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Consecutive C−C Bond Scission of an Allyl Ligand on a WOs_3 Cluster Framework

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Summary: The reaction of $Os_3(CO)_9(C_2R_2)$ *(R = Tol, Ph; Tol = p-*C_6H_4Me*) with* $Cp(CO)_2W{\equiv}CTol$ *(Cp =* η^5*-*C_5H_5*) produces an alkylidyne−alkyne complex* $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2R_2)(\mu_3\text{-}CTol)$ *[**1a** (R = Tol), **1b** (R = Ph)], which is converted to two isomeric allyl complexes* $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^3\text{-}C_3R_2Tol)$ *(**2a,b** and **3a,b**) upon thermolysis. Complexes **3a,b**, in which the allyl ligand is π-coordinated to the tungsten atom, undergo consecutive allyl C−C bond cleavage to afford trialkylidyne complexes* $CpWOs_3(CO)_9(\mu_3\text{-}CR)_2(\mu_3\text{-}CTol)$ *(**5a,b**) via alkylidyne−alkyne complex* $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2R_2)(\mu_3\text{-}CTol)$ *or* $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2RTol)(\mu_3\text{-}CR)$ *(**4a,b**), together with formation of* $CpWOs_3(CO)_8(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_2R_2)(\mu_3\text{-}CTol)$ *or* $CpWOs_3(CO)_8(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_2RTol)(\mu_3\text{-}CR)$ *(**6a,b**) as a minor product.*

There has been considerable current interest in the synthesis and study of cluster complexes due to their potential as models for the behavior of small unsaturated molecules on catalytic metal surfaces.[2] One of the characteristic features of metal cluster chemistry is the promotion of bond scission and bond formation reactions of such small organic ligands.[3] We report herein a facile carbon−carbon bond formation of alkylidyne and alkyne coupling to form an allyl group and consecutive carbon−carbon bond scission reactions of the allyl ligand to afford a trialkylidyne complex on a MOs_3 (M = Mo, W) mixed metal framework.

The reaction of $Os_3(CO)_9(C_2R_2)$ with $Cp(CO)_2W{\equiv}CTol$ in dichloromethane at low temperature (ca. 0 °C, 10 h) produces an alkylidyne−alkyne complex $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2R_2)(\mu_3\text{-}CTol)$ [**1a** (R = Tol), **1b** (R = Ph] in 65% yield, a spiked triangular arrangement of four metal atoms (see Scheme 1). Thermal coupling (45 °C, 3 h, $CHCl_3$) of the alkyne and alkylidyne ligands in complex **1** gives an allyl complex of a tetrahedral metal framework, $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^3\text{-}C_3R_2Tol)$ (**2a,2b**) in quantitative yield, where an allyl ligand is π-coordinated to the osmium atom. Complex **2** may be formed by reductive elimination of the two carbon atoms on the $Os(CO)_2$ center of **1** followed by some bond rearrangements. The allyl ligand of **2** undergoes thermal rearrangement (45 °C, 15 h, $CHCl_3$) to give isomeric allyl complex **3** (75% yield), in which the allyl ligand is π-coordinated to the tungsten center. Results on structural characterization of **1b**, **2a**, **3a**, and **6b** (vide infra) by single crystal X-ray diffraction studies have been shown in Scheme 1 and will be reported in a full paper.[4] Due to the asymmetric nature[5] of the tungsten center of **3**, ^1H NMR spectra (20 °C, $CDCl_3$) of **3a** (R = Tol) and **3b** (R = Ph) show three (δ 2.27, 2.20, and 2.18) and two (δ 2.17 and 2.12, intensity ratio 1.0:1.3) resonances for the methyl groups of the tolyl moieties, respectively.[6] The variable-temperature ^1H NMR spectra of **3a** reveal a typical two site exchange for the two inequivalent side methyl groups (δ 2.27 and 2.20) of the allyl ligand (T_c = 50 °C, 300 MHz), which indicates that localized 2-fold rotation ($k = 31\ s^{-1}$, $\Delta G_c^{\ddagger} = 70\ kJ\ mol^{-1}$) of the carbonyl and cyclopentadienyl ligands on the tungsten atom is taking place above room temperature.

