

**Preliminary communication**

**ALKYLIDYNE–ALKYLIDYNE AND ALKYLIDYNE–CARBONYL COUPLING  
 ON THE TRIOSMIUM FRAMEWORK**

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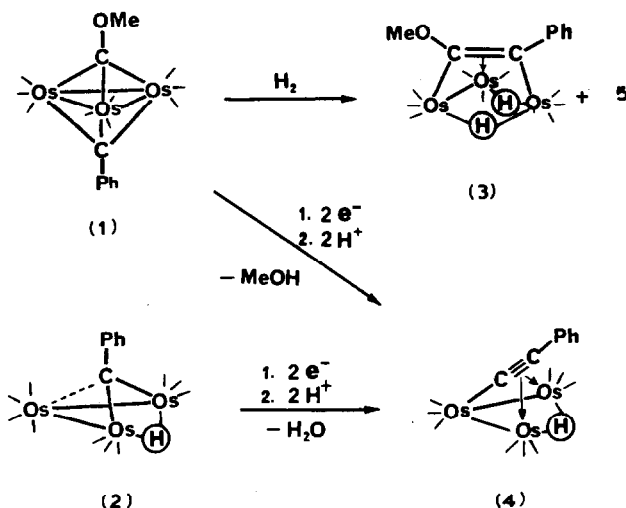
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**Summary**

Hydrogenation of  $\text{Os}_3(\text{CO})_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$  (**1**) at one atmosphere results in alkyldiyne–alkyldiyne coupling, forming the alkyne complex  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3, \eta^2\text{-C}_2(\text{OMe})\text{Ph})$  (**3**). Reduction of **1** by two equiv. of sodium benzophenone ketyl, followed by protonation with tetrafluoroboric acid, yields the phenylacetylide complex  $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3, \eta^2\text{-CCPh})$  (**4**). Sequential reduction/protonation involving  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CPh})$  (**2**) also generates **4**, apparently via benzyldiyne–carbonyl coupling.

Mathieu and coworkers have recently reported the reversible interconversion between the dialkyldiyne complex  $\text{Fe}_3(\text{CO})_9(\mu_3\text{-CMe})(\mu_3\text{-COEt})$  and the alkyne complex  $\text{Fe}_3(\text{CO})_{10}(\mu_3, \eta^2\text{-C}_2(\text{OEt})\text{Me})$  [1]. Related reversible dialkyldiyne coupling/alkyne scission processes have been illustrated in the isoelectronic  $\text{Cp}_3\text{Co}_3(\text{CR})(\text{CR}')$  system [2] and with a trinuclear mixed-metal complex  $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_7(\text{C}_2\text{Tol}_2)$  [3]. Recently, we prepared the first dialkyldiyne triosmium complex,  $\text{Os}_3(\text{CO})_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$  (**1**) [4], as a coproduct with  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CPh})$  (**2**) [5]. We now report examples of alkyldiyne–alkyldiyne coupling with **1** as well as a related alkyldiyne–carbonyl coupling reaction with **2** (see Scheme 1).

Compound **1** undergoes CO substitution in refluxing toluene, when treated with  $\text{PPh}_3$  or  $^{13}\text{CO}$  (1–4 atm); at higher temperatures CO treatment causes disruption of the metal triangle and formation of  $\text{Os}_4$  compounds [6]. However, hydrogenation of **1** in toluene at  $110^\circ\text{C}$  generates the alkyne complex  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3, \eta^2\text{-C}_2(\text{OMe})\text{Ph})$  (**3**) together with  $(\mu\text{-H})_3\text{Os}_3(\text{CO})_9(\mu_3\text{-COMe})$  (**5**) [7]. The ratio of these two products is pressure dependent; yields are 55 and 12% at 1 atm and 23 and 54% at 4 atm, respectively. Spectroscopic data for **3** (FDMS,  $m/e$  962,  $M^+$ ; IR:  $\nu(\text{CO})$ , 2109(w), 2079(vs), 2055(vs), 2023(vs), 2005(s), 1986(m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-30^\circ\text{C}$ ); 7.1 (m,  $\text{C}_6\text{H}_5$ ), 3.62 (s,  $\text{CH}_3$ ),  $-17.44$  (s,  $\mu\text{-H}$ ),  $-20.56$  (s,  $\mu\text{-H}$ )) are in close agreement with those for  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3, \eta^2\text{-C}_2\text{Ph}_2)$  [8], which is not observed as a product. The crystal structure of  $\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3, \eta^2\text{-C}_2(\text{OMe})\text{Me})$



SCHEME 1.

