Oxidative Addition of Cyclopentanone to $WCl_2(PMePh_2)_4$ To Give a Tungsten(VI) Oxo-Alkylidene Complex

Jeffrey C. Bryan and James M. Mayer*

Department of Chemistry, University of Washington
Seattle, Washington 98195

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We recently reported the facile oxidative addition of carbon dioxide and related heterocumulenes X=C=Y (X, Y = O, S, NR) to $WCl_2(PMePh_2)_4$ (**1**), forming novel tungsten(IV) oxo, imido, and sulfido complexes.[1] This is a new type of oxidative addition reaction, involving the cleavage of strong C=O, C=N, or C=S double bonds. We now report the remarkable oxidative addition of a C=O double bond of a ketone forming an oxo-alkylidene complex, apparently via an η^2-ketone (metallaoxirane) intermediate.

A benzene solution of the tungsten(II) complex $WCl_2(PMePh_2)_4$ (**1**)[2] reacts rapidly with 2 equiv of cyclopentanone to form a bis-ketone adduct, $W(\eta^2\text{-}O{=}\overline{CCH_2CH_2CH_2C}H_2)_2Cl_2(PMePh_2)_2$ (**2**), via substitution of two phosphine ligands. Compound **2** decomposes at ambient temperatures to the tungsten(VI) oxo-alkylidene complex $W(O)({=}\overline{CCH_2CH_2CH_2C}H_2)Cl_2(PMePh_2)_2$ (**3**) and cyclopentanone (Scheme I).

The oxo-alkylidene complex **3** has been characterized by comparison of its NMR and IR spectra[3] with the closely related complexes $W(O)({=}CHCMe_3)Cl_2(PR_3)_2$[4] and by an X-ray crystal structure (Figure 1).[5] The molecule can be described as having a distorted octahedral configuration, with a cis relationship between the π-bonding oxo and alkylidene ligands, as found also for $W(O)({=}CHCMe_3)Cl_2(PMe_3)_2$[4] and $W(O)(L)Cl_2(PMePh_2)_2$ (L = CO,[1] $CH_2{=}CH_2$[6]). Similar bond distances and angles are found in these four structures. The cyclopentylidene ligand is bent away from the oxo group (bond angles: O-W-C1 94.9 (4)°, Cl1-W-C1 87.0 (4)°, W-C1-C2 132.2 (10)°, W-C1-C5 120.5 (9)°); the distances and angles within the five-membered ring are indistinguishable from those recently reported for gas-phase cyclopentanone.[7] The $^{13}C\{^1H\}$ NMR spectrum shows a triplet at 329.6 δ with tungsten satellites ($^2J_{PC}$ = 10.0 Hz, $^1J_{WC}$ = 150 Hz) and four singlets (δ 54.8, 49.8, 28.9, and 27.5 ppm) assigned to the α and four methylene carbons of the cyclopentylidene ligand.

The structure of the bis-cyclopentanone adduct **2** has been established spectroscopically[3] and by analogy to the X-ray structure of the related acetone complex $W(\eta^2\text{-}O{=}CMe_2)_2Cl_2(PMePh_2)_2$ (**4**, Figure 2, see below). A bis-η^2-ketone configuration in **2** is indicated by the coupling of phosphorus and tungsten to the carbonyl carbon atoms in the $^{13}C\{^1H\}$ NMR spectrum (107.1 δ, $^2J_{PC}$ = 9 Hz, $^1J_{WC}$ = 24 Hz). The ^1H, ^{13}C, and ^{31}P NMR spectra[3] indicate that the molecule has a twofold axis of symmetry which relates the pairs of phosphine and ketone ligands but leaves the eight hydrogen atoms of each cyclopentyl ring inequivalent.

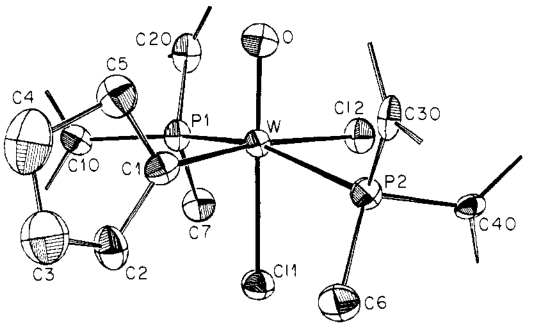


Figure 1. ORTEP drawing of $W(O)({=}\overline{CCH_2CH_2CH_2C}H_2)Cl_2(PMePh_2)_2$ (**3**) with 30% probability thermal ellipsoids. For clarity the hydrogen atoms are omitted, and only the ipso carbon atoms of the phenyl rings are shown. Selected bond distances (Å) and angles (deg) not mentioned in the text are as follows: W-O = 1.708 (8), W-C1 = 1.980 (12), W-P1 = 2.567 (3), W-P2 = 2.563 (3), W-Cl1 = 2.502 (3), W-Cl2 = 2.511 (3), O-W-Cl1 = 178.0 (3), O-W-Cl2 = 94.2 (3), O-W-P1 = 97.4 (3) O-W-P2 = 98.0 (3), Cl1-W-Cl2 = 84.0 (1), P1-W-P2 = 163.5 (1).

