Journal of Organometallic Chemistry, 310 (1986) C47–C50
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

SYNTHESIS AND STRUCTURAL CHARACTERISATION OF $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2C_6H_5)(\mu_2\text{-}CO)_2(CO)_{17}]$: EXAMPLE OF PHOSPHORUS ENCAPSULATED IN A SQUARE ANTI-PRISM OF RUTHENIUM ATOMS AND OF AN UNUSUAL COORDINATION MODE FOR THE BENZYL GROUP

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(Received May 6th, 1986)

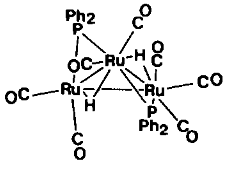
Summary

Reaction of $[Ru_3(CO)_{12}]$ with an equimolar amount of PPh_2H affords a range of products including an octaruthenium species $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2C_6H_5)(\mu_2\text{-}CO)_2(CO)_{17}]$, in which, as established X-ray crystallographically, a phosphorus atom is encapsulated in a square anti-prism of ruthenium atoms and a benzyl group is coordinated to two of these rutheniums through all seven carbon atoms.

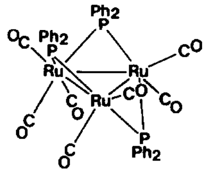
Coordinated triphenylphosphine is known to readily lose a phenyl group under appropriate reaction conditions to afford products containing the bridging diphenylphosphido ligand which, in turn, can be dephenylated to give compounds containing the phenylphosphinidene group and/or encapsulated phosphorus [1]. Examples are provided by thermolysis of $[RhH(CO)(PPh_3)_3]$ which produces either $[Rh_3(\mu_2\text{-}PPh_2)(CO)_3(PPh_3)_2]$ or $[Rh_4(\mu_2\text{-}PPh_2)_4(\mu_2\text{-}CO)_2(CO)_3(PPh_3)]$ depending on the reaction conditions [2,3], the reaction of $[RuHCl(CO)(PPh_3)_3]$ with $Na[Co(CO)_4]$ at 40 °C which yields $[CoRu(\mu_2\text{-}PPh_2)(CO)_5(PPh_3)_2]$ as well as $[RuHCl(CO)_2(PPh_3)_2]$ and $[Ru(CO)_3(PPh_3)_2]$ [4], the reaction of $[Fe_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8]$ with CO at room temperature which gives $[Fe_3(\mu_3\text{-}PPh)_2(CO)_9]$ [5] and the reaction of $[Rh(CO)_2(\text{acetylacetone})]$ with PPh_3 in the presence of caesium benzoate in tetraethylene glycol dimethyl ether at a temperature of 140–160 °C and a 300 atmosphere pressure of CO/H_2 which selectively produces $[Rh_9(\mu_8\text{-}P)(\mu_2\text{-}CO)_{12}(CO)_9]^{2-}$ [6]. The isolation of a ruthenium cluster containing an encapsulated phosphorus in which the latter is derived from diphenylphosphine is now reported.

0022-328X/86/$03.50

We have previously communicated that the reaction of $[\mathrm{Ru_3(CO)_{12}}]$ with an equimolar amount of $\mathrm{PPh_2H}$ in toluene under reflux affords a range of products including $[\mathrm{Ru_3(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}H)_2(CO)_8}]$ (I), $[\mathrm{Ru_3(\mu_2\text{-}PPh_2)_3(\mu_2\text{-}H)(CO)_7}]$ (II), $[\mathrm{Ru_4(\mu_4\text{-}PPh)_2(\mu_2\text{-}CO)(CO)_{10}}]$ (III) and $[\mathrm{Ru_5(\mu_4\text{-}PPh)(CO)_{15}}]$ (IV) [7]. A blue, very minor product in this reaction has now been established X-ray crystallographically, as $[\mathrm{Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2C_6H_5)(\mu_2\text{-}CO)_2(CO)_{17}}]$. The molecular stereochemistry of this compound is illustrated in Fig. 1. The eight ruthenium atoms adopt a square anti-prismatic geometry with a phosphorus encapsulated in the centre of the metal atom framework; the ruthenium–phosphorus distances vary from 2.31(1) to 2.44(1) Å. A benzyl group is coordinated to the skeletal framework via two of the ruthenium atoms with the phenyl ring being essentially symmetrically disposed with respect to one of these two ruthenium atoms (Ru(1)) and the benzylic carbon being located at a bonding distance (2.19(4) Å) from the other (Ru(4)). The coordination at the ruthenium atom is completed by nineteen carbonyl groups with two of these being bridging and the rest terminal.



