characterized as $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$.[12] The ratio of these two products depends on the temperature at which the methylation is conducted; a higher temperature (35 °C) favors the latter whereas a lower temperature (<25 °C) favors the former. In the absence of methylating agent 1 undergoes other rearrangements involving both the carbene and carbyne centers. The details of these reactions are under investigation.

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Registry No. 1, 98015-25-9; (μ–H)Os3(CO)10(μ–COMe), 69048-01-7; [(μ–H)Os3(CO)9(μ–COMe)(η^1–C(O)Ph)], 98015-26-0; (μ–H)Os3(CO)10(μ3–CPh), 95122-80-8; Os3(CO)9(μ3–CPh)(μ3–COMe), 98015-27-1.

Supplementary Material Available: Tables of final positional parameters, anisotropic thermal parameters, and observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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[12] X-ray structure: Churchill, M. R.; Li, Y.-J.; unpublished results. Spectroscopic data: mass spectrum, *m/z* 960 (M^+, ^{192}Os); IR (C_6H_{12}) $\nu(CO)$ 2065 (vs), 2060 (vs), 2024 (s), 2003 (m, br) cm^{-1}; ^1H NMR ($(CD_3)_2CO$, 20 °C) δ 7.90–7.82 (m, 2 H), 7.40–7.16 (m, 3 H), 4.62 (s, 3 H); ^{13}C NMR (CD_2Cl_2, 20 °C) δ 319.4 (s, 1 C, $\equiv$COMe), 234.6 (s, 1 C, $\equiv$CPh), 173.9 (s, 9 C, CO).

Reversible Alkyne Ligand Scission: Formation and Reactivity of $Cp_2W_2Os(CO)_5(\mu\text{-}CTol)(\mu_3\text{-}CTol)$

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Summary: Decarbonylation of $Cp_2W_2Os(CO)_7(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)$ (1) in refluxing methylcyclohexane induces cleavage of the alkyne C-C bond, giving $Cp_2W_2Os(CO)_5(\mu\text{-}CTol)(\mu_3\text{-}CTol)$ (2). This transformation is reversed upon exposure to CO (1 atm, 25 °C, 5 min), but reaction with H_2 (1 atm, 101 °C, 15 min) provides $Cp_2W_2Os(CO)_4(\mu\text{-}CTol)(\mu_3\text{-}CTol)(\mu\text{-}H)H$ (4). Treatment of 4 with CCl_4 gives $Cp_2W_2Os(CO)_4(\mu\text{-}CTol)(\mu_3\text{-}CTol)(\mu\text{-}H)Cl$ (5).

The scission of alkyne ligands is of considerable current interest, as shown by recent reports involving dinuclear,[1] trinuclear,[2] and tetranuclear[3] complexes. Irreversible formation of alkynes from alkylidyne ligands is frequently observed.[4] However, strong inferential evidence for *reversible* alkyne scission/alkylidyne coupling equilibration has only been presented recently, by Vollhardt and co-workers for dialkylidynetricobalt complexes[5] and by Chisholm and co-workers for alkyneditungsten complexes.[6] We now report direct observation of reversibly related alkyne and dialkylidyne mixed-metal trinuclear complexes.

Thermolysis of $Cp_2W_2Os(CO)_7(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)$[7] (1) in refluxing methylcyclohexane flushed with argon (101 °C, 20 min) provides mildly air sensitive $Cp_2W_2Os(CO)_5(\mu\text{-}CTol)(\mu_3\text{-}CTol)$ (2) (>95% by ^1H NMR). The compound is isolated in 88% yield as a dark brown crystalline solid by cooling the concentrated solution to −20 °C; the formulation is established by analytical and spectroscopic data.[8] The key structural features for **2** are revealed in its ^{13}C NMR spectrum.[9] Resonances at δ 384.1 ($^1J_{C-W}$ = 135 Hz) and δ 244.5 ($^1J_{C-W}$ = 89 Hz) are assigned to the doubly bridging and the triply bridging alkylidyne centers, respectively. These signals are well downfield of the signals for the alkyne carbons in the two isomers of 1 (δ 136–162) and show no evidence for C–C coupling.[11] Furthermore, these chemical shifts are compatible with those reported by Stone and co-workers for two related ditungsten–rhenium clusters, $Cp_2W_2Re(CO)_3(\mu\text{-}Br)(\mu\text{-}X)(\mu\text{-}CTol)(\mu_3\text{-}CTol)$ [X = O, δ 341.4, 294.5; X = CO, δ 364.9, 305.2], the structures of which have been established by X-ray crystallography.[12]