Prolonged thermolysis (50 °C, 16 h, $CHCl_3$) of **3a** induces scission of an allyl C−C bond to produce an alkylidyne−alkyne complex of $CpWOs_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)(\mu_3\text{-}CTol)$ (**4a**,[7] 36% yield) together with unreacted **3a** (47%) and a small amount (<10%) of **5a** and **6a**. Three isomers (methyl peaks at δ 2.41, 2.22, and 2.20, intensity ratio 1.2:1.0:1.5) of **4b**[7] have been obtained in the case of the diphenylacetylene complex depending on the allyl C−C bond cleaved. An X-ray study of **4a** (see Figure 1) confirms the allyl carbon−carbon bond cleavage.[8] The tetranuclear molecule contains a "butterfly" arrangement of metal atoms, typical of a 62 valence electron (VE) tetranuclear complex,[10] with coordinated alkylidyne and alkyne ligands. The μ_3-CTol ligand is

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[4] Park, J. T.; et al. To be submitted for publication. All the new compounds **1a−6b** were purified by preparative TLC (silica gel) using appropriate mixtures of *n*-hexane and dichloromethane as eluents.

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[6] Compound **3a**: ^1H NMR ($CDCl_3$, 25 °C) δ 6.31−7.59 (m, 12H), 5.88 (s, 5H), 2.27 (s, 3H), 2.20 (s, 3H), 2.18 (s, 3H); IR (C_6H_{12}) ν(CO) 2072 (s), 2049 (sh), 2038 (vs), 2027 (s), 2002 (m), 1990 (m), 1970 (m), 1949 (w) cm^{-1}. Anal. Calcd for $C_{39}H_{26}O_{10}WOs_3{\cdot}2CH_2Cl_2$: C, 31.19; H, 1.92. Found: C, 31.35; H, 1.95. Compound **3b**: ^1H NMR ($CDCl_3$, 25 °C) δ 6.02−7.68 (m, 14H), 5.91 (s, 5H), 2.17 (s, 3H), 2.12 (s, 3H); ^1H NMR (C_6D_6, 25 °C) δ 6.62−7.54 (m, 14H), 5.24 (s, 5H), 5.23 (s, 5H), 1.90 (s, 3H), 1.85 (s, 3H); IR (C_6H_{12}) ν(CO) 2073 (s), 2050 (sh), 2039 (vs), 2028 (s), 2003 (m), 1990 (m), 1970 (m), 1949 (w) cm^{-1}. Anal. Calcd for $C_{37}H_{22}O_{10}WOs_3{\cdot}2CH_2Cl_2$: C, 30.20; H, 1.69. Found: C, 30.41; H, 1.83.

[7] Compound **4a**: ^1H NMR ($CDCl_3$, 25 °C) δ 6.51−7.11 (m, 12H), 5.13 (s, 5H), 2.42 (s, 3H), 2.23 (s, 3H), 2.21 (s, 3H); IR (C_6H_{12}) ν(CO) 2079 (vs), 2054 (vs), 2033 (vs), 2006 (s), 1989 (s), 1982 (m), 1969 (s), 1952 (w), 1706 (w) cm^{-1}. Anal. Calcd for $C_{39}H_{26}O_{10}WOs_3$: C, 33.24; H, 1.86. Found: C, 33.56; H, 2.08. Compound **4b**: ^1H NMR ($CDCl_3$, 25 °C) δ 6.60−7.16 (m, 14H), 5.15 (s, 5H), 5.14 (s, 5H), 2.41 (s, 3H), 2.22 (s, 3H), 2.20 (s, 3H); IR (C_6H_{12}) ν(CO) 2080 (vs), 2055 (vs), 2034 (vs), 2007 (s), 1990 (s), 1983 (m), 1968 (s), 1953 (w), 1707 (w) cm^{-1}. Anal. Calcd for $C_{37}H_{22}O_{10}WOs_3$: C, 32.18; H, 1.61. Found: C, 32.62; H, 1.63.

