Alkyl Compounds of Diruthenium(III) and Diosmium(III). *X*-Ray Crystal Structure of the First Ruthenium Peralkyl, Hexakis(neopentyl)diruthenium(III)

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The interaction of RMgCl, R = CH_2SiMe_3, CH_2Bu^t with $Ru_2(O_2CMe)_4Cl$ or $Os_2(O_2CMe)_4Cl_2$ leads to the compounds M_2R_6, M = Ru and $M_2(\mu\text{-}O_2CMe)_2R_4$, M = Ru, Os; the structure of $Ru_2(CH_2Bu^t)_6$ has been determined by an *X*-ray crystallographic analysis.

The alkylation or arylation of metal–metal bonded carboxylato bridged complexes, $M_2(\mu\text{-}O_2CR)_4{}^{0,1+,2+}$, M = Cr,[1] Mo,[1,2] Re,[2,3] Ru,[1,2] Os,[4] Rh,[1,2] has usually led to isolable products only in the presence of trimethylphosphine; no homoleptic alkyls have been obtained.

We now report the formation of the alkyls $M_2(\mu\text{-}O_2CMe)_2R_4$, M = Ru, Os and M_2R_6, M = Ru; R = CH_2SiMe_3, CH_2Bu^t by interaction of $Ru_2(O_2CMe)_4Cl$[5] or $Os_2(O_2CMe)_4Cl_2$[6] with the Grignard reagent in tetrahydrofuran at low temperature; the acetato bridged species are intermediates in the reaction and are isolated after short reaction times. The highly coloured, petroleum soluble, and air sensitive crystalline compounds have been fully characterised by elemental analysis, and by ^1H and ^{13}C n.m.r.† and i.r. spectroscopy. The only analogues of the M_2R_6 species are those of Mo and W,[7] which were the first compounds proposed to have M–M triple bonds; the only analogues of the acetato bridged species are those of rhenium[3] (although Re_2R_6 should exist, the carboxylates appear resistant to further alkylation).

The compound $Ru_2(CH_2Bu^t)_6$ has been fully characterised by an *X*-ray structure determination.‡ The molecule (Figure 1) has the R_3MMR_3 ethane-like structure in which the two R_3M groups adopt a mutually staggered configuration. Although it is not isoelectronic with these molecules, the structure is similar to those of $M_2(CH_2SiMe_3)_6$, M = Mo[8] and W,[9] and the corresponding $M_2(NR_2)_6$[10] and $M_2(OR)_6$[11] species. The molecule can be considered as a derivative of the triply bonded $Ru_2{}^{6+}$ core, in which the ten electrons not involved in ligand bonding are distributed amongst the $M_2{}^{6+}$ orbitals as $\sigma^2\pi^4\delta^2\delta^{*2}$.[12] Unexpectedly, the Ru–Ru distance of 2.311(3) Å is *longer* than distances of 2.250—2.290 Å found in the related $Ru_2{}^{5+}$ carboxylate species[13] which have a formal bond order of 2.5.

