

which is a Fe_{14} ring. As shown in Figure 15, the three clusters can be formally constructed from this cyclic fragment. Addition of two $\text{Fe}_2(\mu_2\text{-S})$ fragments gives rise to the two isomers of $[\text{Na}_2\text{Fe}_{18}\text{S}_{30}]^{8-}$. When the two Fe atoms each bind *five* consecutive S atoms of the inner S_{14} ring in the bridging modes $4\mu_3\text{-S} + \mu_4\text{-S}$, the α -isomer is produced. When the binding interactions encompass *six* consecutive S atoms and the modes $6\mu_3\text{-S}$, the β -isomer is generated. The two isomers can be interconverted by the indicated intramolecular sulfide atom attacks on the electrophilic iron centers with consequent topological rearrangement. From isolated yield data based on iron (Figure 3), we infer, but cannot prove, that two isomers exist in equilibrium in alcoholic solution, possibly also with $[\text{FeS}_2]_n^{n-}$, and that the equilibrium is shifted by selective precipitation of one isomer as dependent on solvent and cation.

In a similar manner, the expulsion of two Se anions at diagonally opposite ends of the ring generates two edge-shared Fe_2Se_2 rhombs and two three-coordinate iron sites. Addition of a $\text{Fe}_6(\mu_2\text{-Se})_{10}\text{Se}_2$ chain fragment and formation of one $\text{Fe}-(\mu_2\text{-Se})$ and one $\text{Fe}-(\mu_4\text{-Se})$ bond at each end of the ring builds the three edge-fused bridgehead rhombs and recovers the bicyclic structure of $[\text{Na}_9\text{Fe}_{20}\text{Se}_{38}]^{9-}$.

While the foregoing manipulations are purely conceptual and may not resemble the true assembly mechanisms of the clusters, they do point to a common precursor, $[\text{Fe}^{\text{III}}_{14}\text{Q}_{28}]^{14-}$, stabilized by sodium ions. This species is in turn derivable by cyclization of the polymer $[\text{FeQ}_2]_n^{n-}$, known in linear form in solid-state compounds.^{38de} We prefer an all-Fe(III) formulation of the precursor because, as noted, vertex-shared Fe_2Q_2 rhombs nearly always occur in the Fe(III) state. We observe that, collectively, $[\alpha\text{-Na}_2\text{Fe}_{18}\text{S}_{30}]^{8-}$, $[\beta\text{-Na}_2\text{Fe}_{18}\text{S}_{30}]^{8-}$, and $[\text{Na}_9\text{Fe}_{20}\text{Se}_{38}]^{9-}$ contain the majority of Fe_nQ_m cores known in molecular Fe-Q clusters. These include linear Fe_2Q_2 , linear and cuboidal Fe_3Q_4 , linear

Fe_4Q_6 , and Fe_6Q_9 . We note that $[\beta\text{-Na}_2\text{Fe}_{18}\text{S}_{30}]^{8-}$ is the first synthetic molecular cluster to contain cuboidal Fe_3Q_4 *not* as part of Fe_6Q_9 . A similar cuboidal Fe_3Se_4 unit with three terminal selenide bridges occurs in the phase $\text{Ba}_3\text{Fe}_3\text{Se}_7$ prepared at high temperatures.⁵¹ Lastly, there is perhaps no better example of the apparent assembly of clusters from recognized fragments than that provided by this set of three nanometer-sized clusters, which includes a unique example of cluster isomerism. Given the possibilities provided by the topological analysis, it appears that an extensive family of chalcogenometalates should exist based on metals with a tetrahedral stereochemical preference. The cluster set $[\alpha\text{-Na}_2\text{Fe}_{18}\text{S}_{30}]^{8-}$, $[\beta\text{-Na}_2\text{Fe}_{18}\text{S}_{30}]^{8-}$, and $[\text{Na}_9\text{Fe}_{20}\text{Se}_{38}]^{9-}$ demonstrates the (conceptual) principle that in the presence of an appropriate promoter (here $\text{Na}(\text{PhNCOMe})$) high-nuclearity clusters can be assembled by the termination of a unidimensional polymeric fragment via mono- or bicyclization. This approach may lead to the discovery of new regimes of nanometer-sized clusters.