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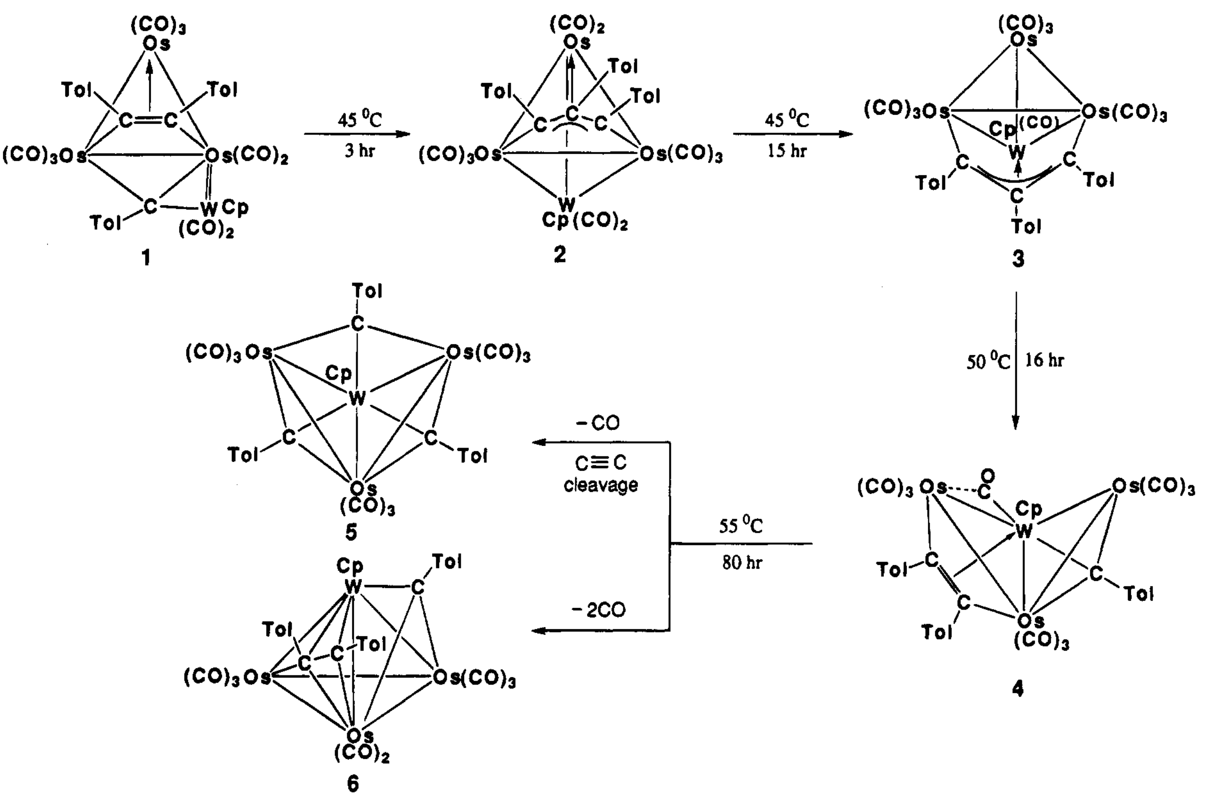
Scheme 1



bonded to the outer face of the W—Os(2)—Os(3) "wing" triangle. The μ_3-η^2-C_2Tol_2 ligand lies on the outer face of the other W—Os(1)—Os(2) "wing" and is formally π-bonded to W and σ-bonded to Os(1) and Os(2) atoms. The carbonyl ligand on the tungsten atom is oriented such as to suggest a weak interaction (semibridging) with the Os(1) center [Os(1)···CO(W) = 2.42(6) Å].

Complex **4** undergoes two parallel thermal reactions: the alkyne C≡C bond cleavage to give a trialkylidyne complex $CpWOs_3(CO)_9(\mu_3\text{-}CTol)_3$ (**5a, 5b**)[11] in 82% yield by loss of a carbonyl ligand and the alkyne rearrangement from a μ_3-(η^2-∥) to a μ_3-(η^2-⊥) alkyne to afford $CpWOs_3(CO)_8(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_2Tol_2)(\mu_3\text{-}CTol)$ (**6a, 6b**) (58 VE) in 10% yield by loss of two carbonyl ligands. However, initial decarbonylation of **4a** with Me_3NO/MeCN and subsequent stirring at 25 °C in dichloromethane for 0.5 h produce only complex **6a** in 42% yield by the latter pathway. Complex **6** can be quantitatively converted back to complex **4** upon carbonylation (80 °C, 1.5 h, toluene, 1 atm of CO). The crystal structure of **5a**,[12] shown in Figure 2, reveals a "butterfly" arrangement (62 VE) of four metal atoms and the presence of three μ_3-CTol ligands. The two equivalent alkylidyne carbon atoms, C(20) and C(30), are bonded to the outer face of both "wings". The third