(I)



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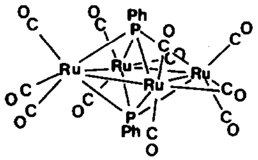

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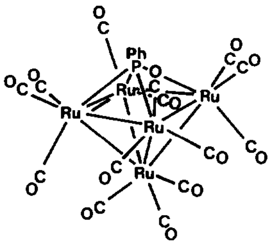

(IV)

Square-anti-prismatic coordination of interstitial main group atoms in metal cluster compounds is unusual [8–10], but has been observed in $[\mathrm{Co_8(\mu_8\text{-}C)(\mu_2\text{-}CO)_{10}(CO)_8}]^{2-}$ [11], $[\mathrm{Rh_9(\mu_8\text{-}P)(\mu_2\text{-}CO)_{12}(CO)_9}]^{2-}$ [6] and $[\mathrm{Rh_{10}(\mu_8\text{-}P)(\mu_2\text{-}CO)_{12}(CO)_{10}}]^{3-}$ [12]. In the $\mathrm{Rh_9}$-cluster, one square face of the anti-prism is capped

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* *Crystal data*: $\mathrm{C_{26}H_7O_{19}PRu_8.CH_2Cl_2}$. $M = 1547.81$, orthorhombic, space group $Pca2_1$, a 23.234(4), b 10.515(2), c 31.144(5) Å. D_c 2.702 g cm^{-3} for $Z = 8$. $F(000) = 5792$. $\lambda(\text{Mo-}K_\alpha)$ 0.71069 Å, $\mu(\text{Mo-}K_\alpha)$ 3.26 mm^{-1}. 6822 unique reflections were measured to $2\theta_{\max}$ 50° and empirically corrected for absorption on a CAD-4 diffractometer (N.C.R.L., C.S.I.R., Pretoria), 4391 of which were classed as observed ($I > 1.5\sigma(I)$). The structure was solved by direct methods (SHELX-86) and refined by full-matrix least squares methods to $R = 0.091$ and $R_w = 0.082$ {Ru, P, Cl ($\mathrm{CH_2Cl_2}$) anisotropic; C, O isotropic; H excluded}. The unit cell contains two crystallographically independent molecules per asymmetric unit. Since both molecules adopt essentially the same geometry, see Fig. 1, the interatomic distances, etc. refer to one molecule only.

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 (Great Britain). Any request should be accompanied by a full literature citation for this communication.