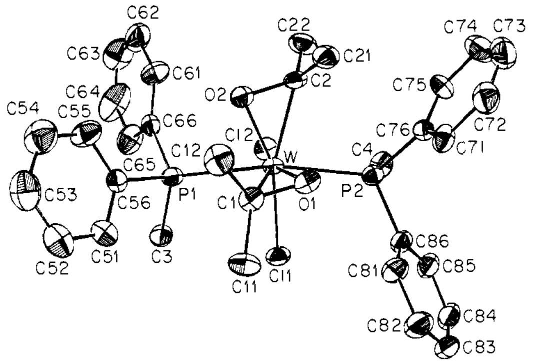
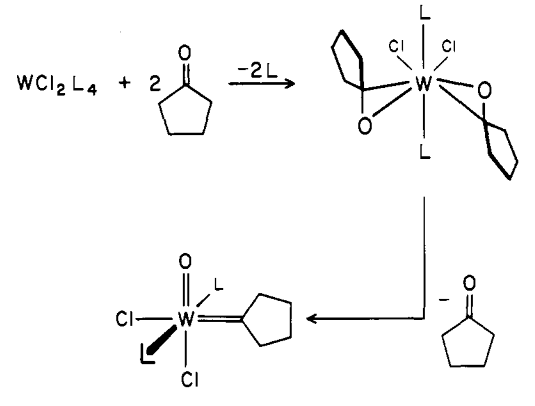


Figure 2. ORTEP drawing of $W(\eta^2\text{-}O{=}CMe_2)_2Cl_2(PMePh_2)_2$ (**4**) with 50% probability thermal ellipsoids. For clarity hydrogen atoms are not shown. Selected bond distances (Å) and angles (deg) not mentioned in the text are as follows: W-O1 = 1.948 (4), W-O2 = 1.933 (4), W-C1 = 2.175 (7), W-C2 = 2.203 (7), W-P1 = 2.626 (2), W-P2 = 2.606 (2), W-Cl1 = 2.432 (2), W-Cl2 = 2.437 (2), O1-W-O2 = 95.3 (2), C1-W-C2 = 104.6 (3), Cl1-W-Cl2 = 82.48 (6), P1-W-P2 = 153.66 (6).

Scheme I Reaction of Cyclopentanone with WCl_2L_4[a]



[a] L = $PMePh_2$.

Analogous bis-η^2-ketone complexes are formed by reaction of **1** with acetone **4**, methyl ethyl ketone **5**, cyclobutanone **6**, and cyclohexanone **7**. These complexes are spectroscopically similar to **2**.[3] The X-ray structure of the acetone complex W-(η^2-O=CMe$_2$)$_2$Cl$_2$(PMePh$_2$)$_2$ (**4**)[8] shows a cis ketone, trans

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(1) Bryan, J. C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 2826-2828.

(2) Sharp, P. R. *Organometallics* **1984**, *3*, 1217-1223.

(3) Full spectroscopic data are included in the Supplementary Material. Selected spectral data are as follows: **2** $^{31}P\{^1H\}$ NMR -6.6 s ($^1J_{WP}$ = 174 Hz), **3** $^{31}P\{^1H\}$ NMR 13.7 s ($^1J_{WP}$ = 332 Hz), IR ν_{W-O} = 952 cm^{-1}, **4** $^{13}C\{^1H\}$ NMR: 96.7 t ($^2J_{PC}$ = 9 Hz); $^{31}P\{^1H\}$ NMR -5.6 s ($^1J_{WP}$ = 171 Hz); IR: ν_{C-O} = 1230 cm^{-1}, $\nu_{C-^{18}O}$ = 1220 cm^{-1}.

(4) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148-155. Schrock, R. R.; Rocklage, S.; Wengrovius, J. H.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73-83. Churchill, M. R.; Rheingold, A. L. *Inorg. Chem.* **1982**, *21*, 1357-1359.

(5) Crystal data for $W(O)({=}\overline{CCH_2CH_2CH_2C}H_2)Cl_2(PMePh_2)_2$ (**3**): monoclinic, $P2_1/c$; a = 16.128 (2) Å, b = 9.923 (2) Å, c = 18.835 (3) Å, β = 96.891 (11)°, V = 2992.8 (10) Å^3, Z = **4**, D_{calcd} = 1.64 g/cm^3. A CAD4 diffractometer was used to collect 5864 data (2° $\leq \theta \leq$ 25°), at 23 ± 3 °C, of which 2774 data with $I > 3\sigma(I)$ were used in the refinements. Structure refined to R = 4.3% and R_w = 4.5%; GOF = 1.14, highest final difference peak, 1.09 e/Å^3 (near W).