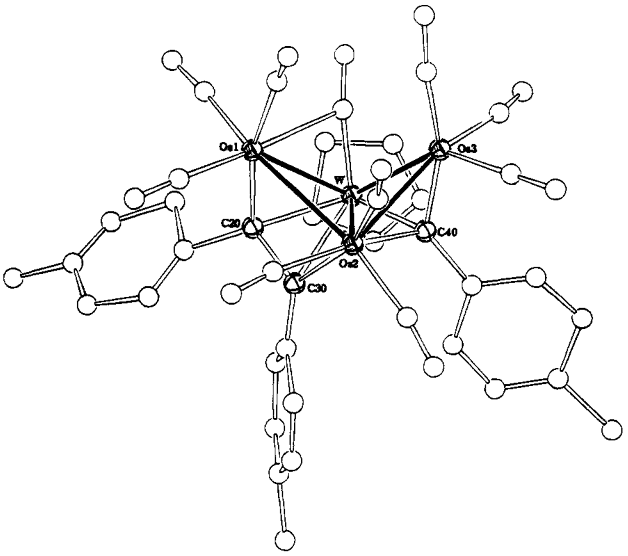


Figure 1. Molecular structure of **4a**. Distances within the molecule: [metal–metal] W–Os(1) = 2.827(3), W–Os(2) = 2.764(3), W–Os(3) = 2.851(3), Os(1)-Os(2) = 2.874(3), Os(2)-Os(3) = 2.848(3) Å; [metal–(μ_3-C)] W–C(40) = 2.02(5), Os(2)-C(40) = 2.13(5), Os(3)-C(40) = 2.06(5) Å; [metal–carbon(μ_3-η^2-alkyne)] W–C(20) = 2.29(5), W–C(30) = 2.39(4), Os(1)-C(20) = 2.18(4), Os(2)-C(30) = 2.11(4) Å; [alkyne C≡C] C(20)-C(30) = 1.49(5) Å.

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(8) Crystal data for **4a**: $C_{39}H_{26}O_{10}WOs_3$; M_r = 1409.08; triclinic; space group $P\bar{1}$ [C^1_i; No. 2]; a = 10.877(3), b = 18.837(2), and c = 10.820(1) Å; α = 100.94(1), β = 103.67(1), and γ = 101.73(1)°; V = 2042.1(6) Å^3; Z = 2; μ(Mo Kα) = 12.21 mm^{-1}. Diffraction data were collected using a CAD4 diffractometer. The structure was solved by SHELXS86[9a] and refined by SHELX-76.[9b] The final discrepancy indices were R = 8.54%, R_w = 9.08%, and GOF = 1.258 for 283 parameters refined against 2562 reflections that had $F_o > 4\sigma F_o$.

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(11) In a typical experiment, a chloroform solution of **4a** (21.2 mg, 15.0 mmol) was stirred at 55 °C for 80 h. Evaporation of the solvent and purification by preparative TLC (dichloromethane:n-hexane = 3:2) provided yellow solid **5a** (17.0 mg, 12.3 mmol, 82%, R_f = 0.45) and brown solid **6a** (2.0 mg, 1.5 mmol, 10%, R_f = 0.39). Compound **5a**: ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.06–7.23 (m, 12H), 5.18 (s, 5H), 2.35 (s, 9H); IR (CCl_4) ν(CO) 2081 (s), 2056 (vs), 2031 (vs), 2015 (w), 2002 (w), 1972 (m) cm^{-1}. Anal. Calcd for $C_{38}H_{26}O_9WOs_3$: C, 33.05; H, 1.90. Found: C, 32.91; H, 1.88. Compound **5b**: ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.07–7.37 (m, 14H), 5.21 (s, 5H), 2.37 (s, 3H); IR (C_6H_{12}) ν(CO) 2080 (s), 2057 (vs), 2031 (vs), 2018 (w), 2003 (w), 1973 (m) cm^{-1}. Anal. Calcd for $C_{36}H_{22}O_9WOs_3$: C, 31.96; H, 1.64. Found: C, 31.64; H, 1.73.

