Unusual C–H bond activation—aldol condensation of aromatic aldehydes with the methyl group of a carbene-like triosmium cluster †

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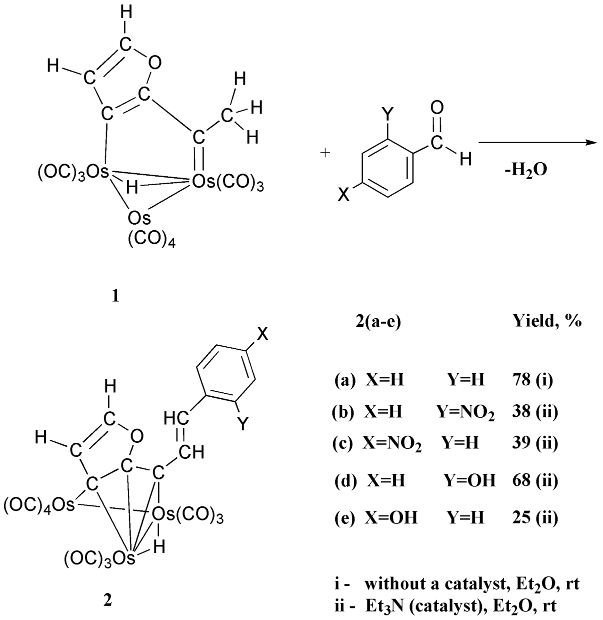
Reactions of the triosmium cluster [$HOs_3(CO)_{10}(\eta^1:\eta^1-OC_4H_2CCH_3)$] with a series of aromatic aldehydes under mild conditions result in condensation of the ligand methyl group with the aldehyde C=O moiety to give typical aldol condensation products.

Aldol condensation reactions have been widely explored since the early days of organic synthesis.[1] The synthetic potential of this type of reaction in organometallic chemistry is mainly related to Fischer carbene complexes, for which there are many important applications.[2–7] In such cases, a general synthetic strategy consists of the generation of a carbanion in the α-position relative to the carbene carbon followed by nucleophilic attack of this species onto the carbonyl carbon of an aldehyde to form a new carbon–carbon bond.[2,3,7] Here we report the condensation reactions of a series of aromatic aldehydes with the methyl group of the organic ligand in [$HOs_3(CO)_{10}(\eta^1:\eta^1-OC_4H_2CCH_3)$] (**1**).[8] These condensations represent unusual examples of C–H bond activation in transition metal clusters and demonstrate a Fischer carbene reactivity pattern of the coordinated organic fragment.

The starting osmium cluster **1** reacts with benzaldehyde and its derivatives according to Scheme 1 to give the condensation products **2a**–**e** in good yield. ‡



Scheme 1

The solid state structure of the benzaldehyde derivative **2a** has been determined through an X-ray crystallographic study. § (Fig. 1). The coordination mode of the organic fragment in **2a** differs fundamentally from that found in **1**.[8] All three carbon atoms of the Os(3)*C(11)C(14)C(15)*Os(2) dimetallacycle, are involved in the interaction with the trinuclear cluster core, yielding an {$\eta^3:\eta^1:\eta^1$} coordination mode for the organic ligand. The involvement of a furan ring double bond, C(11)–C(14), in the interaction with Os(1) renders the ligand a five-electron donor and changes the cluster electron count to 50. The rearrangement of the ligand coordination results in cleavage of a metal–metal bond [Os(1)–Os(3) 3.786 Å] to give an open structure typical for 50 electron triosmium clusters.[9] The coordination of the C(11)–C(14) bond and related bond order reduction is verified by its elongation to 1.426(6) Å. In contrast, the C(12)–C(13) and C(16)–C(17) carbon–carbon bonds, which retain multiple bond character, display values of bond lengths and angles which are typical for C=C double bonds. The room temperature ^1H and ^{13}C NMR spectra of **2a** ‡ are in complete

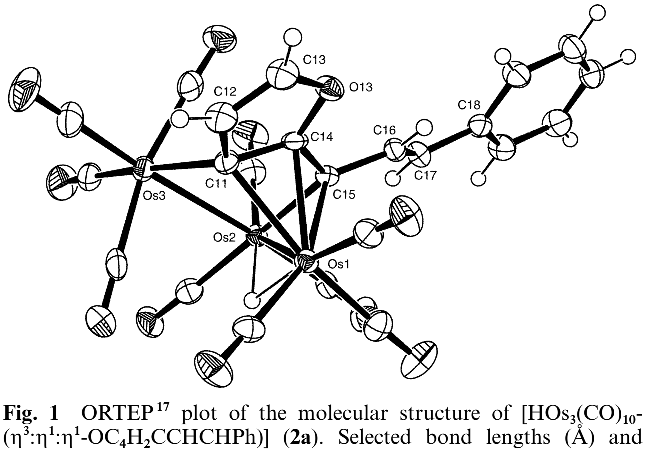


Fig. 1 ORTEP[17] plot of the molecular structure of [$HOs_3(CO)_{10}(\eta^3:\eta^1:\eta^1-OC_4H_2CCHCHPh)$] (**2a**). Selected bond lengths (Å) and angles (°): Os(3)–Os(2) 2.8774(2), Os(2)–Os(1) 2.9058(3), C(11)–Os(3) 2.189(5), C(11)–Os(1) 2.347(5), C(14)–Os(1) 2.274(4), C(15)–Os(2) 2.163(4), C(15)–Os(1) 2.233(4), C(11)–C(14) 1.426(6), C(14)–C(15) 1.425(6), C(11)–C(12) 1.466(6), C(12)–C(13) 1.334(7), C(15)–C(16) 1.479(6), C(16)–C(17) 1.331(7); C(17)–C(16)–C(15) 126.3(4), C(16)–C(17)–C(18) 126.7(5).