(6) Su, F.-M.; Cooper, C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3545-3547.

(7) Tamagawa, K.; Hilderbrandt, R. L.; Shen, Q. *J. Am. Chem. Soc.* **1987**, *109*, 1380-1383.

(8) Crystal data for $W(\eta^2\text{-}O{=}CMe_2)_2Cl_2(PMePh_2)_2$ (**4**): triclinic, $P\bar{1}$; a = 10.1243 (12) Å, b = 11.898 (2) Å, c = 14.760 (2) Å, α = 108.763 (9)°, β = 107.131 (9)°, γ = 96.664 (10)°, V = 1564.5 (8) Å^3, Z = 2, D_{calcd} = 1.64 g/cm^3. A CAD4 diffractometer was used to collect 5822 data (2° $\leq \theta \leq$ 25°), at 23 ± 2 °C, of which 4139 data with $I > 3\sigma(I)$ were used in the refinements. Structure refined to R = 3.6% and R_w = 3.7%; GOF = 1.05, highest final difference peak, 0.76 e/Å^3 (near W).

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phosphine, cis chloride configuration (Figure 2), as proposed for **2** and suggested earlier for the analogous bis-ethylene complex, $W(CH_2{=}CH_2)_2Cl_2(PMePh_2)_2$.[2] The C–O bond distances of 1.390 (8) Å and 1.379 (8) Å are considerably longer than in free acetone (1.210 (4) Å[9]) and approach the C–O single bond length of 1.41 Å.[10] The long C–O bond distances, the large deviation from planarity of the acetone ligands (average angles O–C–C = 113.6 (6)°, C–C–C = 111.4 (6)°), and the ^{13}C chemical shift of the carbonyl carbons (96.7 ppm vs 203.5 ppm for free acetone) all suggest a large contribution from a metallaoxirane resonance form and substantial oxidation of the tungsten(II) center.[11,12] To our knowledge, complexes **2** and **4–7** are the first bis-η^2-ketone complexes, and they are rare examples of η^2-binding of a ketone ligand without electron-withdrawing substituents.[11]

Complex **4** decomposes at ambient temperatures to nonstoichiometric amounts of acetone, $W(O)Cl_2(PMePh_2)_3$,[13] and paramagnetic tungsten complex(es); an oxo–alkylidene complex has not been observed. The decomposition of complexes **5–7** and the reasons for the difference in reactivity between **2** and **4** are currently under investigation. Complex **1** does not react with diethyl ketone, probably because its steric bulk, or with γ-butyrolactone or ethyl acetate, presumably for electronic reasons. The addition of aldehydes (RC(O)H, R = Me, Et, *t*-Bu) to **1** gives a number of products.

The oxidative addition of cyclopentanone is a remarkable reaction because of the strength of the C═O bond (~160 kcal/mol[14]): it is the strongest bond that has been simply cleaved to two fragments that remain on a single metal center.[15] This is a four-electron oxidative addition reaction that occurs under very mild conditions, presumably favored by the formation of a strong[16] tungsten–oxygen multiple bond. The reaction contrasts with the typical reduction of ketones by metals leading to pinacolates and olefins via C–C coupling.[17] Cleavage of cyclopentanone may occur directly from an η^2-ketone adduct or possibly via a metallacycle formed by the head-to-tail coupling of two cyclopentanones.[18] Mechanistic studies are in progress.

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Supplementary Material Available: Spectroscopic and analytical data for **2–7** and tables of atomic coordinates, bond distances and angles, anisotropic temperature factors, and hydrogen atom coordinates for **3** and **4** (14 pages); tables of observed and calculated structure factors for **3** and **4** (35 pages). Ordering information is given on any current masthead page.

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(9) Iijima, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3526–3530.

(10) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 19.

(11) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223–8227, and references therein. Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421–5422.

(12) Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 7952–7959. Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 1590–1591. Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1983**, *244*, C53–C56. Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33–61.

(13) Carmona, E.; Sânchez, L.; Poveda, M. L.; Jones, R. A.; Hefner, J. G. *Polyhedron* **1983**, *2*, 797–801.

(14) Glockler, G. *J. Phys. Chem.* **1958**, *62*, 1049–1054.

(15) The cleavage of CO seems to require more than one metal center: LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6382–6384. The cleavage of N_2 requires added acid: Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625. The cleavage of ketones by metal–alkylidene complexes forms olefins: Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399–5400.

(16) Sanderson, R. T. *Inorg. Chem.* **1986**, *25*, 3518–3522.

