrained to rigid, planar hexagons (d(C–C) = 1.395 Å). The crystallographic asymmetric unit consists of half of the W complex (on a $\bar{1}$ site) and a molecule of CH_2Cl_2. With a data-to-parameter ratio of 11.4, the structure was refined to $R_F = 3.78\%$ ($R_{wF} = 3.94\%$); the largest peak on the final difference map, 0.854 e Å^{-3}, is located within the CH_2Cl_2 solvent molecule. Computer programs used in data collection and structure solution and refinement are from the SHELXTL[12] and P3 program libraries. Atomic scattering factors were taken from literature sources.[12,13] Table II lists atomic coordinates; bond lengths and angles are contained in Table III. Additional data are available as supplementary material.

Results and Discussion

Photodisproportionation of the Linear Oxo Bridge in $[(\mathrm{MoO}\{S_2CN(CH_2Ph)_2\}_2)_2O]$. Most of the known examples of linear oxo bridges between d^1 metal centers involve complexes of Mo(V), typically with dithiocarbamate, xanthate, thiophosphate or other bis-chelate sulfur ligands,[1] and since there are no literature reports on the photochemistry of such complexes, we began by examining the photolysis of $[(\mathrm{MoO}\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (**4**).[8] This was chosen because, although otherwise typical, this bis(benzyldithiocarbamato) complex is the only simple bis(alkyldithiocarbamato) complex of the $\mathrm{Mo^V}_2O_3$ core reported to have significant solubility in simple organic solvents.[8] Another attractive feature of this system is that the potential photodisproportionation products $[(\mathrm{Mo^{IV}O}\{S_2CN(CH_2Ph)_2\}_2]$[10b] (**8**) and $[(\mathrm{Mo^{VI}O_2}\{S_2CN(CH_2Ph)_2\}_2]$[10c] (**9**) are known compounds.

It was immediately apparent that **4** was indeed photosensitive—it was difficult to obtain consistent electronic spectra of the material, and the extinction coefficient in benzene of the major visible absorption at 519 nm depended markedly on the history of the sample. We were, however, able to establish that a solution handled in the dark had an initial ϵ_{519} of 19 000 M^{-1} cm^{-1}. This is larger than the reported ϵ_{519}[8] by a factor of 2.8, and since **4** would be expected to participate in the thermal disproportionation equilibrium shown in Scheme II the most reasonable interpretation is that **4** is photosensitive and that photodisproportionation in solution under ambient lighting results in a photostationary state to the right of the thermal equilibrium. A typical spectrum of **4** is shown in Figure 1.

The photosensitivity of **4** is so marked that the optical density at 519 nm of an unstirred solution of **4** in benzene decreased 11% when left in the spectrophotometer for 5 min. Thermal recombination is, however, rapid, and the optical density fully recovered when the cell was stirred in the dark for 10 min.

The extreme sensitivity of **4** precluded definitive determination of its optical spectrum, but we have satisfied ourselves that the dark value of 19 000 for ϵ_{519} is close to the true value and is not significantly influenced by thermal or photodisproportionation of

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(12) Sheldrick, G. M. *SHELXTL User's Manual, Issue 5.1*; Nicolet: Madison, WI, 1984.

(13) *International Tables for X-Ray Crystallography*; Ibers, J., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. IV, pp 72–98.

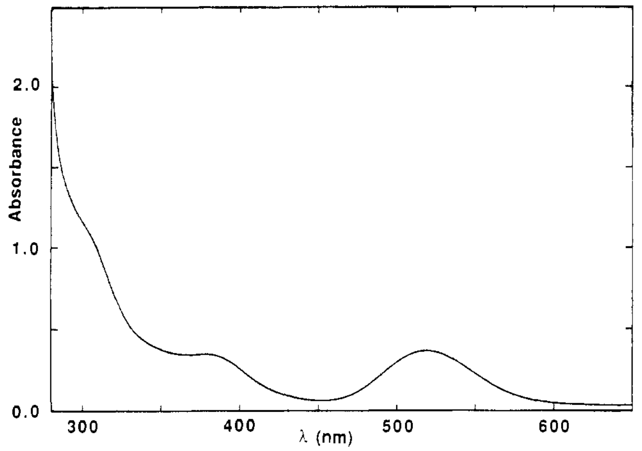

Figure 1. Electronic spectrum of a solution of $[(\mathrm{MoO}\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (**4**) in CH_2Cl_2 that had been handled in the dark.