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Supplementary Material Available: Listing of X-ray crystallographic data for the compounds in Table I and tables of intensity collections, atom positional and thermal parameters, and calculated hydrogen atom positions (17 pp); listing of calculated and observed structure factors (143 pp). Ordering information is given on any current masthead page.

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Communications to the Editor

On the Nature of the Olefination Reaction Involving Ditungsten Hexaalkoxides and Aldehydes or Ketones

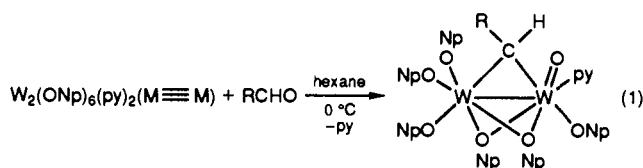
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Pertinent to the development of any reagent for organic synthesis is a knowledge of its scope, limitations, reaction mechanism, and competing side reactions. We are investigating the use of ditungsten hexaalkoxides for the reductive coupling of aldehydes and ketones to olefins.¹ This reaction proceeds in two stages: (1) the reductive cleavage of the carbonyl group of the aldehyde or ketone to yield a μ -alkylidene oxo ditungsten compound (eq 1)² and (2) formation of the olefinic C-C bond and rupture of the carbonyl C-O bond of the second aldehyde or ketone. We report here observations that provide insight into the nature of the initial C-O bond cleavage and subsequent C-C bond formation.



The addition of cyclopropanecarboxaldehyde (1 equiv) to $\text{W}_2(\text{ONp})_6(\text{py})_2$, where Np = neopentyl and py = pyridine, in hexane at 0°C gives the cyclopropylmethylidene complex $\text{W}_2(\text{ONp})_6(\mu\text{-CH}(\text{C}_3\text{H}_5))(\text{O})(\text{py})$ as dark red crystals in ca. 70% yield.³ The structure of this complex is shown in Figure 1⁴ and resembles the previously characterized related complexes $\text{W}_2(\text{ONp})_6(\mu\text{-CHAR})(\text{O})(\text{py})$.⁵ To our knowledge, this is the first structurally characterized cyclopropylmethylidene complex,⁶ and

(3) All reactions were carried out under dry and oxygen-free atmospheres (N_2) and employed purified, deoxygenated solvents. Satisfactory elemental analyses were obtained.

(4) Crystal data for $\text{W}_2(\text{O})(\text{OCH}_2\text{-}i\text{-Bu})_6(\mu\text{-C}_3\text{H}_5)(\text{py})$ at -170°C : $a = 12.606(2) \text{ \AA}$, $b = 19.923(4) \text{ \AA}$, $c = 10.583(2) \text{ \AA}$, $\alpha = 104.52(1)^\circ$, $\beta = 112.21(1)^\circ$, $\gamma = 95.16(1)^\circ$, $Z = 2$, $d_{\text{calcd}} = 1.48 \text{ g cm}^{-3}$, and space group $P1$. For $\text{W}_2(\text{O})(\text{OCH}_2\text{-}i\text{-Bu})_6(\mu\text{-OC}_{12}\text{H}_{16})$ at -169°C : $a = 11.227(2) \text{ \AA}$, $b = 20.634(3) \text{ \AA}$, $c = 10.730(2) \text{ \AA}$, $\alpha = 104.73(1)^\circ$, $\beta = 98.31(1)^\circ$, $\gamma = 75.56(1)^\circ$, $Z = 2$, $d_{\text{calcd}} = 1.55 \text{ g cm}^{-3}$, and space group $P1$.

