Formation of the Trinuclear Osmium Cluster $[Os(\eta\text{-}C_6H_6)(\mu\text{-}H)]_3\{\mu^3\text{-}(CH_2)_3CH\}$ involving Activation of the Three Methyl Groups of 2-Methylpropane

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Co-condensation of osmium atoms and a benzene : 2-methylpropane mixture gives $[Os(\eta\text{-}C_6H_6)(\mu\text{-}H)]_3\{\mu^3\text{-}(CH_2)_3CH\}$; the analogous reaction with C_6D_6 : 2-methylpropane gives $[Os(\eta\text{-}C_6D_6)(\mu\text{-}H)]_3\{\mu^3\text{-}(CH_2)_3CH\}$.

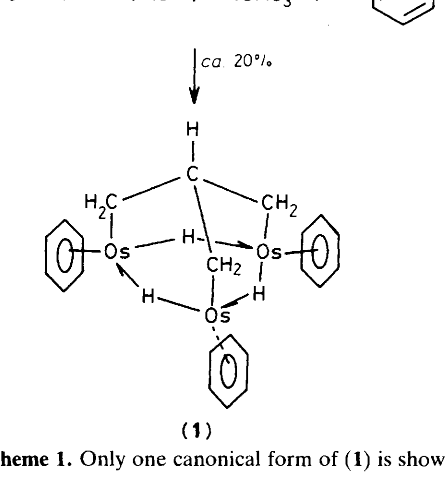
We have shown that metal atoms react with mixtures of alkanes and ligands such as benzene or trimethylphosphine giving compounds containing ligands derived from the alkanes. Examples are tungsten atoms with cyclopentane : PMe_3 giving $W(\eta\text{-}C_5H_5)(PMe_3)H_5$,[1] chromium atoms with cyclohexane : PMe_3 giving $Cr(\eta\text{-}C_6H_6)(PMe_3)_3$,[2] and rhenium atoms with alkane : benzene giving the binuclear compounds $[\{Re(\eta\text{-}C_6H_6)\}_2(\mu\text{-}H)_2(\mu\text{-alkylidene})]$.[3] Here we report the formation of a trinuclear osmium cluster involving an unprecedented triple carbon–hydrogen bond activation process.

Co-condensation of osmium atoms and a benzene : 2-methylpropane mixture (1 : 1), followed by extraction of the less volatile products with cyclohexane gives, upon concentration of the extract, yellow air-sensitive crystals of the compound $[Os(\eta\text{-}C_6H_6)(\mu\text{-}H)]_3\{\mu^3\text{-}(CH_2)_3CH\}$, (**1**).

In a typical experiment osmium atoms (0.7 g) were co-condensed with C_6H_6 : 2-methylpropane (70 cm^3 of a 1 : 1 mixture) giving *ca.* 250 mg of (**1**) (20% yield, based on osmium leaving the furnace).

The compound (**1**) is thermally stable in solution to 150 °C and has been characterised by microanalysis, the mass spectrum, and detailed n.m.r. studies.† In particular, the ^1H n.m.r. spectrum shows a binomial septet for the apical hydrogen due to coupling to the six equivalent Os–CH_2 hydrogens only. The adamantane-like structure proposed for (**1**) is shown in Scheme 1.

Co-condensation of osmium atoms and a C_6D_6 : 2-methyl propane (1 : 1) mixture gives the compound $[Os(\eta\text{-}C_6D_6)(\mu\text{-}H)]_3\{\mu^3\text{-}(CH_2)_3CH\}$, showing that the three μ-H groups arise from the 2-methylpropane.



(**1**)

Scheme 1. Only one canonical form of (**1**) is shown.

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† N.m.r. data for (**1**): ^1H, $C_6D_5CD_3$ at room temperature: δ 4.41 [18 H, s, 3η-C_6H_6], 4.2 [1 H, septet, *J* 6.6 Hz, CH], 1.4 [6 H, d, *J* 6.6 Hz, 3CH_2], −17.09 [3 H, s, 3 Os–H–Os]; ^{13}C, 60 °C: 70.0 [d, 3η-C_6H_6], 56.96 [d, CH], 30.26 [t, CH_2]. *m/z* (P^+ at 864).

The compound (**1**) provides a striking model for a surface adsorbed alkane. The mechanism of the formation of (**1**) is unknown but it surely must involve intermediate steps in which unsaturated metal centres of discrete osmium intermediates activate the C–H bonds of 2-methylpropane. We have shown that co-condensation of osmium atoms with pure benzene gives $Os(\eta\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)$ yet less than 1% of this compound is detected (n.m.r.) in the osmium–benzene–2-methylpropane reaction mixture.[4]

This study and previously reported reactions between alkanes and metal atoms show that it is unlikely that alkanes are 'inert' solvents in reactions involving highly unsaturated transition metal compounds, even when there is an excess of an established ligand.

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