4 by recording the spectrum of a solution, handled in red light, to which an equivalent of **9** had been added—this did not significantly affect the observed ϵ_{519}. A small equilibrium constant for the dissociation in Scheme II would be reasonable, given the reported values of 2.0×10^{-3} mol L^{-1} for R = Et in $ClCH_2CH_2Cl$ at 25 °C[6a] and 4.1×10^{-3} for R = Pr in chlorobenzene at 41 °C.[6b]

Preparation of $[W(CO)_3\{S_2CN(CH_2Ph)_2\}_2]$, a W(II) Precursor for W(VI) and W(V) Oxo Complexes. It was clear at this stage that the d^1–d^1 oxo-bridged dimer **4** was indeed subject to a photodisproportionation reaction analogous to that which we had observed for $\mathbf{1}^{2+}$ but that more detailed studies of the reaction would be limited by the rapidity of the thermal disproportionation equilibrium in Scheme II. This suggested that the analogous tungsten oxo-bridged dimer might be more amenable to quantification—if the thermal recombination reaction were slower, it would be straightforward to carry out quantum yield studies and determine the action spectrum (wavelength dependence of the quantum yield) of the complex.

Unfortunately, however, parallels between the oxo chemistry of tungsten and that of molybdenum are not well developed, and there are no sets of W(V), W(VI), and W(IV) oxodithiocarbamato complexes analogous to those in Scheme II.[1] Well-established reports of tungsten oxodithiocarbamate complexes are, in fact, limited to the three complexes $[WO_2(S_2CNR_2)_2]$ (R = Me, Et, *n*-Pr) reported in preliminary form by McDonald and co-workers[14,15] and to the report on $[WO_2(S_2CNR_2)_2]$ (R_2 = Me_2 and $(CH_2)_5$) by Yu and Holm, which appeared while this manuscript was in preparation.[18] We therefore set out to prepare such a set of complexes and again chose the *N*,*N*-dibenzyldithiocarbamato ligand with the hope that, as in the molybdenum case, this would enhance the solubility of the complexes, particularly of the target W(V) dimer $[(\mathrm{WO}\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (**5**).

Most preparations of *N*,*N*-dialkyldithiocarbamato complexes of Mo(V) dimers containing $\mathrm{Mo^V}_2O_3$ cores and of related complexes involve the reaction of $M[S_2CNR_2]$ salts with molybdate at controlled pHs and/or in the presence of reducing agents.[9,19–21] The reproducibility of these approaches has, however, been criticized,[22] and we therefore chose to approach the preparation of **5** by controlled oxidation of $[W(CO)_3\{S_2CN(CH_2Ph)_2\}_2]$ (**10**). The preparation of the molybdenum analogue of **5** by oxidation of $[Mo(CO)_3\{S_2CN(CH_2Ph)_2\}_2]$[8] suggested that **5** should be accessible from **10**, and Templeton's report[23] of IR evidence for the formation of **10** indicated that this should, in turn, be an accessible W(II) substrate.

Templeton's preparation of **10** involved addition of $Na[S_2CN(CH_2Ph)_2]$ to $[W(CO)_4I_2]$,[23] and other simple $[W(CO)_3(S_2CNR_2)_2]$ (R = Me, Et) complexes have been prepared from the corresponding bromide $[W(CO)_4Br_2]$.[24] The dichloride $[W(CO)_4Cl_2]$ is, however, more readily available than the bromide or the iodide,[7] and we therefore developed a new preparation of **10** by reaction of $Na[S_2CN(CH_2Ph)_2]$ with $[W(CO)_4Cl_2]$ in ethanol at −78 °C. The low temperature is critical to the success of the reaction—previous attempts to prepare dithiocarbamate complexes from $[W(CO)_4Cl_2]$ have been unsuccessful,[8] and this reflects the instability of $[W(CO)_4Cl_2]$ at ambient temperatures. The recrystallization was carried out under CO, but this is probably not essential since **10** has less tendency to lose a carbonyl than the analogous molybdenum complexes, which readily and reversibly form the dicarbonyls.[25]

Oxidation of $[W(CO)_3\{S_2CN(CH_2Ph)_2\}_2]$. Direct oxidation of **10** in THF over 5 h provided convenient access to the yellow W(VI) dioxo complex $[WO_2\{S_2CN(CH_2Ph)_2\}_2]$ (**6**) in 91% recrystallized yield. The composition of the complex was established analytically and spectroscopically as detailed in the Experimental Section, and the presence of two terminal W=O stretching absorptions in IR spectra at 939 (vs) and 893 (vs) cm^{-1} strongly suggests a cis orientation of the oxo groups such that they give rise to IR-active antisymmetric and symmetric stretching combinations.

