Stoichiometric Alkyne Metathesis at Metal Cluster Compounds: Interconversion of Os_3W Alkyne–Alkylidyne and Dimetalloallyl Clusters

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*Summary: Treatment of $Os_3(CO)_{10}(C_2Me_2)$ with $CpW(CO)_2(\equiv CTol)$ produced the alkylidyne–alkyne cluster $CpWOs_3(CO)_{10}(\mu_3\text{-}CMe)(CMeCTol)$ (**2**) and the dimetalloallyl complex $CpWOs_3(CO)_9[C(Me)C(Me)C(Tol)]$ (**3**) in sequence. Thermolysis of **3** induced the selective scission of one C—C bond to give a second alkylidyne–alkyne cluster, $CpWOs_3(CO)_8(\mu_3\text{-}CTol)(C_2Me_2)$ (**4**), providing a model of alkyne metathesis through a dimetalloallyl intermediate.*

We have recently prepared and examined the reactivity of Os_3W clusters with ligated C_4 hydrocarbons by addition of tungsten acetylide complexes to Os_3 alkyne complexes.[1] Our work has been motivated by attempts to develop a generalized strategy to mixed-metal clusters[2] and to learn about the reaction pathway of chemisorbed hydrocarbon intermediates on metal surfaces.[3] This investigation is now extended to tetranuclear Os_3W cluster compounds with the asymmetric C_3 dimetalloallyl ligand $\mu_3\text{-}\eta^3\text{-}C(Tol)C(Me)C(Me)$. Before our investigation of these tetranuclear dimetalloallyl clusters, others have also studied syntheses and reactivities of dinuclear and trinuclear derivatives.[4] Among the various chemical reactions probed, that of forming and breaking the C—C bond is important because it provides valuable mechanistic insight into alkyne metathesis.[5] In this paper, we report a novel example of transformation of ligand pairs [μ_3-CMe + MeC_2Tol] to [μ_3-CTol + MeC_2Me] through the ligand $\mu_3\text{-}\eta^3$-[C(Tol)C(Me)C(Me)]. This experimental result substantiates an earlier report by Stone and coworkers, who demonstrated that two ligated C_3 allyl fragments, differing in the arrangement of substituents, were produced via cleavage and formation of a C—C bond, providing compelling evidence for scrambling of [CR + $R'C_2R'$] and [CR′ + $R'C_2R$] fragments.[6] Such rearrangement on metal complexes is noteworthy because it could in theory allow a dimetalloallyl species to be considered a possible intermediate of catalytic alkyne metathesis.

The alkyne cluster $Os_3(CO)_{10}(C_2Me_2)$ (**1**) reacts with approximately 3 equiv of $CpW(CO)_2(\equiv CTol)$ in refluxing toluene solution (30 min) to afford the red-orange alkylidyne–alkyne complex $CpWOs_3(CO)_{10}(\mu_3\text{-}CMe)(CMeCTol)$ (**2**) and dark green dimetalloallyl complex $CpWOs_3(CO)_9[C(Me)C(Me)C(Tol)]$ (**3**) in 27 and 38% yields, respectively. These two cluster compounds were fully characterized by spectroscopic[7] and X-ray measurements.[8]

The X-ray analysis of **2** indicated that it consists of a Os_3W butterfly arrangement with the W atom located at the hinge position (Figure 1). The alkylidyne group, which connects to both wingtip Os atoms with two long bonds (2.23(2) and 2.13(2) Å) and to the W atom with a short interaction (2.01(2) Å), carries a methyl substituent but not a tolyl substituent. This information suggests that the alkylidyne ligand is derived from the 2-butyne ligand but not from the CTol unit of $CpW(CO)_2(\equiv CTol)$. In addition, the ligated alkyne [C(Me)C(Tol)], generated from coupling of the second CMe unit and the incoming CTol fragment, lies on the W–Os(1)–Os(2) face opposite