Complex 2 reacts readily with carbon monoxide (1 atm, 5 min) at room temperature to generate alkyne complex 1 (95% recovery from 1 → 2 → 1 cycle). A reasonable picture of the probable reaction sequence linking 1 and 2 can be constructed (see Scheme I), based largely on the structures of related compounds characterized by Stone and co-workers.[12,13] The μ_3-η^2 (∥) alkyne configuration shown by 1[7] is that expected for a 48e complex, and loss of one CO ligand should give a 46e species, $Cp_2W_2Os(CO)_6(C_2Tol_2)$ (3), with a μ_3-η^2 (⊥) configuration.[14] In fact, the iron analogue of 3, namely, $Cp_2W_2Fe(CO)_6(\mu_3\text{-}\eta^2\text{-}C_2Tol_2)$, has been isolated and shown to have the perpendicular configuration,[15] no analogue of 1 was observed. However, this osmium/iron stability reversal has been evident before: 48e $Os_3(CO)_{10}(C_2Ph_2)$ is stable,[16] whereas

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[1] (a) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74. (b) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *Organometallics* **1984**, *3*, 1770.

[2] Clauss, A. D.; Shapley, J. R.; Wilker, C. N.; Hoffmann, R. *Organometallics* **1984**, *3*, 619 and references therein.

[3] Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182.

[4] Vollhardt, K. P. C.; Walborsky, E. C. *J. Am. Chem. Soc.* **1983**, *105*, 5507. Also see Allison et al.[5] especially ref 4 therein.

[5] Allison, N. T.; Fritch, J. R.; Vollhardt, K. P. C.; Walborsky, E. C. *J. Am. Chem. Soc.* **1983**, *105*, 1384.

[6] Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794.

[7] (a) Shapley, J. R.; Park, J. T.; Churchill, M. R.; Bueno, C. Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 7385. (b) Busetto, L.; Green, M.; Howard, J. A. K.; Hessner, B.; Jeffery, J. C.; Mill, R. M.; Stone, F. G. A. Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 1101. (c) Churchill, M. R.; Bueno, C.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 640. (d) Busetto, L.; Green, M.; Hessner, B.; Howard, J. A. K.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 519. Note that this complex forms two isomers both of which are present in the solid as well *as interconvertible in solution.*

[8] $Cp_2W_2Os(CO)_5(\mu\text{-}CTol)(\mu_3\text{-}CTol)$: FD mass spectrum ($^{184}W$,$^{192}Os$), *m/z* 1036 ($M^+$), 1004 ($M^+$ − CO); IR ($C_6H_{11}CH_3$) $\nu(CO)$ 2040 (vs), 1979 (s), 1951 (m) cm^{-1}; ^1H NMR (360 MHz, C_6D_6) δ 7.24–6.46 (8 H, m), 4.88 (10 H, s), 240 (3 H, s), 2.01 (3 H, s). Anal. Calcd for $W_2Os_1C_{31}H_{24}O_5$: C, 35.99; H, 2.34; W, 35.55. Found: C, 35.85; H, 2.30; W, 35.55.

[9] **2**: ^{13}C NMR (90.4 MHz, $C_6D_5CD_3$, −75 °C) δ 384.1 (μ-CR, $^1J_{C-W}$ = 135 Hz), 244.5 (μ_3-CR, $^1J_{C-W}$ = 89 Hz), 231.5 (W–CO, $^1J_{C-W}$ = 165 Hz), 186.4, 182.4 (1:2, Os–CO). The intensity of the tungsten satellites for both alkylidyne carbon resonances indicates the alkylidynes are connected to two identical tungsten centers. The carbon-13 enriched samples were obtained from the reaction of the $CpW(^*CO)_2{}^*CTol$ and $H_2Os_3(^*CO)_{10}$.[10]

[10] Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C.; Wasserman, H. J. *Inorg. Chem.* **1983**, *22*, 1579.

[11] The coupling constants ($^1J_{C-C}$) observed at −92 °C for the alkyne carbons in the two isomers of 1 are 22 and 24 Hz.

[12] Carriedo, G. A.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1597.

[13] Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89.