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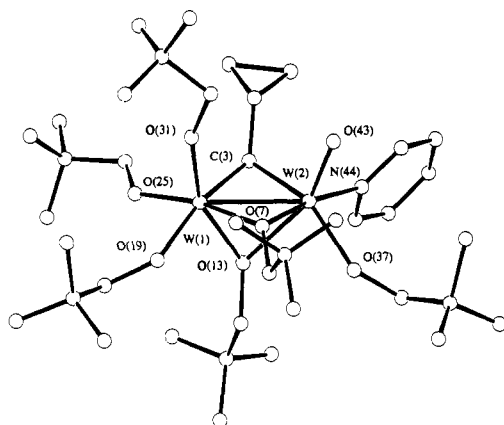


Figure 1. Ball-and-stick drawing of $W_2(O)(\mu\text{-CH-c-C}_3\text{H}_5)(\text{OCH}_2\text{-}t\text{-Bu})_6(\text{py})$. Selected distances (angstroms) and angles (degrees) are as follows: $W\text{-}W = 2.6586$ (6), $W(1)\text{-}O(43) = 1.713$ (5) Å, $W(1)\text{-}C(3) = 2.171$ (8), $W(2)\text{-}C(3) = 2.156$ (8), $W\text{-}C\text{-}W = 75.8$ (2).

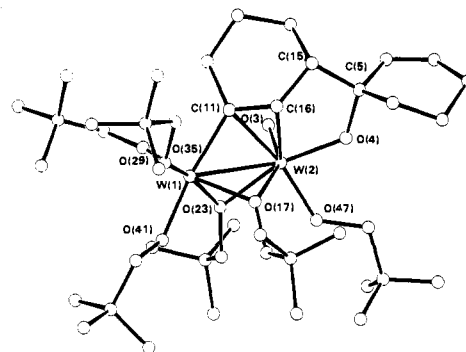
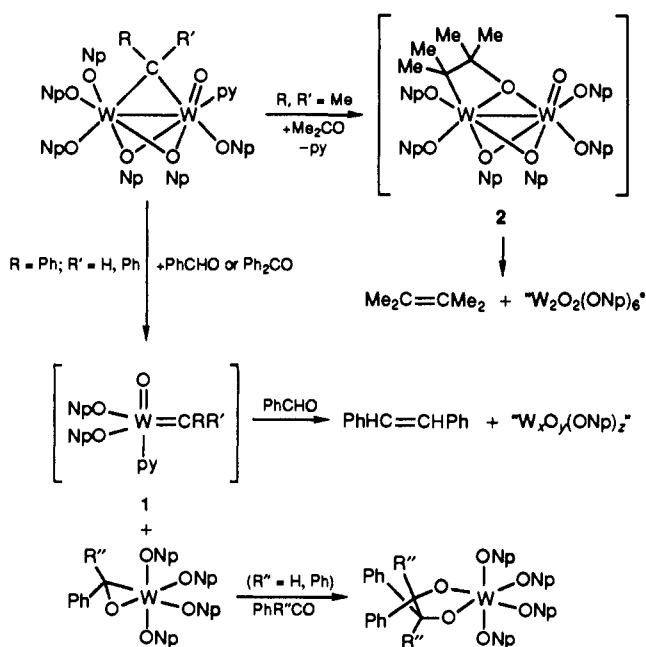


Figure 2. Ball-and-stick drawing of the $W_2(O)(\mu\text{-OC}_{12}\text{H}_{16})(\text{OCH}_2\text{-}t\text{-Bu})_6$ molecule. Selected bond distances (angstroms) and angles (degrees) are as follows: $W\text{-}W = 2.8247$ (5), $W(1)\text{-}C(11) = 2.106$ (5), $W(2)\text{-}O(3) = 1.705$ (4), $W(2)\text{-}C(11) = 2.106$ (5), $W(2)\text{-}C(16) = 2.309$ (5), $W(2)\text{-}O(4) = 1.949$ (4), $C(11)\text{-}C(16) = 1.394$ (8). The bridging hydrocarbon fragment can be viewed as a $\mu\text{-}\eta^1, \eta^2\text{-vinyl}$ ligand and the $W(2)\text{-}O(4)$ bond as typical of a $W\text{-}OR$ bond.