The two previous reports of tungsten(VI) dioxodithiocarbamate complexes $[WO_2(S_2CNR_2)_2]$[14,18] involved a rather indirect approach in which W(II) complexes $[W(CO)_3(S_2CNR_2)_2]$ were oxidized by the Mo(V) oxo dimer $[(\mathrm{MoO}\{S_2P(OEt)_2\}_2)_2O]$. Oxygenation offers a simpler and more direct approach that would allow access to many analogues of **6**.

The observation of a purple color during oxidation suggested the intermediacy of the desired W(V) oxo-bridged dimer $[(\mathrm{WO}\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (**5**), and it proved possible to isolate this material in excellent (92%) yield by carrying out the oxidation in CH_2Cl_2 over a restricted period (90 min) and precipitating **5** by addition of pentane over 3 h. The high yield in this procedure is surprising, and we suspect that the reaction is mechanistically complex—the solubility of **5** in this low-polarity medium is very limited, and the **5** produced in the later stages may actually be formed by conproportionation of W(VI) oxidation products and W(II) starting material. The procedure as described in the Experimental Section does, however, give reproducible yields of **5**.

The dimer **5** was characterized analytically and spectroscopically as detailed in the Experimental Section—the most notable spectroscopic feature is the presence of a single W=O stretching absorption at 953 (s) cm^{-1} and a single W—O—W stretching absorption at 699 (s) cm^{-1}, consistent with the anti geometry observed (see below) for the W_2O_3 moiety.[26] The disappointing solubility of **5** in organic solvents (e.g. 0.1 g in 200 mL of CH_2Cl_2) made it impractical to obtain ^{13}C NMR spectra of the complex.

It is unlikely that the W(V) oxo-bridged dimer **5** is a necessary intermediate in the formation of the dioxo complex **6**, although it is true that **5** can be converted to **6** in good yield by prolonged (14 h) oxidation in CH_2Cl_2. Most interestingly, the reaction time can be drastically shortened (to 1 h) if the reaction mixture is irradiated, and we have established that the principal visible absorption of **5** at 517 nm is photoactive by using filters to cut

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(14) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chim. Acta.* **1976**, *19*, L67.

(15) Other reports by Lozano et al.[16] and by Brown et al.[17] have been shown to be at least partially incorrect,[18] and the electronic spectra claimed to be those of $[(\mathrm{WO}(S_2CNR_2)_2)_2O]$ complexes, for example,[16c] are inconsistent with those reported below for structurally characterized $[(\mathrm{WO}(S_2CN\{CH_2Ph\}_2)_2)_2O]$.

(16) (a) Lozano, R.; Doadrio, A. L.; Alarcon, E.; Roman, J.; Doadrio, A. *Rev. Chim. Mineral.* **1983**, *20*, 109. (b) Lozano, R.; Alarcon, E.; Doadrio, A. L.; Doadrio, A. *Polyhedron* **1983**, *2*, 435. (c) Lozano, R.; Alarcon, E.; Doadrio, A. *Polyhedron* **1984**, *3*, 25.

(17) Brown, D. A.; Glass, W. K.; Toma, H. J.; Waghorne, W. E. *J. Chem. Soc., Dalton Trans.* **1987**, 2531.

(18) Yu, S.-B.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 4385.

(19) Malatesta, L. *Gazz. Chim. Ital.* **1939**, *69*, 752.

(20) Jowitt, R. N.; Mitchell, P. C. H. *J. Chem. Soc. A* **1970**, 1702.

(21) Casey, A. T.; Mackey, D. J.; Martin, R. L.; White, A. H. *Aust. J. Chem.* **1972**, *25*, 477.

(22) Newton, W. E.; Corbin, J. L.; Bravard, D. C.; Searles, J. E.; McDonald, J. W. *Inorg. Chem.* **1974**, *13*, 1100.

(23) Templeton, J. L.; Ward, B. C. *Inorg. Chem.* **1980**, *19*, 1753.