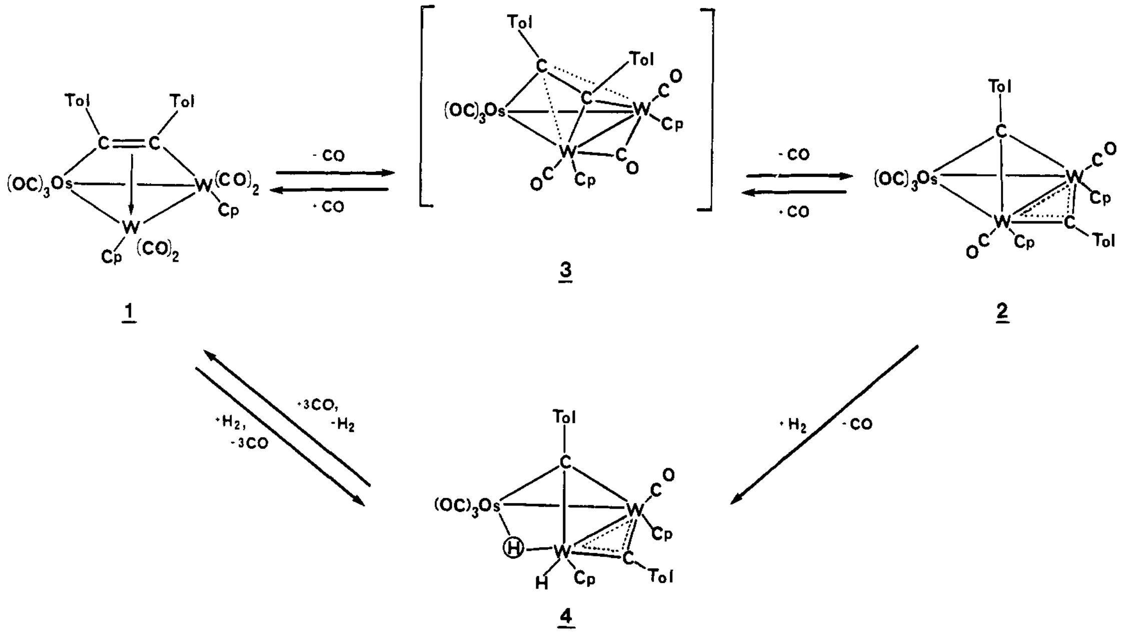
[14] Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.

[15] Busetto, L.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 101.

[16] Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1975**, *97*, 7172.

0276-7333/85/2304-1900$01.50/0

Scheme I



46e $Os_3(CO)_9(C_2Ph_2)$ is an observable but highly reactive intermediate;[17] 46e $Fe_3(CO)_9(C_2Ph_2)$ is isolable and the original example of the ⊥ configuration,[18] yet there is no evidence for 48e $Fe_3(CO)_{10}(C_2Ph_2)$. The particular ability of iron in stabilizing the ⊥ configuration has been discussed.[19] Thus, although 3 has not been observed directly, it is highly precedented. The unique aspect of 3, however, is the ease with which a second CO ligand is lost, which apparently triggers scission of the coordinated alkyne ligand. No comparable reaction is seen for $Os_3(CO)_9(C_2Ph_2)$, even under forcing conditions.[17]

In contrast to its reaction with CO, complex 2 reacts with molecular hydrogen (101 °C, 1 atm, 30 min) to form the mildly air-sensitive complex $Cp_2W_2Os(CO)_4(\mu\text{-CTol})(\mu_3\text{-CTol})(\mu\text{-H})H$ (4) (>95% by ^1H NMR; 66% isolated).[20] The hydride ^1H NMR resonances for 4 occur at δ −1.87 and −13.15, which can be assigned to a terminal and a bridging hydride ligand, respectively. The tungsten satellites of the hydride resonances show that the terminal hydride is bound to a tungsten atom and the bridging hydride is coordinated on a tungsten–osmium edge.[21] The mutual hydride–hydride coupling (J_{H-H} = 6.5 Hz) is similar to the coupling constant ($J_{H-H} \approx$ 4 Hz) in the triosmium complexes $H(\mu\text{-H})Os_3(CO)_{10}L$, in which the terminal and the bridging hydride ligands share a common vertex of the metal triangle.[22] The ^{13}C NMR spectrum of 4 again substantiates the proposed structure (Scheme I), in that the alkylidyne centers are clearly distinct (δ 371 and 244), the tungsten atoms are not equivalent, and the bridging hydride is coupled to two of the osmium carbonyls. The terminal hydride in 4 is replaced by chloride upon treatment with excess CCl_4 at room temperature, yielding $Cp_2W_2Os(CO)_4(\mu\text{-CTol})(\mu_3\text{-CTol})(\mu\text{-H})Cl$ (5) (>95% by ^1H NMR; 79% isolated). Again the formulation and proposed structure is evident from the ^1H and ^{13}C NMR results.[23]

Complex 4 can be obtained directly from 1 by substituting hydrogen for argon (101 °C, 40 min) in the procedure used to prepare 2, and it also reacts with carbon monoxide to give the parent alkyne complex 1 under more severe conditions (1 atm, 101 °C, 15 min) than for 2. Complex 5 does not return to 1 when treated with carbon monoxide (1 atm, 101 °C, 2 h) under similar conditions.