Scheme I

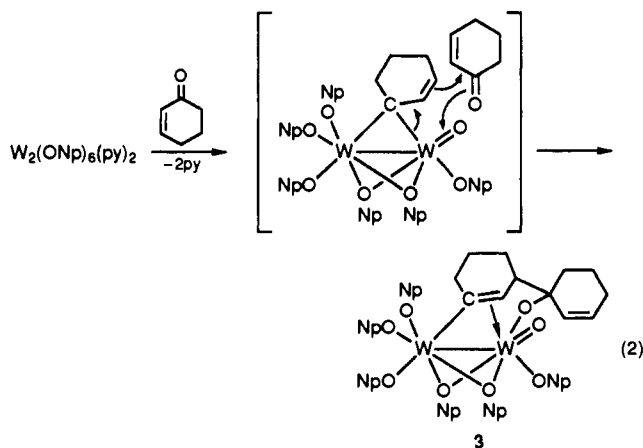


the retention of the cyclopropyl ring in the deoxygenation reaction suggests that the cleavage of the $C=O$ bond proceeds in an effectively concerted manner. In other words, any intermediate in which large amounts of electron spin density or charge are built up on the α -carbon must be very short-lived. Anions, cations, radicals, and carbenes adjacent to a cyclopropyl ring are known to undergo rapid ring opening to a homoallyl or cyclobutyl system.⁷ Thus, the fact that the 3-membered ring remains intact throughout the reaction strongly suggests both a high degree of covalent $W\text{-}C$ σ -bonding in the product and the effectively concerted nature of $C=O$ bond rupture and $C\text{-}W/O\text{-}W$ bond formation.

The second step in the olefination reaction involves the addition of an aldehyde or ketone to the alkylidene-bridged complex. The initially formed alkylidene moiety is efficiently transformed to olefin (as determined by using labeled compounds incorporating $\mu\text{-}^{13}\text{CMe}_2$ and $\mu\text{-}^{13}\text{CPh}$), but the added aldehyde or ketone may participate in the nonproductive formation of pinacolate complexes $W(\text{ONp})_4(\text{pinacolate})$. The latter compounds are formed to a

greater extent for aryl-substituted aldehydes and ketones. We have previously characterized the compound $W(\text{ONp})_4(\eta^2\text{-OCPh}_2)$ ⁸ and shown that this reacts with added aldehydes and ketones to give $W(\text{ONp})_4(\text{pinacolate})$.⁸ We propose that this nonproductive reaction proceeds by way of a reaction as shown in Scheme I.

The mononuclear $W(6+)$ oxo alkylidene complex **1** formed in Scheme I may participate in olefin formation in a manner well-documented for Schrock-type carbene complexes.⁹ That intermediate **1** forms for aromatic-substituted alkylidenes and not for aliphatics could be explained by conjugation between the $M=C$ bond of **1** and the aromatic π -system. The proposed dinuclear pathway shown in Scheme I involving a dimetallaoxacyclopentane **2** has to our knowledge no precedent. A dinuclear pathway is, however, implicated by reactions wherein pinacolate formation is very minor and also by the finding that cyclohexenone (2 equiv) and $W_2(\text{ONp})_6(\text{py})_2$ yield the novel compound of formula $W_2\text{-}(O)(\text{ONp})_6(\text{OC}_{12}\text{H}_{16})$, whose structure is shown in Figure 2.⁴ The latter compound is the product of the vinylogous coupling of a μ -cyclohexenylidene ligand with cyclohexenone as shown in eq 2.



This reaction is analogous to the coupling of an ordinary dinuclear alkylidene complex with a ketone (to give complex **2** in Scheme I), which in the olefination reaction is followed by metallacycle cleavage to yield alkene, a reaction which cannot readily occur for **3**.

Further studies are in progress.¹⁰

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(10) We thank the National Science Foundation for support.