(24) Broomhead, J. A.; Young, C. G. *Aust. J. Chem.* **1982**, *35*, 277.

(25) Colton, R.; Scollary, G. R.; Tomkins, I. B. *Aust. J. Chem.* **1968**, *21*, 15.

(26) Cotton, F. A.; Hunter, D. L.; Ricard, L.; Weiss, R. *J. Coord. Chem.* **1974**, *3*, 259.

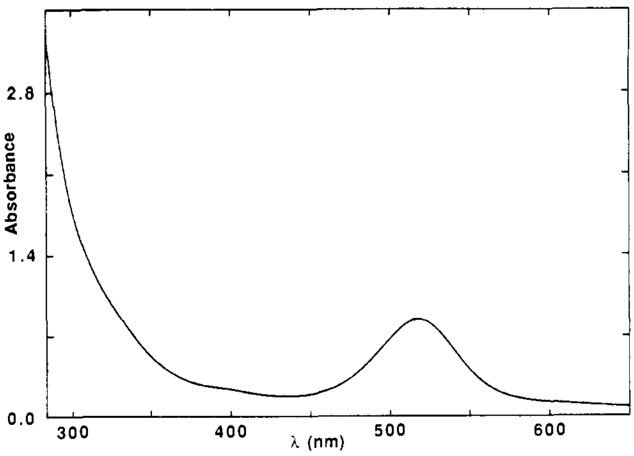

Figure 2. Electronic spectrum of a solution of $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (**5**) in CH_2Cl_2 that had been handled in the dark.

off radiation with $\lambda < 515$ nm.

The photoacceleration of the oxidation of **5** is most reasonably interpreted in terms of an initial photodisproportionation of **5** to **6** and a W(IV) oxo complex $[WO\{S_2CN(CH_2Ph)_2\}_2]$ (**11**) (which may form a solvent adduct—see section on reduction of **6** below) followed by direct oxidation of **11** (or its adduct) to **6**.

The photosensitivity of **5** was confirmed when we examined its optical spectrum (Figure 2). Although the general features of this spectrum are reproducible, the extinction coefficient for the major visible absorption at 517 nm is again highly dependent on sample history—samples that had been protected from ambient light and samples to which an equivalent of **6** had been added indicated a lower limit of 15000 for ϵ_{517}, but samples handled under ambient light more typically gave apparent values of 4000 for ϵ_{517}, suggestive of a photostationary state that was extensively dissociated.

Solid-State Structure of $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]$. Although there are many established examples of Mo(V) complexes containing M_2O_3 units, and six of these have been established crystallographically to contain linear oxo bridges,[27-32] there are only limited reports of analogous W(V) complexes containing M_2O_3 units,[16-18] and no examples have been structurally characterized. This led us to carry out a single-crystal X-ray diffraction study of **5** that established the molecular structure shown in Figure 3.

Complex **5** crystallizes in the $P2_1/n$ space group with two molecules in the unit cell. The bridging oxygen atom O(1) resides on a crystallographic inversion center ($^1/_2$, 0, 0), and half of the atomic coordinates were symmetry generated by inversion through this center. This leads to a W–O(1)–W(a) angle of 180° and an O(2)–W–W(a)–O(2a) torsion angle of 180°. The W atom has a distorted octahedral coordination environment, with cis angles ranging from 67.6 to 110.4° and trans angles ranging from 156.0 to 157.5°. The W═O and W—O bond lengths of 1.708 (6) and 1.875 (1) Å fit well with other reported values for metal-oxygen double and single bonds.[33] As observed for analogous Mo_2O_3 complexes with bis-chelate sulfur ligands[27-30] the M–S distances vary widely (2.487 (2) to 2.720 (2) Å)—this has been variously ascribed to trans effects[28] or steric interactions,[27] but an electronic explanation seems most probable.

