Synthesis and *X*-Ray Crystal Structure of Hexakis(trimethylphosphine)-tris-μ-methylene-diruthenium(III)†

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Summary The reaction between the dinuclear ruthenium-(II.III)-bridged acetate $Ru_2(O_2CMe)_4Cl$ and $MgMe_2$ in presence of PMe_3 produces the complex $Ru_2(CH_2)_3(PMe_3)_6$ (A) in low yield; higher yields are obtained if the trimeric μ_3-oxo-centred acetate $[Ru_3O(O_2CMe)_6(H_2O)_3]\cdot(O_2CMe)$ is used and the structure of (A) has been determined by *X*-ray crystallography and contains three methylene bridges.

RELATIVELY few compounds containing a bridging $-CH_2-$ (methylene) unit have been isolated.[1] The compound $Ru_2(CH_2)_3(PMe_3)_6$ (A) was first isolated in very low yield

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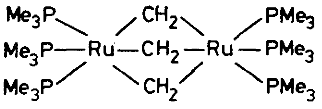
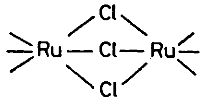
† No reprints available.

from the reaction of $Ru_2(O_2CMe)_4Cl$ with dimethylmagnesium in the presence of trimethylphosphine as red, air-sensitive, diamagnetic crystals; the main product was *cis*-$RuMe_2(PMe_3)_4$.[2]



(A)



(B)

We have obtained compound (A) in much higher yields (*ca.* 40%) from $[Ru_3O(O_2CMe)_6(H_2O)_3]\cdot(O_2CMe)$ under similar conditions. N.m.r. and i.r. data were insufficient to characterise the compound structurally so that an *X*-ray diffraction study has been made.

Crystal data: $C_{21}H_{60}P_6Ru_2$, $M = 700{\cdot}7$, monoclinic, $a = 22{\cdot}174(5)$, $b = 9{\cdot}352(2)$, $c = 16{\cdot}925(4)$ Å, $\beta = 106{\cdot}06(3)°$, $U = 3372{\cdot}8$ Å^3, D_m not measured, $Z = 4$, $D_c = 1{\cdot}380$ g cm^{-3}, space group $P2_1/n$, $F(000) = 1456$, μ(Mo-K_α = 11·3 cm^{-1}, λ(Mo-K_α) = 0·71069 Å. The intensities of 5921 unique reflections ($1{\cdot}5 < \theta < 25°$) were measured from a crystal sealed under nitrogen using a Nonius CAD4 diffractometer, Mo-K_α radiation, and an $\omega/2\theta$ scan technique. The Ru and P positions were obtained from the best E-map computed with the SHELX[3] program and other atoms from electron density syntheses. Blocked full-matrix least-squares refinement of the structure (non-hydrogen atoms anisotropic, H atoms isotropic) has given an R value of 0·0292 for 4561 significant $[I_0 > 1{\cdot}5\sigma(I_0)]$ reflections.‡

The molecular structure found is shown in the Figure, the complex thus being identified as a unique triply methylene-bridged dinuclear ruthenium(III) compound. The overall co-ordination geometry is that of a confacial bioctahedron as in $[Ru_2Cl_3(PPhEt_2)_6]^+$,[4] $Ru_2Cl_4(PPhEt_2)_5$,[5] and $Ru_2Cl_5(PBu^n_3)_4$,[6] all of which contain the unit (B). The Ru–Ru distance of 2·650(1) Å and acute (*ca.* 78·0°) Ru–C–Ru bridge angles in our complex are consistent with the presence of a single Ru–Ru bond, as required by the compound's diamagnetism.

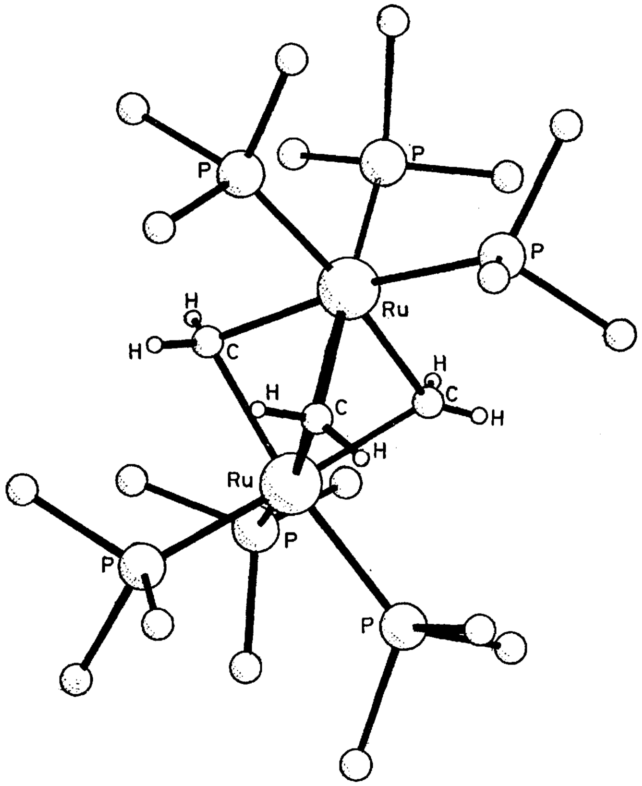


FIGURE. The molecule of $Ru_2(CH_2)_3(PMe_3)_6$. Important molecular geometry parameters are: Ru–P, 2·332—2·340(1) and Ru–C, 2·103—2·112(6) Å; ∠C-Ru-C, 81·7—87·5(3) and ∠P-Ru-P, 94·5—96·4(2)°.

The formation of methylene bridges presumably arises by transfer of hydrogen from Ru–Me groups in an intermediate complex. There seems now no reason why methylene-bridged compounds comparable to halogen-bridged compounds of transition metals should not be stable and isolable, provided suitable rational synthetic methods can be developed.

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‡ The atomic co-ordinates 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.

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