Registry No. 3, 139071-24-2; *c*-C₃H₅CHO, 1489-69-6; W₂(ONp)₆(py)₂, 88608-50-8; W₂(ONp)₆(μ-CH(C₃H₅))(O)(py), 139071-23-1; 2-cyclohexenone, 930-68-7.

Supplementary Material Available: NMR and crystallographic data comprised of a summary of data collection and refinement, VERSORT and stereodrawings, tables of atomic coordinates, and complete listings of bond distances and angles (32 pages); listings of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

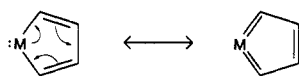
Osmacyclopentatriene Complexes: Structural Characterization of [Os(C₄Me₄)(en)₂](CF₃SO₃)₂

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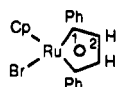
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Metallacyclopentadiene complexes have attracted considerable interest, because they are considered important intermediates in alkyne cyclization.² However, very few metallacyclopentatriene complexes which, as shown, are resonance forms of metallacyclopentadienes have been prepared and characterized.^{3,4}



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structural evidence suggests that it may be better described as a five-membered aromatic metallacycle, a resonance structure between metallacyclopentadiene and metallacyclopentatriene for the following reasons: (i) The bond distances of C(1)-C(2) [1.403 (8) Å] and C(2)-C'(2) [1.377 (12) Å] are almost identical. In other metallacyclopentadiene compounds, the difference between the carbon-carbon single bond and double bond is ca. 0.10-0.15 Å: Mague, J. T. *Inorg. Chem.* **1970**, *9*, 1610. Gastinger, R. G.; Rausch, M. D.; Sullivan, D. A.; Palenik, G. J. *J. Am. Chem. Soc.* **1976**, *98*, 719. Gastinger, R. G.; Rausch, M. D.; Sullivan, D. A.; Palenik, G. J. *J. Organomet. Chem.* **1976**, *117*, 355. Suzuki, H.; Itoh, K.; Ishii, Y.; Simon, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 8494. Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454. O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 6232. (ii) The 1.942 (6) Å Ru-C(1) bond distance is in the range of the longest bond lengths of the previously reported Ru-C double bond length, 1.83-1.91 Å: Clark, G. R. *J. Organomet. Chem.* **1977**, *134*, 51. Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Thomas, S. J. *Chem. Soc., Dalton Trans.* **1979**, 1929. Selegue, J. P. *Organometallics* **1982**, *1*, 217. Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2203. Selegue, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 5921. Crocker, M.; Green, M.; Orpen, A. G.; Neumann, H.-P.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1351. (iii) The chemical shift of the two hydrogens on the metallacycle at δ 7.82 is significantly downfield of the vinyl proton signal at δ 6.8 in 1,1,4,4-tetraphenyl-1,3-butadiene: Weast, R. C.; Grasselli, J. G. *Handbook of Data on Organic Compounds*, 2nd ed.; CRC Press: Boca Raton, FL, 1989; Vol. 1, p 464. (b) For examples of delocalization in the metallacyclopentadiene structure, see: Mague, J. T. *Inorg. Chem.* **1970**, *9*, 1610. Pierpont, C. G.; Downs, H. H.; Itoh, K.; Nishiyama, H.; Ishii, Y. *J. Organomet. Chem.* **1976**, *124*, 93.

