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Thermal C-O Bond Scission in a μ_3-η^2-Coordinated Acyl. Structural Characterization of a Doubly Bridging Four-Electron Oxo Ligand

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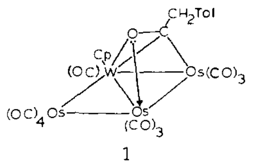
We recently described the synthesis and structure of the heterometallic tetranuclear cluster $CpWOs_3(CO)_{11}[\mu_3\text{-}\eta^2\text{-}C(O)CH_2Tol]$ (**1**, Cp = η^5-C_5H_5, Tol = *p*-$C_6H_4CH_3$), in which the bridging dihapto acyl ligand shows an "activated" C–O bond (d(C–O) = 1.372 (20) Å).[1] We now report that heating complex **1** (toluene, 110 °C) induces scission of the acyl C–O bond and provides the oxo–alkylidyne complex $CpWOs_3(CO)_6(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (**2**).[2] The oxo ligand in **2** forms a markedly unsymmetrical bridge that overall provides four electrons to the compound. These results have implications for Fischer–Tropsch style hydrocarbon synthesis and for the reactivity of polynuclear oxo complexes.



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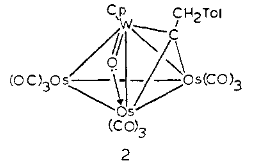

2

The molecular configuration of **2** is illustrated in Figure 1.[3] The nearly planar tetrametallic framework in **1** has been folded at the W–Os "hinge" into a pseudotetrahedral arrangement in **2**. The oxo ligand bridges a WOs edge adjacent to the WOs_2 face capped by the alkylidyne ligand, but the O(10)···C(15) separation is a distant 3.15 Å. The W–O distance in **2** is considerably shorter than that in **1** (1.812 (7) vs. 2.150 (10) Å); however, the corresponding Os–O distances and W–O–Os angles are comparable (2.169 (8) vs. 2.115 (10) Å and 83.5 (3)° vs. 80.0 (4)°, respectively). Compound **2** appears to be coordinatively saturated; i.e., it does not react readily with CO (1 atm) or PPh_3, and it has overall the 60 valence electrons needed for electronic saturation.[6]

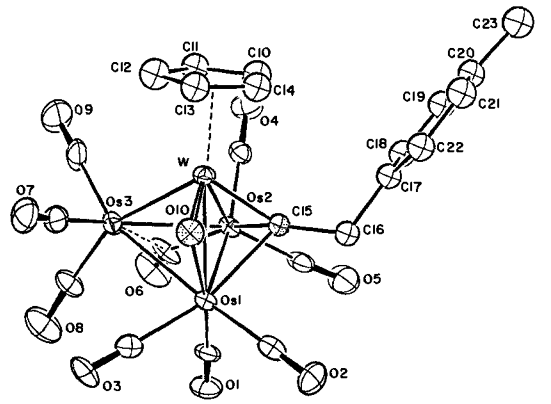

Figure 1. ORTEP diagram of the molecular structure of $CpWOs_3(\mu\text{-}O)(\mu_3\text{-}CCH_2Tol)$ (**2**). Important distances: metal–metal, W–Os(1) = 2.663 (1), W–Os(2) = 2.814 (1), W–Os(3) = 2.655 (1), Os(1)–Os(2) = 2.836 (1), Os(1)–Os(3) = 2.875 (1), Os(2)–Os(3) = 2.772 (1) Å; metal–(μ_3-C), W–C(15) = 2.030 (12), Os(1)–C(15) = 2.291 (12), Os(2)–C(15) = 2.100 (10); metal–(μ-O), W–O(10) = 1.812 (7), Os(1)–O(10) = 2.169 (20).

The oxo ligand is best viewed as forming a double bond to the tungsten atom and acting as a donor to the adjacent osmium atom, i.e., W=O→Os. This donation leads to a ca. 0.1 Å lengthening of the W=O bond in comparison with terminal W=O bonds in related compounds.[7] Previous examples of four-electron oxo ligands in cluster compounds have involved face-bridging μ_3-O species.[8] Apparently in **2**, forming a second bond to tungsten is more favorable than forming a single bond to Os(3).

Compound **1** is derived from the interaction of $CpW(CO)_2(CTol)$ and $H_2Os_3(CO)_{10}$;[1] the formation of **2** regenerates an alkylidyne moiety but with an added methylene group. Taken together these reactions form the homologation sequence shown in eq 1. Acyl species have been widely discussed as possible

$$RC \xrightarrow{+2H} RCH_2 \xrightarrow{+CO} RCH_2C(=O) \xrightarrow{-O} RCH_2C \quad (1)$$

intermediates in hydrocarbon chain growth during Fischer–Tropsch synthesis;[9] however, reduction to a hydroxyalkyl species prior to C–O bond scission has been assumed. Recent work has demonstrated facile reductive cleavage of acyl or formyl ligands by a variety of hydride reagents[10] or in bihapto cases by nucleophilic attack at carbon[11a] or electrophilic attack at oxygen.[11b] The present work shows unassisted C–O bond scission directly from an η^2-acyl complex, which suggests that the sequence in eq 1 might form the basis of a catalytic chain growth cycle.

