Synthesis and *X*-Ray Crystal Structures of the First Tetrahedral Osmium(IV) Compounds, Tetrakis(cyclohexyl)osmium(IV) and Tetrakis(*o*-methylphenyl)osmium(IV)

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The compounds OsR_4, R = cyclohexyl, *o*-methylphenyl, have been isolated by the interaction of the appropriate Grignard reagents with $Os_2(O_2CMe)_4Cl_2$ and OsO_4 respectively; both complexes have been characterized by *X*-ray crystallography.

Although neutral, homoleptic tetra-alkyls and aryls for early transition metals (Ti, Zr, Hf, V, Cr)[1] and also for Mo[2] and W[3] have been isolated at ambient, or more usually at low temperatures, and some of them crystallographically characterized [$M(CH_2Ph)_4$, M = Ti,[4] Zr,[5] Hf,[4] $V(2,4,6\text{-}Me_3C_6H_2)_4$,[6] $Cr(CH_2CMe_2Ph)_4$,[7] $Cr(CPh{=}CMe_2)_4$ [8]], no analogous compounds for the platinum group metals have been obtained.

OsR_4
(**1**) R = $c\text{-}C_6H_{11}$
(**2**) R = $o\text{-}MeC_6H_4$

We now report the synthesis of osmium compounds *via* preparative routes somewhat different from those utilized to obtain the other tetra-alkyls where metal halides or alkoxides have been almost exclusively used. The cyclohexyl $Os(c\text{-}C_6H_{11})_4$ (c = cyclo) (**1**) has been obtained by interaction of the Grignard reagent with the binuclear Os^{III} acetate $Os_2(\mu\text{-}O_2CMe)_4Cl_2$, probably *via* a disproportionation reaction, whereas $Os(o\text{-}MeC_6H_4)_4$ (**2**) has been prepared by reduction of OsO_4 with the Grignard reagent. Previously $Os_2(O_2CMe)_4Cl_2$ has only been partially alkylated to give $Os_2(\mu\text{-}O_2CMe)_2R_4$ [9] ($R = CH_2SiMe_3$, CH_2Bu^t), while OsO_4 has been used directly in alkylations only in the two cases of $OsO(CH_2SiMe_3)_4$ [10] and $OsO_2(2,4,6\text{-}Me_3C_6H_2)_2$ [11] and indirectly in synthesis of nitrido-osmium alkyls.[12]

Both these red-purple petroleum-soluble and air-stable crystalline compounds (**1**) and (**2**) have been fully characterized by elemental analysis, ^1H and ^{13}C n.m.r. and i.r. spectroscopy, and *X*-ray crystallography.† Of particular interest is their thermal stability, especially of the cyclohexyl complex which might have been expected to be susceptible to β-hydrogen elimination; cyclohexyl complexes are relatively scarce[13] and the only analogue $Ti(c\text{-}C_6H_{11})_4$ [14] is unstable above −30 °C. To our knowledge the $o\text{-}MeC_6H_4$ ligand has not been previously used for the preparation of homoleptic tetra-aryls although well defined $M(2,4,6\text{-}Me_3C_6H_2)_4$ compounds (M = Ti,[15] V,[16] Cr,[17] Mo[2]) have

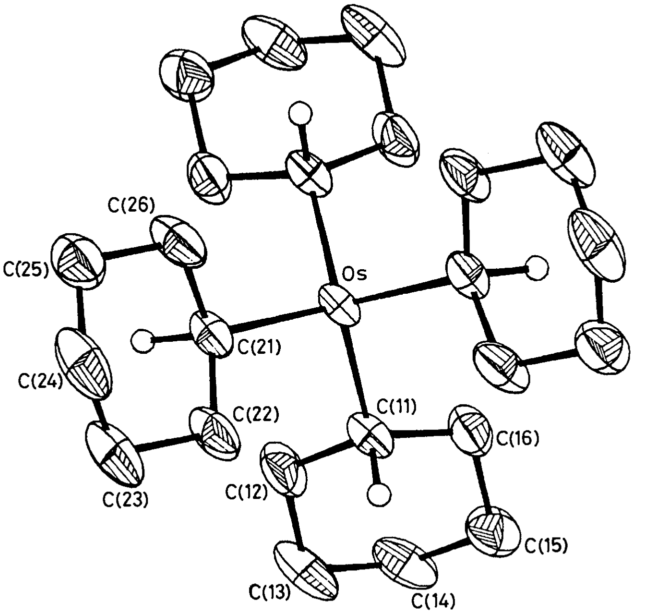

Figure 1. The structure of $Os(c\text{-}C_6H_{11})_4$, (**1**).