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(7) Spectral data for **2**: MS (FAB, ^{192}Os, ^{184}W) *m/z* 1258 (M^+); IR (C_6H_{12}) ν(CO), 2077 (s), 2049 (vs), 2030 (s), 2026 (m), 2009 (m), 1996 (m), 1981 (m), 1969 (m), 1955 (m), 1939 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 294 K) δ 7.38 (d, 2H, $J_{H-H} = 8.0$ Hz), 7.19 (d, 2H, $J_{H-H} = 8.0$ Hz), 5.22 (s, 5H), 4.49 (s, 3H), 3.14 (s, 3H), 2.30 (s, 3H). Anal. Calcd for $C_{27}H_{18}O_{10}Os_3W$: C, 25.80; H, 1.44. Found: C, 25.40; H, 1.52. Spectral data for **3**: MS (FAB, ^{192}Os, ^{184}W) *m/z* 1230 (M^+); IR (C_6H_{12}) ν(CO), 2067 (m), 2030 (vs), 1995 (w), 1982 (s), 1949 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 294 K) δ 7.75 (d, 1H, $J_{H-H} = 7.6$ Hz), 7.33 (d, 1H, $J_{H-H} = 7.6$ Hz), 7.04 (d, 1H, $J_{H-H} = 7.6$ Hz), 5.84 (d, 1H, $J_{H-H} = 7.6$ Hz), 4.65 (s, 5H), 3.69 (s, 3H), 2.58 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 294 K) δ 197.6, 190.6 (broad, 3C), 189.4 (broad, 3C), 185.9, 185.6 (CO), 166.5 ($J_{W-C} = 49$ Hz), 154.0 ($J_{W-C} = 45$ Hz), 151.9, 135.3, 132.6, 129.1, 129.0, 128.6, 127.4, 87.6 (5C, Cp), 40.1 (Me), 26.0 (Me), 20.9 (Me). Anal. Calcd for $C_{26}H_{18}O_9Os_3W$: C, 25.41; H, 1.48. Found: C, 25.41; H, 1.57.

(8) Crystal data for **2**: $C_{26}H_{18}O_{10}Os_3W$, $M_r = 1253.24$, triclinic space group $P\bar{1}$, $a = 9.580(2)$ Å, $b = 12.513(4)$ Å, $c = 14.957(7)$ Å, $\alpha = 72.17°$, $\beta = 81.08(3)°$, $\gamma = 79.30(2)°$, $V = 1668(1)$ Å^3, $Z = 2$, $D_c = 2.741$ mg/cm^3, $F(000) = 1240$, μ(Mo Kα) = 15.21 mm^{-1}, $R_F = 0.047$, $R_w = 0.048$, GOF = 2.48. Crystal data for **3**: $C_{25}H_{18}O_9Os_3W$, $M_r = 1216.86$, orthorhombic space group *Pbcn*, $a = 29.065(4)$ Å, $b = 9.476(3)$ Å, $c = 22.839(5)$ Å, $V = 6291(3)$ Å^3, $Z = 8$, $D_c = 2.570$ mg/cm^3, $F(000) = 4334$, μ(Mo Kα) = 15.86 mm^{-1}, $R_F = 0.049$, $R_w = 0.043$, GOF = 1.41.

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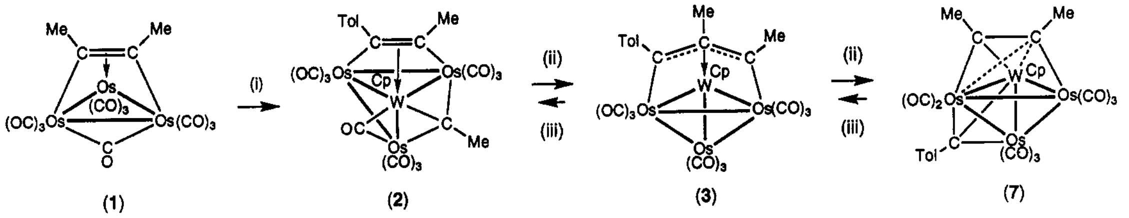
Scheme 1



[a] Legend: (i) $CpW(CO)_2(CTol)$; (ii) –CO; (iii) +CO.