has been determined [9]. Finally, treatment of  $\text{Os}_3(\text{CO})_9(\mu_3\text{-}^*\text{CPh})(\mu_3\text{-}^*\text{COMe})$  [each  $^*\text{C}$  ca. 50%  $^{13}\text{C}$ ] with hydrogen gives  $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\mu_3, \eta^2\text{-}^*\text{CPh}^*\text{COMe})$ , the  $^{13}\text{C}$  NMR spectrum of which shows signals for the alkyne carbons at  $\delta$  197.1 (C-OMe) and 80.0 (C-Ph) ppm with  $^1J(\text{C-C})$  27 Hz. Assignment of the alkyne carbons is based on the chemical shifts reported for alkoxy-substituted alkynes,  $\text{R-C}\equiv\text{C-OR}'$ , in which  $\equiv\text{C-R}$  are found well upfield of  $\equiv\text{C-OR}$  [10] and the alkylidyne carbon shifts observed in 1 ( $\delta$  319.4, C-OMe; 234.6 ppm, C-Ph) [6].

Since the transformation of 1 into 3 is formally a two-electron reduction process, we have sought to approach the same results by first reducing 1 directly, followed by protonation. However, slow addition of sodium benzophenone ketyl solution (25 mM in THF, 2 equiv.) to 1 at room temperature under nitrogen, followed by protonation ( $\text{HBF}_4$ , 1 M in  $\text{Et}_2\text{O}$ , 5 equiv.), instead produces the known phenylacetylide complex  $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\mu_3, \eta^2\text{-CCPh})$  (4) [11], isolated in 95% yield. The  $^{13}\text{C}$  NMR spectrum of 4 generated from  $\text{Os}_3(^*\text{CO})_9(\mu_3\text{-}^*\text{CPh})(\mu_3\text{-}^*\text{COMe})$  shows that the acetylide carbon at  $\delta$  134.5 ppm and the phenyl-substituted carbon at  $\delta$  67.6 ppm are coupled, with  $^1J(\text{C-C})$  51 Hz [12]. On the other hand, formation of  $(\mu\text{-H})\text{Os}_3(^*\text{CO})_9(\mu_3, \eta^2\text{-CCPh})$  from  $\text{Os}_3(^*\text{CO})_9(\mu_3\text{-CPh})(\mu_3\text{-COMe})$  shows that the phenylacetylide complex is indeed derived from coupling of the two alkylidyne moieties. This last result rules out the possibility of alkylidyne-carbonyl coupling in the formation of 4 from 1 (cf. [13]), but we were moved to investigate this possibility with  $(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_3\text{-CPh})$  (2). In fact, sequential treatment of 2 with sodium benzophenone ketyl solution and tetrafluoroboric acid in a fashion identical to that described above yields 4 in 90% yield as the only observed product.

The reductive coupling involving 1 is readily interpreted in terms of the alkyne complex  $[\text{Os}_3(\text{CO})_9(\text{C}_2(\text{OMe})\text{Ph})]^{2-}$  as an intermediate with subsequent protonation of this species occurring both on the methoxy group (releasing methanol) and on the metal framework to give 4. Similarly, the transformation of 2 into 4 likely involves benzylidyne-carbonyl coupling, generating  $[\text{HOs}_3(\text{CO})_9(\text{C}_2(\text{O})\text{Ph})]^{2-}$ , followed by double protonation at the oxygen and loss of water. The bridging hydride

is not involved, since protonation with  $\text{CH}_3\text{CO}_2\text{D}$  yields **4** without deuterium incorporation. Our observation is closely related to results reported by Mathieu that reduction of  $[\text{Fe}_3(\text{CO})_{10}(\mu_3\text{-CMe})]^-$  leads to  $[\text{Fe}_3(\text{CO})_9(\mu_3, \eta^2\text{-CCMe})]^-$  via  $[\text{Fe}_3(\text{CO})_9(\mu_3, \eta^2\text{-C(O)CMe})]^{2-}$  [14]. Furthermore, Shriver and coworkers have shown that two-electron reduction of  $[\text{M}_3(\text{CO})_{10}(\mu_3\text{-COC(O)Me})]^-$  gives  $[\text{M}_3(\text{CO})_9(\mu_3\text{-CCO})]^{2-}$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ), apparently via alkylidyne-carbonyl coupling concomitant with loss of an acetate group [15]. Finally, Deeming, et al., have observed similar addition/elimination reactions of nucleophiles with the triosmium acetylide complex  $\text{HOs}_3(\text{CO})_9(\text{CCH})$  [16].

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