Pyrolysis of **2** in boiling toluene under N_2 results in its conversion to $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}C{=}CHTol)(\mu\text{-}H)$ (**3**), whereas bubbling H_2 through the solution provides $CpWOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}CHCH_2Tol)(\mu\text{-}H)$ (**4**) quantitatively (see eq 2).[12] The

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(1) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *Inorg. Chem.* **1983**, *22*, 1579.

(2) Compound **2**: dark brown crystals from CH_2Cl_2/CH_3OH; IR (C_6H_{12}) ν(CO) 2075 (m), 2040 (s), 2028 (vs), 2008 (vw), 1997 (w), 1989 (m), 1972 (m), 1961 (w), 1954 (vw) cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C) δ 7.3–7.1 (m, 4 H), 5.75 (s, 5 H), 5.25 (d, 1 H, J = 15.2 Hz), 4.46 (d, 1 H, J = 15.2 Hz), 2.36 (s, 3 H); MS (70 eV), m/z 1210 (M^+), 1210 – 28X, X = 1–9 (M^+ – XCO). Anal. Calcd for $C_{23}H_{14}O_{10}WOs_3$: C, 22.93; H, 1.17. Found: C, 23.16; H, 0.95. The ^{13}C NMR signal for the nonprotonated carbon atom is shifted significantly downfield for **2** (δ 220.8) compared to **1** (δ 163.3). Pyrolysis of **1** in refluxing $C_6H_5CH_3$ gives **2** (<0.5 h) but significant amounts of **3** also. The highest yield of **2** is obtained by first treating **1** with Me_3NO (1 equiv) in CH_3CN, evaporating to dryness, and then heating a $C_6H_5CH_3$ solution of the residue briefly (<15 min) to reflux. Preparative TLC (*n*-C_5H_{12}:CH_2Cl_2 2:3, R_f = 0.26) provides **2** in 80% yield.

(3) Crystal data for **2**: $C_{23}H_{14}O_{10}WOs_3$, M_r = 1204.8; triclinic; space group $P\bar{1}$ [C_i^1; No. 2]; a = 9.704 (3) Å, b = 9.783 (3) Å, c = 14.599 (4) Å; α = 108.11 (2)°, β = 93.80 (2)°, γ = 94.57 (2)°; V = 1307 (6) Å^3; D_c = 3.06 g cm^{-3}; Z = 2; μ(Mo Kα) = 200.9 cm^{-1}. Diffraction data were collected[4] with a Syntex $P2_1$ diffractometer, and the structure was solved by MULTAN.[5] Full-matrix least-squares refinement of positional and thermal parameters (anisotropic for the $WOs_3(CO)_9(\mu\text{-}O)$ moiety, isotropic for other non-hydrogen atoms) led to convergence with R_F = 3.9%, R_{wF} = 3.5%, and GOF = 1.95 for all 3438 data.

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(6) Compare the closely related compound $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_2H$: Shapley, J. R.; Park, J. T.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182.

(7) (a) $CpW(O)(Ph)(C_2Ph_2)$, 1.69 (2) Å: Bokiy, N. G.; Gatilov, Y. V.; Struchkov, Y. T.; Ustynyuk, N. A. *J. Organomet. Chem.* **1973**, *54*, 213. (b) $W(O)Cl_2(CHCMe_3)(PEt_3)$, 1.661 (11) Å: Churchill, M. R.; Missert, J. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 3388. (c) $W(O)Cl_2(CHCMe_3)(PMe_3)_2$, 1.697 (15) Å: Churchill, M. R.; Rheingold, A. L. *Inorg. Chem.* **1982**, *21*, 1357. (d) $Cp_2W_2Fe(CO)_5(C_2Tol_2)(O)$, 1.726 (7) Å: Busetto, L.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 101.

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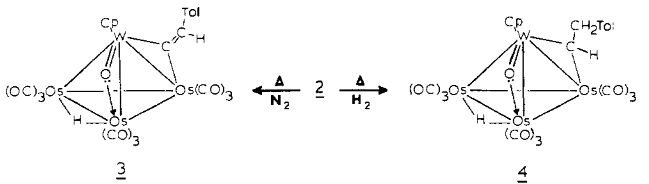

(2)

conversion of **2** to **3** or **4** does not involve loss of a ligand (i.e., CO) in order to provide a site of unsaturation for the oxidative addition of a C–H or an H–H bond. However, if the μ-oxo ligand can move reversibly from a bridging (4e$^-$ donor) to a terminal (2e$^-$ donor) position, an unsaturated intermediate is generated. This intriguing possibility is the object of further investigation.

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Registry No. 1, 85335-18-8; **2**, 88609-62-5; **3**, 88589-02-0; **4**, 88609-63-6; Os, 7440-04-2; W, 7440-33-7.

Supplementary Material Available: Listing of positional and thermal parameters for all atoms in **2** and a description of the synthesis and characterization of **3** and **4** (4 pages). Ordering information is given on any current masthead page.