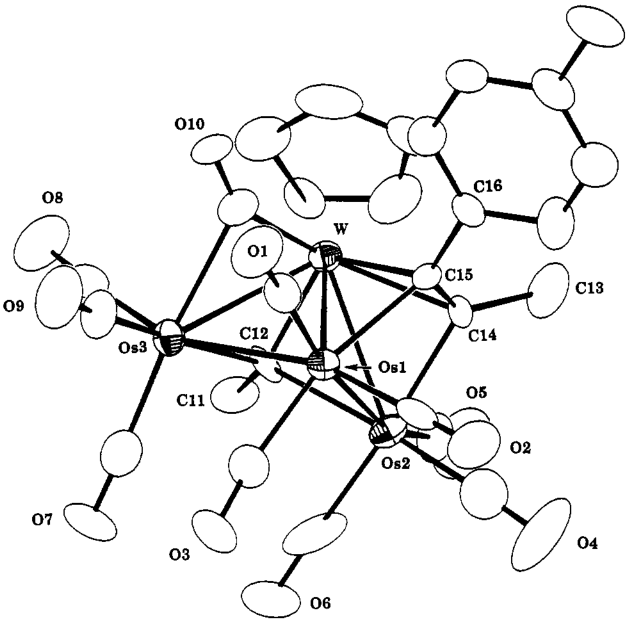


Figure 1. Molecular structure of **2** and the atomic numbering scheme. Selected bond lengths (Å): W–Os(1) = 2.832(1), W–Os(2) = 2.778(2), W–Os(3) = 2.767(1), Os(1)–Os(2) = 2.787(1), Os(1)–Os(3) = 2.889(2), W–C(12) = 2.01(2), Os(2)–C(12) = 2.23(2), Os(3)–C(12) = 2.13(2), C(11)–C(12) = 1.55(2), W–C(14) = 2.27(1), Os(2)–C(14) = 2.17(2), W–C(15) = 2.27(1), Os(1)–C(15) = 2.16(2), C(13)–C(14) = 1.49(3), C(14)–C(15) = 1.35(2), C(15)–C(16) = 1.48(3).

the bridging ethylidyne group with two short Os—C bonds and two long W—C bonds, showing characteristics of the typical 2σ + π bonding mode.[9]

For complex **3**, the structure adopts a distorted Os_3W tetrahedral core, on which the W atom is capped by a Cp ligand, and each Os atom is coordinated by three orthogonal terminal CO ligands (Figure 2). The 2-butyne and tolylalkylidyne fragments coupled to form an allyl functional group, which lies over the top of one Os_2W triangle and is coordinated to the atoms Os(1) and Os(3) via a σ-bond and to the W atom via a π-allyl interaction. Simple electron counting gives 58 valence electrons for this molecule, suggesting that the molecule is unsaturated and contains a multiple bonding interaction. However, the molecule has no apparent localized M=M double bond, as lengths of all the Os—W bonds are in the narrow range 2.682–2.722 Å and are all substantially shorter than that of other Os—Os single bonds (2.891–2.794 Å). Thus, the unsaturation is distributed over all four metal centers, comparable to what is observed in the unsaturated 56-electron compound $H_4Re_4(CO)_{12}$.[10] An essentially identical dimetalloallyl bonding mode is observed in the 60-electron tetrahedral cluster $Os_4(CO)_{11}(\mu\text{-}H)(\mu\text{-}\eta^3\text{-}C_4H_5)$[11] and in many other trinuclear allyl cluster compounds.[12] Consistent with the solid-state structure, the ^{13}C NMR spectrum shows five Os–CO signals at δ 197.6, 190.6, 189.4, 185.9, and 185.6 in the ratio 1:3:3:1:1, presumably implying the presence of three $Os(CO)_3$ units, two of which undergo rapid tripodal CO exchange. Three additional signals appeared at δ 166.5 (J_{W-C} = 49 Hz), 154.0 (J_{W-C} = 45 Hz), and 151.9 and are clearly due to the dimetalloallyl carbon atoms.

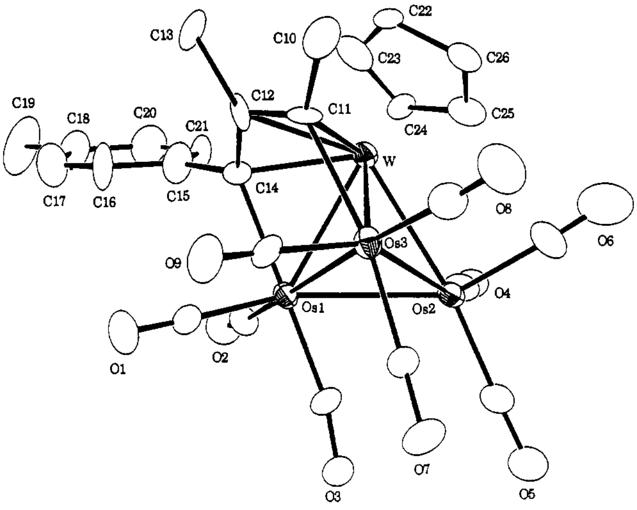


Figure 2. Molecular structure of **3** and the atomic numbering scheme. Selected bond lengths (Å): W–Os(1) = 2.668(2), W–Os(2) = 2.722(2), W–Os(3) = 2.682(2), Os(1)–Os(2) = 2.805(2), Os(1)–Os(3) = 2.891(2), Os(2)–Os(3) = 2.794(2), W–C(11) = 2.13(2), W–C(12) = 2.34(2), W–C(14) = 2.19(2), Os(1)–C(14) = 2.18(3), Os(3)–C(11) = 2.24(3), C(11)–C(12) = 1.39(4), C(12)–C(14) = 1.43(3).