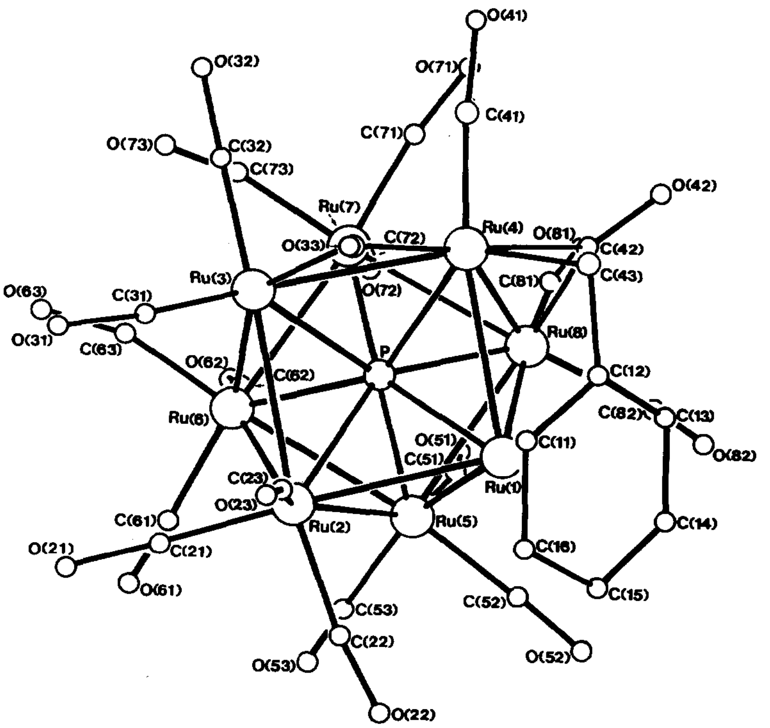
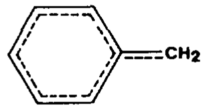


Fig. 1. The molecular stereochemistry of $[Ru_8(\mu_8\text{-}P)(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2C_6H_5)(\mu_2\text{-}CO)_2(CO_{17}]$. Ru(1)–Ru(2), 2.839(5); Ru(1)–Ru(4), 2.864(5) Ru(1)–Ru(5), 2.832(5); Ru(1)–Ru(8), 2.822(5); Ru(2)–Ru(3), 2.961(5); Ru(2)–Ru(5), 2.905(5); Ru(2)–Ru(6), 2.867(5); Ru(3)–Ru(4), 2.857(5); Ru(3)–Ru(6), 2.948(5); Ru(3)–Ru(7), 2.919(5); Ru(4)–Ru(7), 3.007(5); Ru(4)–Ru(8), 2.830(5); Ru(5)–Ru(6), 2.956(5); Ru(5)–Ru(8), 2.980(5); Ru(6)–Ru(7), 2.916(5); Ru(7)–Ru(8), 2.931(5) Å. Ru–P distances are in the range 2.31(1)–2.43(1) Å.

by a further rhodium atom while in the Rh_{10}-cluster both square faces are capped by rhodium atoms. Compounds in which the benzyl group functions as a monohapto ligand are numerous, coordinating via the benzylic carbon either terminally as in $[Nb(C_5H_5)_2(CH_2C_6H_5)_2]$ [13] and $[Mo_2(NMe_2)_4(CH_2C_6H_5)_2]$ [14] or in the bridging mode as in $[Mn_2(\mu\text{-}CH_2C_6H_5)_2(CH_2C_6H_5)_2(PMe_3)_2]$ [15]. Similarly, examples of compounds containing the benzyl or related groups functioning as hexahapto ligands i.e. coordinating through the benzene ring as in $[Cr(\eta^6\text{-}C_6H_5CH_3)(CO)_2CNBu^t)]$ [16] are equally prolific. However, we have not found any reported examples of compounds in which a benzyl group bridges two metal atoms, formally bonded to each other, in a monohapto-hexahapto coordination mode.

An alternative description of the coordination of the $CH_2C_6H_5$ group is one in which the group functions as a benzylic system, bonding to the metal cluster across one of its edges as a heptahapto ligand. The interatomic distances and angles



associated with the benzylic carbon are no different from those normally observed for the benzyl group coordinated in the monohapto mode however [17], and thus the coordination is probably best described as monohapto-hexahapto.

Acknowledgements. The authors express their sincere thanks to the South African Council for Scientific and Industrial Research, the University of Natal, and Fonds der Chemischen Industrie for financial support, Johnson–Matthey Limited for the loan of ruthenium salts and Dr. P.H. van Rooyen of the N.C.R.L., C.S.I.R., Pretoria for the intensity data collection.

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17 See references 13, 14 and 15 for instance.