This work leads to two new conclusions: (a) The 46e W_2Os complex 3 further decarbonylates, inducing scission of the alkyne ligand. This behavior contrasts with that of the isoelectronic Os_3 complex, and we attribute the difference to the formation of strong W–C multiple bonds. (b) The tendency to have either an alkyne ligand or two alkylidyne ligands is not determined solely by the availability of other ligands, i.e., simply by coordinative saturation or unsaturation. In this case CO causes coupling, but H_2, which can clearly bind tightly in place of CO, does not.

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Registry No. 1 (isomer 1), 81368-76-5; 1 (isomer 2), 79991-95-0; **2**, 98015-29-3; **4**, 98050-00-1; **5**, 98050-01-2.

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(18) Blount, J. F.; Dahl, L. F.; Hoogzand, C.; Hubel, W. *J. Am. Chem. Soc.* **1966**, *88*, 292.

(19) Busetti V.; Granozzi, G.; Aime, S.; Gobetto, R.; Osella, D. *Organometallics* **1984**, *3*, 1510.

(20) $Cp_2W_2Os(CO)_4(\mu\text{-CTol})(\mu_3\text{-CTol})(\mu\text{-H})H$: FD mass spectrum ($^{184}W$, ^{192}Os), *m/z* 1010 (M^+); IR (C_6H_{12}) ν(CO) 2048 (vs), 1979 (vs), 1960 (vs), 1896 (w)cm^{-1}; ^1H NMR (360 MHz, C_6D_6) δ 7.30–6.20 (8 H, m), 5.58 (5 H, s), 4.98 (5 H, s), 2.51 (3 H, s), 2.17 (3 H, s), −1.87 (1 H, m, $^2J_{H-H}$ = 6.5 Hz, $^1J_{H-W}$ = 100 Hz, $^2J_{H-W}$ = 11 Hz), −13.15 (1 H, m, $^2J_{H-H}$ = 6.5 Hz, $^1J_{H-W}$ = 29 Hz); ^{13}C NMR (90.4 MHz, $C_6D_5CD_3$) δ 370.9 (μ-CR, J_{C-W} = 132 Hz), 244.4 (μ_3-CR, J_{C-W} = 90 Hz, 64 Hz), 210.6 (W–CO, J_{C-W} = 178 Hz), 181.7, 178.8 ($^2J_{C-H}$ = 1.8 Hz), 177.3 ($^2J_{C-H}$ = 9.2 Hz). Anal. Calcd for $W_2Os_1C_{30}H_{26}O_4$: C, 35.73; H, 2.60. Found: C, 35.23; H, 2.54.

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(22) Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304 and references therein.

(23) $Cp_2W_2Os(CO)_4(\mu\text{-CTol})(\mu_3\text{-CTol})(\mu\text{-H})Cl$: FD mass spectrum ($^{184}W$, ^{192}Os), *m/e*, 1044 (M^+); IR (C_6H_{12}) ν(CO) 2056 (vs), 1990 (vs), 1968 (vs), 1907 (w) cm^{-1}; ^1H NMR (360 MHz, C_6D_6) δ 7.44–6.80 (8 H, m), 5.72 (5 H, s), 5.16 (5 H, s), 2.57 (3 H, s), 2.27 (3 H, s), −11.09 (1 H, s, $^1J_{H-W}$ = 67 Hz); ^{13}C NMR (90.4 MHz, $C_6D_5CD_3$) δ 372.4 (μ-CR, $^1J_{C-W}$ = 137, 121 Hz), 247.3 (μ_3-CR, $^1J_{C-W}$ = 88, 54 Hz), 216.4 (W–CO, $^1J_{C-W}$ = 173 Hz), 180.9, 179.5, 178.1 ($^2J_{C-H}$ = 9.1 Hz). Anal. Calcd for $W_2Os_1C_{30}H_{25}O_4Cl_1$: C, 34.55; H, 2.42. Found: C, 34.68; H, 2.42.