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† Electronic supplementary information (ESI) available: synthesis and characterisation data for **2a**–**e**. See http://www.rsc.org/suppdata/dt/b2/b200707j/

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agreement with the solid state structure, indicating that the structure is retained in solution and that it is stereochemically rigid on the NMR time scale. The IR and NMR spectroscopic data of **2b**–**e** (see the ESI †) match the data obtained for **2a**, indicating that similar structures are formed in the condensation of various benzaldehyde derivatives with **1** and the apparent general character of the reactivity pattern presented.

The organic fragment in **2a** is a typical example of an aldol condensation product where addition of a C–H bond of the coordinated organic moiety to benzaldehyde, followed by H_2O release, gives the structure shown in Fig. 1. The observed chemical behaviour indicates activation of the C–H bonds of the methyl group in **1**, which allows the aldol condensation to occur under quite mild conditions. A similar effect of coordination on the chemical properties of C–H bonds α to a carbene carbon atom and the acidic nature of the α-protons in Fischer carbene complexes are well recognized.[10] For example, an activation of this sort enables α-proton abstraction by alkyl lithium reagents[2,7,11] to give carbanions, which react further with aldehydes to afford condensation products analogous to **2**. The reaction conditions shown in Scheme 1 suggest considerable C–H bond activation in **1**, enabling the condensation reaction with benzaldehyde to occur in the absence of a catalyst, whereas other benzaldehyde substituted derivatives react in the presence of a relatively weak base, *viz.* NEt_3. There is only one example of a similar condensation of a Fischer carbene, $[(CO)_5Cr{=}C(OEt)CH_3]$,[3] with aromatic aldehydes, which is catalyzed by $NEt_3/(CH_3)_3SiCl$.

The organic ligand in **1** shares a few common structural and spectroscopic features with mononuclear Fischer carbenes. In particular, the electron count for the closed triangular framework in **1** requires donation of three electrons from the $\eta^1:\eta^1\text{-}C_4OH_2CCH_3$ fragment,[8] which in turn implies an osmium–carbon double bond as shown in Scheme 1, which is verified by an analysis of bond lengths. The reactivity pattern described in the present communication testifies in favour of this formal assignment and points to a substantial contribution of the carbene resonance form into the bonding of the organic moiety to an osmium atom of the cluster core. The ^{13}C NMR spectrum of **1** ‡ is especially indicative, displaying thirteen low field resonances corresponding to ten carbonyl groups and three coordinated carbons, of which twelve are located in the expected interval of 190–170 ppm, whereas the thirteenth is shifted much further downfield so that it appears at 227.6 ppm. This is in line with the usual deshielding of terminal carbene carbons[12,13] and agrees well with the values found for other triosmium carbene clusters.[14–16] Therefore the ^{13}C NMR signal can be assigned to the carbene atom in **1**.

The observed reactivity and spectroscopic data suggest an unusual "enhanced carbene" type activation of the organic moiety in **1** to give rise to aldol condensation reactivity, which has not been previously observed in the chemistry of transition metal clusters.

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Notes and references

‡ Spectroscopic data for **1**: NMR δ_C ($CDCl_3$): 227.6 ($C{=}Os$), 189.9–172.3 12 signals corresponding to 10 CO and 2 coordinated carbons of the ligand; 156.2, 133.5 (furanyl ring *C*H carbons), 39.1 (CH_3).

For **2a**: IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2100m, 2068m, 2056vs, 2002m (sh), 2012s, 1988m (sh). NMR δ_H ($CDCl_3$): 8.13–8.03 [2 H, AB protons of C(16)–C(17) double bond, $J = 15$ Hz], 7.96, 7.04 (2 H, AB protons of furanyl ring, $J = 3$ Hz,), 7.78–7.35 (5 H, Ph-protons), −15.07 (1 H, s, μ-*H*Os); δ_C ($CDCl_3$): 206.8–169.2, 13 signals corresponding to 10 CO and 3 coordinated carbons [C(11), C(14), C(15)]; 148.6, 146.0 C(16) and C(17); 130.6,124.9, 122.6, 129.6, 121.0, 120.3 non-coordinated phenyl and furanyl ring carbons. FAB-MS (*m*/*z*) 1034 (M^+), 1007 ($M^+ - 1$ CO), 976 ($M^+ - 2$ CO), 949 ($M^+ - 3$ CO), 919 ($M^+ - 4$ CO), 889 ($M^+ - 5$ CO). Detailed reaction procedures for the syntheses of **2a**–**e** and a complete set of spectroscopic data are given in the ESI.

§ Crystallographic data for **2a**: $C_{23}H_{10}O_{11}Os_3$, $M = 1032.91$ g mol^{-1}, triclinic, $a = 9.52160(10)$, $b = 9.66420(10)$, $c = 13.9842(2)$ Å, $\alpha = 97.8138(6)$, $\beta = 91.0860(7)$, $\gamma = 96.8966(8)°$, $V = 1264.82(3)$ Å^3, $T = 150(2)$ K, space group $P\bar{1}$, $Z = 2$, $D_c = 2.712$ Mg m^{-3}, μ(Mo-Kα) = 0.71073 Å, 19096 reflections measured, 4929 [R(int) = 0.0393] which were used in all calculations. The final R_1 [$I > 2\sigma(I)$] was 0.0225 and $wR(F^2) = 0.0556$ [$I > 2\sigma(I)$]. CCDC reference number 174515. See http://www.rsc.org/suppdata/dt/b2/b200707j/ for crystallographic data in CIF or other electronic format.

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