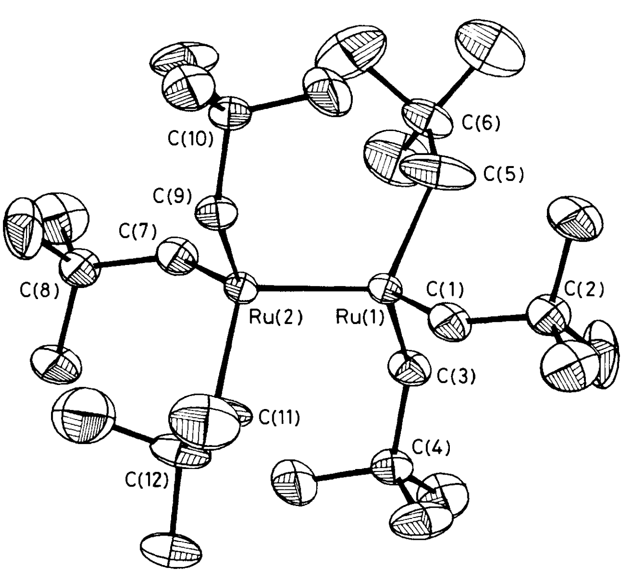

Figure 1. The molecular structure of hexakis(neopentyl)diruthenium(III). Selected bond lengths and bond angles are: Ru(1)–Ru(2) 2.311(3), Ru(1)–C(1), –C(3), –C(5) 2.031(8), 2.033(8), 2.043(9), Ru(2)–C(7), –C(9), –C(11) 2.032(8), 2.023(8), 2.051(9) Å; Ru(2)–Ru(1)–C(1), –C(3), –C(5) 101.7(3), 114.5(3), 117.4(4), Ru(1)–Ru(2)–C(7), –C(9), –C(11) 101.4(3), 115.1(3), 106.3(4), C_α–Ru–C_α 101.6(4)—117.8(4)°.

The ruthenium compounds are the first neutral homoleptic alkyls of the platinum group elements.§ The Ru_2R_6 compounds are also the first neutral species with a $Ru_2{}^{6+}$ core and

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† Representative data [for $Ru_2(\mu\text{-}O_2CMe)_2(CH_2Bu^t)_4$] δ, in C_6D_6: ^1H, 2.69 (s, 8H, Bu^tCH_2), 1.71 (s, 6H, $MeCO_2$), 1.28 (s, 36H, Me_3CCH_2); $^{13}C\{^1H\}$, 185.7 (s, $MeCO_2$), 52.6 (s, Bu^tCH_2), 33.6 (s, Me_3CCH_2), 30.1 (s, Me_3CCH_2), 23.2 (s, $MeCO_2$).

‡ *Crystal data:* $C_{30}H_{66}Ru_2$, $M = 629.03$, triclinic, space group $P\bar{1}$, $a = 20.013(3)$, $b = 9.848(2)$, $c = 9.757(2)$ Å, $\alpha = 117.83(3)$, $\beta = 86.89(3)$, $\gamma = 97.82(2)°$, $U = 1684.7$ Å^3, $Z = 2$, $D_c = 1.24$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 8.15$ cm^{-1}, $\lambda = 0.71069$ Å. 6028 Data measured (CAD4 diffractometer), 4717 observed [$I > 1.5\sigma(I)$]. $R = 0.047$.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ Homoleptic Pd and Pt compounds, *e.g.*, $[PtMe_6]^{2-}$ are ionic; see P. M. Maitlis, P. Espinet, and M. H. Russell in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon Press, 1982, vol. 6, Ch. 38.4 and F. R. Hartley, *ibid.*, Ch. 39.5. No Rh or Ir compounds appear to be known.

a multiple bond unsupported by bridging groups; the only other Ru_2^{6+} species is the cation $Ru_2L_2^{2+}$, where L is a N_4-macrocyclic ligand.[14] The formation of the ruthenium(III) species from $Ru_2^{II,III}(O_2CMe)_4Cl$ under alkylation conditions is possibly due to the disproportionation shown in equation (1) giving unstable ruthenium(II) species, since the yields of the Ru_2^{III} compounds are below 50%.

$$2Ru_2^{II,III\ 5+} \rightarrow Ru_2^{II,II\ 4+} + Ru_2^{III,III\ 6+} \qquad (1)$$

It is obvious that other similar complexes with bulky RO, ArO, R_2N, R_2P, RS, *etc.*, groups should be accessible directly from the acetate chlorides or from these alkyls; syntheses of such compounds as well as reactions of the alkyls, *e.g.* with acids, are under study. Also, since the intermediates $M_2R_4(\mu\text{-}O_2CMe)_2$ react quantitatively on alkylation, mixed species should be readily accessible.

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