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(12) The synthesis and characterization of 3 and 4 are described in the supplementary material. The structures have been determined by X-ray diffraction studies: Churchill, M. R.; Li, Y. J., unpublished results.

Mechanisms of Hole-Catalyzed Reactions: Ab Initio Theoretical Reaction Paths for Olefin Cation Radical/Olefin Cycloaddition

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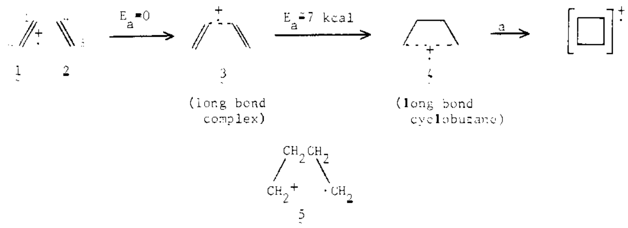
The existence of cation radical chain mechanisms for certain organic reactions, originally established for a few, apparently somewhat esoteric, reactions, has proved to be a pioneering observation.[1-4] Recent experimental and theoretical observations in the field of cation radical chemistry[5,6] have lead to an enhanced appreciation of the generality of this new mechanistic type and to recognition of its importance as a fundamental catalytic principle, termed hole catalysis.[7]

The phenomenon of hole catalysis is made feasible by the astonishingly low activation energies of many cation radical reactions, including most pericyclic reactions.[6] Consequently, the simple process of ionization (electron transfer to a catalyst hole), followed by a cation radical chain sequence, and terminated by electron acceptance represents a catalytic route of impressive efficiency and generality. The hole-catalyzed Diels–Alder[5] and olefin cyclodimerization[1,8] reactions are outstanding examples of hole-catalyzed reactions, which already have demonstrable utility in organic synthesis. The prototype of the latter reaction, the cycloaddition of ethene cation radical and ethene, is an attractive subject for a fully optimized, extended basis set ab initio theoretical reaction path study. Reaction path calculations of this quality have not previously been reported for any hole-catalyzed reaction, and very few such calculations have been published for any reaction path involving four or more "heavy atoms". The calculations reported here illuminate for the first time and with substantial credibility several basic aspects of cation radical cycloadditions, some of which differ sharply from those traditionally imputed to reaction paths of neutrals.

Scheme I



^{a} Only feasible when hole-delocalizing substituents are present.

For convenience, the ethene/ethene cation radical cycloaddition path was calculated commencing with the fully optimized cyclobutane cation radical (product) which, as previously reported, has a long-bond structure of trapezoidal geometry (**4**),[9] and then progressively lengthening the long bond to afford, eventually, the two ethenic fragments (**1** and **2**). The path was calculated initially using a minimum basis set (STO-3G) to provide a basis, subsequently, for evaluating the necessity for the more expensive extended basis set calculations in future theoretical studies of cation radical reactions. The energy of each point on the reaction path was minimized with respect to all geometric variables using a convergence criterion of 1×10^{-4} au for general points and 1×10^{-5} au for energy extrema. The energy profile of the STO-3G path (Figure 1) is essentially that of a concerted reaction, except that a shallow minimum is encountered at a reaction coordinate value $R_{23} = 4.400$ Å corresponding to a loose π complex between a moiety that is approximately an ethene cation radical ($R_{34} = 1.429$ Å) and one that resembles an ethene molecule ($R_{12} = 1.349$ Å). The shorter pericyclic carbon-carbon distance is $R_{14} = 3.121$ Å, and the carbon framework is planar. Although the transition state ($R_{23} = 4.350$, $R_{12} = R_{34} = 1.423$ Å) is only 0.34 kcal mol^{-1} above the total energies of the isolated ethene plus ethene cation radical fragments, the calculated activation energy for the formation of the cyclobutane cation radical from the π complex is 4.26 kcal mol^{-1}.

The 3-21G basis set has been recommended as a split valence set that gives results comparable to those of the 4-31G basis set, but with appreciably greater economy.[10] The fully optimized 3-21G reaction path, calculated in the same way as the STO-3G path, is significantly different from the latter (Figure 1, Table I). With the extended basis set, no minimum is found for a loose π complex such as that encountered with STO-3G. The transition state is actually 12.65 kcal mol^{-1} below the energies of the isolated fragments, but an activation energy of 7.14 kcal mol^{-1} is required to form the cyclobutane cation radical (**4**) from a stable intermediate (**3**) ($R_{23} = 3.062$, $R_{14} = 2.227$, $R_{12} = 1.381$, $R_{34} = 1.378$ Å). The latter is not readily dissociated ($E_a = 19.80$ kcal mol^{-1}) to ethenic fragments in competition with cyclization ($E_a = 7.14$ kcal mol^{-1}). Unlike the STO-3G complex, the 3-21G intermediate

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(7) The term "hole" specifically refers to an "electron hole". Any entity that can accept a single electron is considered to have an electron hole. Hole catalysis refers to catalysis initiated by transfer of an electron hole from a hole catalyst to a substrate. Cation radicals, of course, represent one important class of species having an electron hole.

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