The most interesting feature of the structure of **5** is the anti orientation adopted by the terminal oxo groups. The terminal oxo groups in the best known examples of complexes containing d^1–d^1 linear oxo bridges adopt syn orientations,[27,28] but more recent examples include both syn[29] and anti[30-32] orientations. An extended Hückel MO treatment has suggested that the angle between M═O terminal bonds in M_2O_3 units must be 0 or 180° if, in d^1–d^1 cases, the valence electrons are to be spin paired[28] (as in **5**), and in the case of **5** this is achieved by adopting the anti conformation with a 180° twist angle. The structure contrasts with that found in $[\{WO(neopentyl)_3\}_2O]$—this d^0–d^0 complex also contains a linear oxo bridge, but the terminal oxo groups are colinear with the bridge.[34]

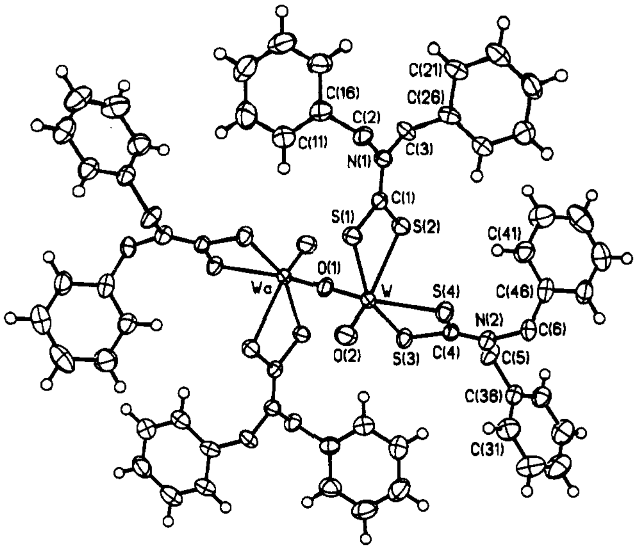

Figure 3. Molecular structure and numbering scheme for $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (**5**). Thermal ellipsoids are drawn at the 40% probability level; all hydrogen atoms are depicted as spheres of arbitrary radius.

Reduction of $[WO_2\{S_2CN(CH_2Ph)_2\}_2]$: Preparation of $[WO(PEt_3)\{S_2CN(CH_2Ph)_2\}_2]$ by Oxygen Atom Transfer to PEt_3. The photosensitivity of **5** strongly suggested that **5** was indeed subject to a photodisproportionation reaction analogous to that observed for **4**, and we attempted to prepare the proposed W(IV) product $[WO\{S_2CN(CH_2Ph)_2\}_2]$ (**11**) by reduction of **6**.

It has been known since the pioneering studies of Barral et al.[6b] that molybdenum complexes of the type $[MoO_2(S_2CNR_2)_2]$ (R = Et, *n*-Bu, *i*-Bu) can transfer oxygen atoms to acceptors like PPh_3 and thereby undergo reduction to Mo(IV) monooxo complexes.[10a,b] This reaction has been extensively studied because of its involvement in cycles for the catalytic oxidation of organic substrates[6b] and as a potential model for the role of the molybdenum centers in molybdenum oxo transferases.[36,37]

At the time that our work was underway, no analogous examples were known of oxo atom transfer from $M^{VI}O_2$ complexes of tungsten to an oxygen atom acceptor, and it had been reported that the reaction of $[WO_2(S_2CNMe_2)_2]$ with tertiary phosphines gave products that could not be characterized.[14] Although it was reasonable that a $W^{VI}O_2$ complex would be more stable than a $Mo^{VI}O_2$ complex, it seemed unlikely that oxygen atom transfer from **6** to an oxygen atom acceptor was impossible. We accordingly examined the reaction of **6** with a range of tertiary phosphines like PPh_3, PMe_2Ph, and PEt_3, and observed that all of these reduced **6**. Only in the case of PEt_3, however, was it possible to obtain a crystalline product, and this required the presence of excess PEt_3. The isolated product was shown by combustion analysis, IR, ^1H NMR, and ^{13}C NMR methods to be $[WO(PEt_3)\{S_2CN(CH_2Ph)_2\}_2]$ (**7**), a phosphine adduct of the desired W(IV) complex **11**.

A PMe_3 complex closely related to **7** has been previously prepared by a rather different route, in which addition of an-

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(27) Ricard, L.; Estienne, J.; Karagiannidis, P.; Toledano, P.; Fischer, J.; Mitschler, A.; Weiss, R. *J. Coord. Chem.* **1974**, *3*, 277.

(28) Blake, A. B.; Cotton, F. A.; Wood, J. S. *J. Am. Chem. Soc.* **1964**, *86*, 3024.

(29) Zubieta, J. A.; Maniloff, G. B. *Inorg. Nucl. Chem. Lett.* **1976**, *12*, 121.

(30) Knox, J. R.; Prout, C. K. *Acta Crystallogr. Sect. B* **1969**, *B25*, 2281.