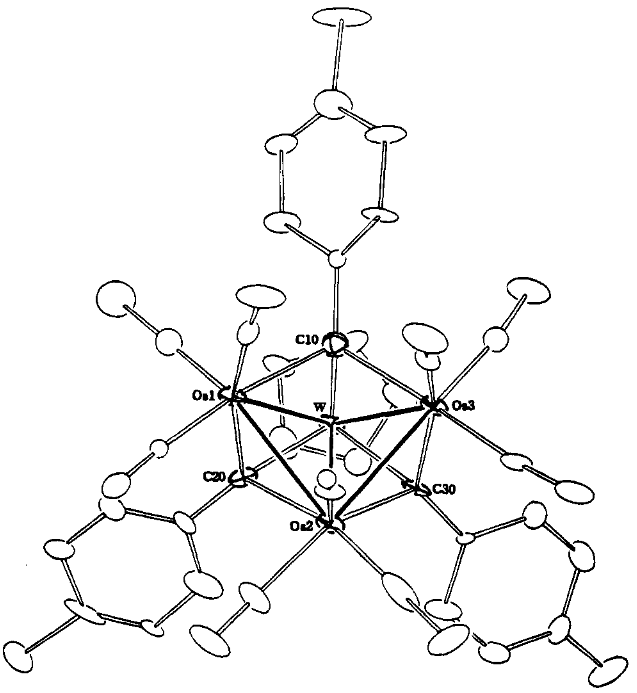

Figure 2. Molecular structure of **5a**. Distances within the molecule: [metal–metal] W–Os(1) = 2.831(2), W–Os(2) = 2.819(1), W–Os(3) = 2.797(3), Os(1)-Os(2) = 2.856(2), Os(2)-Os(3) = 2.834(2) Å; [metal–(μ_3-C)] W–C(10) = 1.97(3), W–C(20) = 2.03(2), W–C(30) = 1.94(3), Os(1)-C(10) = 2.27(3), Os(1)-C(30) = 2.07(2), Os(2)-C(20) = 2.29(2), Os(2)-C(30) = 2.33(3), Os(3)-C(10) = 2.28(3), Os(3)-C(20) = 2.10(2) Å.

unique μ_3-CTol ligand, centered on C(10), spans the tungsten (or "hinge") position and the two "wing-tip" osmium atoms, Os(1) and Os(3). Complex **5a** shows a single resonance (δ 2.35) for the two inequivalent methyl groups of the tolyl moieties, and the two isomers of **5b** also exhibit a single resonance (δ 2.37) for the methyl group of each isomer. This observation indicates that complex **5** in solution may undergo a degenerate metal framework rearrangement that interchanges the three alkylidyne moieties, which can be interpreted as breaking and making Os–Os bonds.[13] The μ_3-(η^2-$\perp$) alkyne bonding mode in tetrahedral cluster **6** with 58 VE can be understood by analogy with that well established for an alkyne–M$_3$ unsaturated cluster with 46 VE.[14] Complex **6b** also exists as three isomers which are derived from three isomers of **4b** (three Cp and three methyl ^{1}H resonances for **6b** in toluene-d_8: see supplementary material).

Monitoring the pyrolysis of **1a** in CDCl$_3$ at 40 °C by ^{1}H NMR spectroscopy reveals that complex **2a** is formed rapidly in the beginning, but as the reaction proceeds, complex **3a** becomes dominant (consecutive first-order kinetics). An analogous kinetic study with **3a** at 50 °C shows that complexes **2a** and **3a** are in equilibrium in a ratio of ca. 1:4 and rapid formation of **4a** is followed by slower formation of both **5a** and **6a**. The corresponding Mo analogue of **1a** undergoes analogous sequential reactions much faster than WOs$_3$ complexes.

The coupling of an alkylidyne with an alkyne to form an allyl ligand (**1** → **2**) has been previously reported in several cases.[15] The analogous coupling reaction (**4** → **3**) was expected in the thermolysis reaction of **4**; nevertheless, the C≡C bond scission of the alkyne ligand has been observed. There have been several reports that describe the cleavage of alkyne triple bonds in cluster complexes,[16] but unprecedented is the present consecutive C–C bond cleavage from an allyl group to afford trialkylidyne moieties via an alkylidyne–alkyne intermediate (**3** → **4** → **5**). To the best of our knowledge compound **5a** represents the first example of a trialkylidyne cluster derived from the cleavage of the C–C bonds of a coordinated allyl ligand.

Further studies on the reactivity, fluxionality, and kinetics of these complexes are in progress.

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Supplementary Material Available: A listing of spectroscopic data for complexes **1a,b**, **2a,b**, and **6a,b**, tables of experimental details of the X-ray diffraction studies, positional parameters, isotropic thermal parameters, and bond distances and angles for **4a** and **5a**, and ORTEP diagrams (13 pages). Ordering information is given on any current masthead page.

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(12) Crystal data for **5a**: C$_{38}$H$_{26}$O$_9$WOs$_3$; M_r = 1381.07; monoclinic; space group $P2_1/c$ [C^5_{2h}; No. 14]; a = 20.263(4), b = 9.890(1), and c = 20.011(8) Å; β = 114.80(2)°; V = 3640.5(3) Å^3; Z = 4; μ(Mo Kα) = 13.70 mm^{-1}. Diffraction data were collected and treated as described for **4a**. The final discrepancy indices were R = 7.8%, R_w = 8.0%, and GOF = 0.7979 for 460 parameters refined against 3609 reflections that had $Fo > 4\sigma F_o$.

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