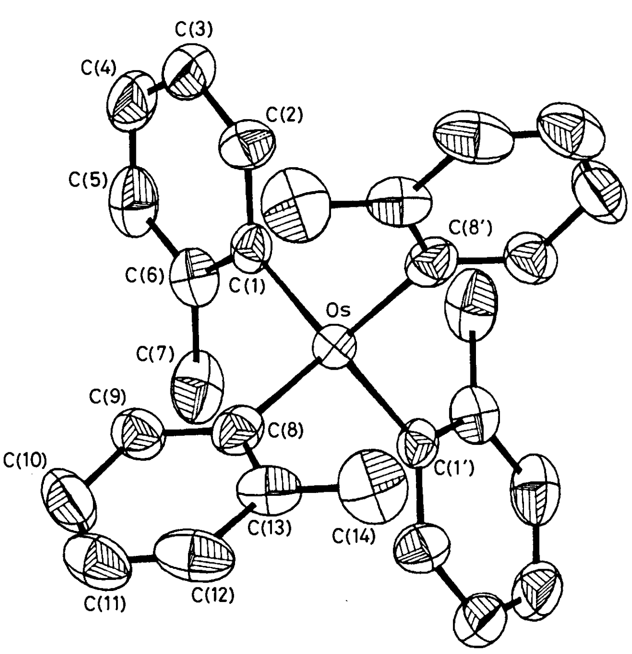

Figure 2. The structure of $Os(o\text{-}MeC_6H_4)_4$, (**2**).

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† *Crystal data.* For (**1**) $C_{24}H_{44}Os$, $M = 522.81$, monoclinic, $a = 17.636(3)$, $b = 8.528(2)$, $c = 17.507(3)$ Å, $\beta = 118.41(3)°$, $U = 2315.8$ Å^3, space group *C2/c*, $Z = 4$, $D_c = 1.50$ g cm^{-3}, $\lambda(Mo\text{-}K_\alpha) = 0.71069$ Å, $\mu = 34.35$ cm^{-1}. For (**2**) $C_{28}H_{28}Os$, $M = 554.73$, orthorhombic, $a = 16.321(3)$, $b = 8.083(2)$, $c = 8.510(2)$ Å, $U = 1122.7$ Å^3, space group *Pba*2, $Z = 2$, $D_c = 1.64$ g cm^{-3}, $\lambda(Mo\text{-}K_\alpha) = 0.71069$ Å, $\mu = 54.48$ cm^{-1}. Data for both compounds were recorded using a CAD4 diffractometer with monochromated Mo-K_α radiation and an ω–2θ scan technique and corrected for absorptions. The structures were solved by routine heavy atom procedures and refined by least-squares. For (**1**), $R = 0.029$ for 1718 observed [$I > 1.5\sigma I$] out of 2037 unique measured data (202 parameters refined); for (**2**), $R = 0.0193$ for 855/1058 unique observed data (180 parameters refined). The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

received considerable attention mainly due to their thermal stability and chemical inertness as opposed to the well known instability of phenyl compounds *via* reductive elimination[18] and *ortho*-hydrogen abstraction[1,19] decomposition pathways.

The compounds are the first examples of tetrahedrally co-ordinated Os^{IV}, d^4; only octahedral and distorted octahedral Os^{IV} have been observed previously. Both compounds have similar structures (Figures 1 and 2); in each case the molecule has crystallographic $C2$ symmetry and the co-ordination geometry is slightly flattened tetrahedral, with C–Os–C angles of 106.1(4)—117.1(8)° for the aryl (**2**) and 105.3(2)—117.1(2)° for the alkyl (**1**). The Os–C distances in (**2**) are slightly smaller than those in (**1**) [1.98(1), 2.02(1) *vs.* 2.026(6), 2.030(3)Å], which may correlate with the expected differences in covalent radii for sp^2 and sp^3 carbons.

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