(31) Bino, A.; Cohen, S.; Tsimering, L. *Inorg. Chim. Acta* **1983**, *77*, 279.

(32) El-Essawi, M.; Weller, F.; Stahl, K.; Kersting, M.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1986**, *542*, 175.

(33) See representative data in Table III of ref 1a.

(34) Feinstein-Jaffe, I.; Gibson, D.; Lippard, S. J.; Schrock, R. R.; Spool, A. *J. Am. Chem. Soc.* **1984**, *106*, 6305.

(35) Deleted in proof.

(36) *Molybdenum Enzymes*; Spiro, T. G., Ed.; Wiley Interscience: New York, 1985.

(37) Bray, R. C. *Rev. Biophys.* **1988**, *21*, 299.

hydrous $Na[S_2CNMe_2]$ to $[WOCl_2(PMe_3)_3]$ gave $[WO(PMe_3)(S_2CNMe_2)_2]$ (**12**).[38] The temperature dependence of the dynamic ^1H NMR spectra of **12** has been interpreted in terms of a fluxional process (possibly involving rupture of a W-S bond), which equilibrates the inequivalent ligands in a structure with a cis orientation of the oxo and phosphine ligands—the appearance of four distinct benzylic resonances in ^{13}C spectra of **7** suggests a similar low-symmetry structure (Scheme III), but we see no comparable evidence for a low-energy fluxional rearrangement of **7**. The low symmetry within **7** was further confirmed by the observation in ^1H NMR spectra of a complex (18 resolved lines) resonance for the phosphine methylenes—this was closely simulated by PANIC[11] on the assumption that the methylene hydrogens are diastereotopic (see Experimental Section for parameters).

While this work was being prepared for publication, we were informed that Yu and Holm had independently discovered that $[WO_2(S_2CNR_2)_2]$ ($R_2 = Me_2$, $(CH_2)_5$) can be reduced to W(V) oxo-bridged dimers $[\{WO(S_2CNR_2)_2\}_2O]$ by $P(OMe)_3$,[39] from which they inferred the intermediate formation of the W(IV) oxo species $[WO(S_2CNR_2)_2]$. Our preparation of **7** remains the only case in which oxo atom transfer is used to reduce a $W^{VI}O_2$ complex to an isolated $W^{IV}O$ complex, and since a trialkylphosphine would be expected to be a somewhat less powerful oxo acceptor than a trialkyl phosphite (ca 13 kcal mol^{-1} from the data in Table V of ref 18), the success of reduction with PEt_3 suggests that oxo transfer from $W^{VI}O_2$ complexes may be less difficult than had been assumed.

It is notable that we have only been able to isolate a PEt_3 adduct of $[WO\{S_2CN(CH_2Ph)_2\}_2]$ (**11**)—attempts to limit the reduction of **6** to the production of **11** by using 1 equiv of PEt_3 have not led to tractable products, and we suspect that, in sharp contrast to the analogous molybdenum complexes, W(IV) oxo complexes $[WO(S_2CNR_2)_2]$ are only stable as adducts of donor ligands.

Conclusions

Photochemical. The sensitivity of $[(MoO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (**4**) and of $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (**5**) to ambient lighting is most reasonably interpreted in terms of facile photodisproportionation into the $M^{IV}O$ and $M^{VI}O_2$ complexes **8** plus **9** and **6** plus **11**, respectively, and the photoacceleration of the oxidation of **5** supports this suggestion. In conjunction with our previous observation of photodisproportionation of $\mathbf{1}^{2+}$ [4] and Richman's demonstration of photodisproportionation of $[\{Fe(TPP)\}_2O]$,[5] these results imply that photodisproportionation is probably a general reaction of complexes with a linear oxo bridge between two metal centers with odd (d^1–d^1 and d^5–d^5 in the cases above) electron centers.

We have not yet carried out detailed photophysical studies of **4** or **5**, and these will be experimentally challenging in both cases for a variety of reasons—the facility of the equilibrium thermal disproportionation of **4** precludes simple classical quantum yield studies and trapping experiments, while the limited solubility of **5** and the apparent inaccessibility by independent synthesis of the $W^{IV}O$ product **11** restricts photophysical studies of disproportionation of **5**. Until such studies have been completed, detailed speculation on the mechanism of the photodisproportionation is inappropriate, but it is certainly possible that it occurs from a distorted charge-transfer excited state as established by Richman for the $[\{Fe(TPP)\}_2O]$ case.[5b] It is interesting that the photoacceleration of the oxidation of **5** can be carried out by using long wavelength ($\lambda > 515$ nm) light, since this would indicate that the intense visible absorption at 517 nm, which must have charge-transfer character, is photoactive.