(17) (a) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405–411. Giese, B. *Radicals in Organic Synthesis*; Pergamon: Oxford, 1986; pp 122–124, 185–188. Blatchford, T. P.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1984**, 1295–1296. Cotton, F. A.; DeMarco, D.; Falvello, L. R.; Walton, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 7375–7376. Sharpless, K. B.; Umbreit, M. A.; Nieh, M. T.; Flood, T. C. *J. Am. Chem. Soc.* **1972**, *94*, 6538–6540. (b) The cleavage of an quinolinyl phenyl ketone to give CO_2 and a bridging carbene has been reported: Suggs, J. W.; Wovkulich, M. J.; Lee, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 5546–5548.

(18) See, for example: Browning, J.; Empsall, H. D.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 381–387.

The Mechanism of Microbial Denitrification

E. Weeg-Aerssens,[†] J. M. Tiedje,*[†] and B. A. Averill*[‡]

Department of Crop and Soil Sciences
Michigan State University
East Lansing, Michigan 48824-1124
Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

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Denitrification,[1] the reduction of NO_3^- to N_2O and N_2 by soil bacteria, is a key process in the nitrogen cycle that controls the amount of fixed nitrogen available for plant growth; estimates indicate that 25–30% of fertilizer nitrogen is lost via denitrification.[2] Nitrite and nitrous oxide are known to be free intermediates in the pathway[1] (eq 1)

$$NO_3^- \rightarrow NO_2^- \rightarrow ? \rightarrow N_2O \rightarrow N_2 \qquad (1)$$

Efforts to design specific inhibitors of denitrification suitable for agricultural use require a knowledge of the mechanism of the first enzyme unique to denitrification, nitrite reductase. The mechanism of this key step in denitrification, reduction of NO_2^- to N_2O, has been controversial,[3] with evidence presented for NO as an obligatory free intermediate,[3-5] and for formation of N_2O either by dimerization of free nitroxyl (HNO)[6,7] (eq 2) or by nucleophilic attack of a second NO_2^- on an enzyme-bound nitrosyl intermediate[8,9] (eq 3). The existence of the nitrosyl intermediate common

$$NO_2^- + E \rightleftarrows E{\cdot}NO_2^- \underset{H_2O}{\overset{H_2O}{\rightleftharpoons}} E{\cdot}NO^+ \rightarrow E + HNO \rightarrow (1/2)N_2O \qquad (2)$$

$$NO_2^- + E \rightleftarrows E{\cdot}NO_2^- \underset{H_2O}{\overset{H_2O}{\rightleftharpoons}} E{\cdot}NO^+ \xrightarrow{NO_2^-} E{\cdot}N_2O_3 \rightarrow N_2O \qquad (3)$$

to eq 2 and 3 has been conclusively demonstrated[6,10] by $H_2{}^{18}O$ exchange and by trapping experiments with N_3^- and NH_2OH. We report herein the results of isotope exchange and trapping studies which resolve this controversy by demonstrating that $H_2{}^{18}O$, $^{14}N_3^-$, and $^{15}NO_2^-$ compete for the same enzyme-bound nitrosyl intermediate, as required by eq 3.

Cell-free extracts of *Pseudomonas stutzeri*, a typical denitrifier known to contain a heme *cd*-nitrite reductase,[11] were used, because we have found that whole cells are relatively impermeable to azide. Table I[12] shows the relative isotopic composition of N_2O produced

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[†] Michigan State University.

[‡] University of Virginia.

(1) Payne, W. J. *Denitrification*; John Wiley and Sons: New York, 1981.

(2) Hauck, R. D. In *Terrestrial Nitrogen Cycles*; Clark, F. E., Rosswall, T., Eds.; Swedish Natural Research Council (N.S.R.): Stockholm, 1981; Ecol. Bull. No. 33, p 558.

(3) Henry, Y.; Bessieres, P. *Biochimie* (*Paris*) **1984**, *66*, 259–289.

(4) Grant, M. E.; Cronin, S. E.; Hochstein, L. I. *Arch. Microbiol.* **1984**, *140*, 183–186.

(5) Shapleigh, J. P.; Payne, W. J. *J. Bacteriol.* **1985**, *163*, 837–840.

(6) Kim, C.-H; Hollocher, T. C. *J. Biol. Chem.* **1984**, *259*, 2092–2099.

(7) Garber, E. A. E.; Hollocher, T. C. *J. Biol. Chem.* **1982**, *257*, 4705–4708.

(8) Averill, B. A.; Tiedje, J. M. *FEBS Lett.* **1982**, *138*, 8–11.

(9) Aerssens, E.; Tiedje, J. M.; Averill, B. A. *J. Biol. Chem.* **1986**, *261*, 9652–9656.

(10) Garber, E. A. E.; Hollocher, T. C. *J. Biol. Chem.* **1982**, *257*, 8091–8097.

(11) Kodama, T. *Plant Cell Physiol.* **1970**, *11*, 231–239.