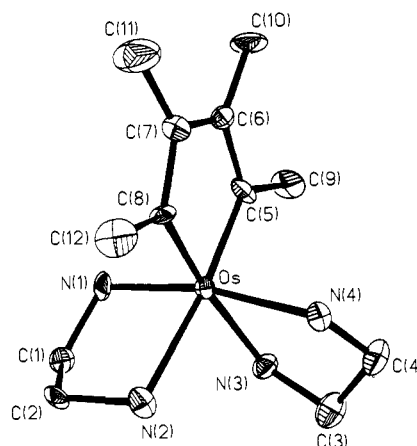


Figure 1. Molecular structure and labeling scheme for **1**: Os-N(1) 2.101 (7), Os-N(2) 2.239 (7), Os-N(3) 2.274 (8), Os-N(4) 2.120 (7), Os-C(5) 1.940 (8), Os-C(8) 1.931 (8), C(5)-C(6) 1.461 (13), C(6)-C(7) 1.357 (12), C(7)-C(8) 1.448 (12) Å; N(1)-Os-N(2) 78.3 (3), N(1)-Os-N(3) 92.8 (3), N(2)-Os-N(3) 84.2 (3), N(1)-Os-N(4) 168.0 (3), N(1)-Os-C(5) 94.9 (3), N(2)-Os-C(5) 172.9 (3), N(3)-Os-C(5) 98.5 (3), N(4)-Os-C(5) 95.4 (3), N(1)-Os-C(8) 94.9 (3), N(2)-Os-C(8) 96.9 (3), N(3)-Os-C(8) 172.2 (3), N(4)-Os-C(8) 92.6 (3), C(5)-Os-C(8) 81.3 (4), Os-C(5)-C(6) 116.1 (6), C(5)-C(6)-C(7) 111.9 (7), C(6)-C(7)-C(8) 115.3 (8), Os-C(8)-C(7) 115.1 (6)°.

In this communication, we wish to report the synthesis and characterization of two novel metallacyclopentatrienes, *cis*-[Os(C₄Me₄)(en)₂]²⁺ (**1**) and *cis*-[Os(C₁₀H₁₄)(en)₂]²⁺ (**2**), prepared as the bis(trifluoromethanesulfonate) salts (en = ethylenediamine). The method of preparation which depends on the reaction of alkynes with an η²-dihydrogen complex of bis(ethylenediamine)osmium(II) merits special mention. In earlier work in this laboratory,^{5a} it was shown that a compound prepared over two decades ago,^{5b} and then described as dihydridobis(ethylenediamine)osmium(IV), has a *trans* arrangement of the en ligands and that the purported two hydrides actually constitute an η²-H₂ unit occupying one face of the plane. The opposite face is occupied by a ligand which, in the absence of a more nucleophilic candidate, is a molecule of the solvent. It was also shown that the dihydrogen is readily replaced by strong π acid ligands.

When an acetone solution of *trans*-[Os(en)₂(η²-H₂)(H₂O)]-(CF₃SO₃)₂ (**3**) (0.53 mmol, 0.13 M) and 2-butyne (7.2 mmol) is heated at 59 °C for 21 h, the yellow green solution turns dark green. A new compound, [Os(C₄Me₄)(en)₂](CF₃SO₃)₂ (**1**), is isolated in 95% yield by precipitation with ether. The ¹H NMR spectrum of **1** in acetone-*d*₆ shows four broad peaks for amine protons at δ 7.74, 6.55, 6.27, 6.11 and four multiplets for the methylene protons at δ 3.12, 3.96, 2.75, 2.57, which indicates that the original planar symmetry has been reduced to C₂, the two *trans*-ethylenediamine ligands of **3** having rearranged to the *cis* position. Two singlets at δ 2.22 and 0.60, each corresponding to six protons, are observed for the methyl groups; that is, 2 equiv of the alkyne molecules have coupled on the metal center to form a metallacycle. The strong π back-bonding tendency of osmium(II) amine moieties^{5c} suggests that the conventional metallacyclopentadiene structure, which has two M-C single bonds, would be disfavored in comparison to the metallacyclopentatriene structure with two Os-C double bonds. The ¹³C{¹H} NMR spectrum of **1** does show a singlet at δ 266.6, which is consistent with the existence of carbene carbons in the proposed osmacyclopentatriene structure. An intramolecular alkyne cyclization also occurs to generate complex **2**, *cis*-[Os(C₁₀H₁₄)(en)₂](CF₃SO₃)₂, when **3** (0.206 mmol, 51.5 mM) is treated with 2,8-

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