Synthetic. Controlled oxidation of $[W(CO)_3\{S_2CN(CH_2Ph)_2\}_2]$ (**10**) allows access to the W(VI) dioxo complex $[WO_2\{S_2CN(CH_2Ph)_2\}_2]$ (**6**) or the d^1–d^1 dimer $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (**5**). Reduction of **6** with PEt_3 leads to $[WO(PEt_3)\{S_2CN(CH_2Ph)_2\}_2]$ (**7**), a PEt_3 adduct of the $W^{IV}O$ complex, which would be the expected product of oxygen atom transfer from **6** to PEt_3—this is the first example in which reaction of a W(VI) dioxo complex with an oxygen atom acceptor has been observed to give an isolable W(IV) oxo complex.

Acknowledgment. This work was supported in part by the Office of Naval Research. We thank Professor R. H. Holm for prepublication communication of the information in ref 18.

Supplementary Material Available: Tables of full crystal data, anisotropic temperature factors, and hydrogen atom coordinates for $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ (3 pages); a listing of calculated and observed structure factors (22 pages). Ordering information is given on any current masthead page.

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(38) Carmona, E.; Sachez, L.; Poveda, M. L.; Jones, R. A.; Hefner, J. G. *Polyhedron* **1983**, *2*, 797.

(39) Holm, R. H. Personal communication. Details of this work have been published.[18]

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Regioselective Coupling of a Fluoromethylidyne Ligand of Nonacarbonylbis(μ_3-fluoromethylidyne)triiron with Alkynes

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Nonacarbonylbis(μ_3-fluoromethylidyne)triiron, $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ (**1**), reacts with alkynes $H{-}C{\equiv}C{-}R$ (**2a–f**), forming diferra–allyl clusters $Fe_3(CO)_8(\mu_3\text{-}CF)(\mu_3\text{-}CF{-}CH{-}CR)$ (**3a–f**). According to the spectroscopic data of the products **3a–f**, the carbon–carbon bond formation occurs selectively at the sterically less hindered site of the alkyne. The structure of $Fe_3(CO)_8(\mu_3\text{-}CF)(\mu_3\text{-}CF{-}CH{-}C{-}O{-}C_2H_5)$ (**3c**) has been established by an X-ray crystal structure determination, monoclinic, $P2_1/c$, $a = 15.396$ (4) Å, $b = 8.153$ (4), $c = 14.915$ (3) Å, $\beta = 103.24$ (6)°. With the alkynes $H_3C{-}C{\equiv}C{-}R$ (**2g–l**), the regioselectivity of the carbon–carbon bond formation is less distinct. The clusters $Fe_3(CO)_8(\mu_3\text{-}CF)[\mu_3\text{-}CF{-}C(CH_3){-}CR]$ (**3(I)g–l**) and the isomers $Fe_3(CO)_8(\mu_3\text{-}CF)(\mu_3\text{-}CF{-}CR{-}CCH_3)$ (**3(II)g–l**) are obtained. The ratio of the isomers strongly depends on the steric demand and the electronic effects of the substituent R.

Introduction

In contrast to the well-established chemistry of the nonacarbonyl(μ_3-alkylidyne)tricobalt clusters[1] and their derivatives obtained by metal-exchange reactions,[2] only a few nonacarbonylbis(μ_3-alkylidyne)triiron clusters $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(C{-}OCH_3)$,[3] $Fe_3(CO)_9(\mu_3\text{-}CF)_2$,[4] $Fe_3(CO)_9(\mu_3\text{-}C{-}CH_3)(\mu_3\text{-}C{-}$

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(1) Kemmitt, R. D. W.; Russel, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1982; Vol. 5. Penfold, B. R.; Robinson, B. H. *Acc. Chem. Res.* **1973**, *6*, 73. Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97.

(2) Beurich, H.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 2385. Beurich, H.; Blumhofer, R.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 2409.

(3) Wong, W.-K.; Chiu, K. W.; Wilkinson, G.; Galas, A. M.-R.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1983**, 1557.

0020-1669/90/1329-4396$02.50/0