The order of formation of these clusters was established. Our experimental evidence indicates that the alkylidyne–alkyne cluster **2** was formed prior to **3**, as the latter contains one CO ligand less than the former and because when the reaction time is decreased from 30 to 20 min, the yield of **2** increased to 39%, whereas the yield of **3** diminished to 21%. Furthermore, complex **3** appears to undergo a unique thermal transformation to form the second alkylidyne–alkyne cluster $CpWOs_3(CO)_8(\mu_3\text{-}CTol)(C_2Me_2)$ (**4**)[13] in over 80% yield, through a process involving elimination of CO and selective scission of the C—C bond of the dimetalloallyl ligand. The X-ray diffraction study of **4** shows that it consists of tolylalkylidyne and 2-butyne ligands coordinated to a Os_2W triangle and to one adjacent Os_2W face, respectively; the alkyne adopted the unusual μ_3-η^2($\perp$) mode for electron-deficient clusters.[14] In accord with this

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assignment, the ^{13}C NMR spectrum shows seven CO signals with one signal possessing double intensity corresponding to two coincident CO ligands, one triply bridging alkylidyne signal at δ 267.1 (J_{W-C} = 97 Hz), and two alkyne signals at δ 170.1 (J_{W-C} = 71 Hz) and 161.0.

Attempts were also made to investigate the reverse process **4** → **3** → **2**. Exposing a solution of **3** under CO at room temperature has produced **2** as a transient species, but upon raising the temperature or increasing the reaction time, we isolated the saturated tetrahedral dimetalloallyl cluster $CpWOs_3(CO)_{10}[C(Me)C(Me)C(Tol)]$ as the final product. On the other hand, heating a solution of **4** with CO regenerated only a small amount of **3**, indicating that re-formation of the allyl C—C bond is not completely accessible. Hence, the process **2** → **3** → **4** is best considered irreversible under this circumstance. This sequence is thus akin to the cleavage of alkyne in tetranuclear Os_3W and Co_2Fe_2 clusters,[15] rather than the respective process observed in trinuclear OsW_2 and RuW_2 alkyne complexes, which is completely reversible.[16] Extensive discussion of these reactions will be described in the near future.

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Supplementary Material Available: Tables of crystal data, bond distances, positional parameters, and anisotropic thermal parameters for **2** and **3** (10 pages). Ordering information is given on any current masthead page.

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(13) Selected crystal data for **4**: orthorhombic space group $Pna2_1$, a = 19.066(4) Å, b = 9.032(2) Å, c = 18.059(4) Å. Spectral data for **4**: MS (FAB, ^{192}Os, ^{184}W) m/z 1202 (M$^+$); IR (C_6H_{12}) ν(CO), 2069 (vs), 2037 (vs), 2000 (vs), 1991 (s), 1970 (s), 1953 (w), 1936 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K) δ 7.02 (d, 2H, J_{H-H} = 8.0 Hz), 6.71 (d, 2H, J_{H-H} = 8.0 Hz), 5.49 (s, 5H), 3.49 (s, 3H), 2.96 (s, 3H), 2.35 (s, 3H), ^{13}C NMR (100 MHz, THF-d_8, 256 K) δ 203.9, 198.3, 197.7, 185.3, 182.6, 180.8, 177.9 (2C) (CO), 267.1 (J_{W-C} = 97 Hz, *C*Tol), 170.1 (J_{W-C} = 71 Hz, *C*Me), 161.0 (*C*Me), 137.7, 130.3 (2C), 128.8 (2C), 115.9, 100.9 (5C, Cp), 28.0 (Me), 27.1 (Me), 22.2 (Me). Anal. Calcd for $C_{25}H_{18}O_8Os_3W$: C, 25.01; H, 1.51. Found: C, 24.69; H, 1.54.

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