Preparation and X-Ray Crystallographic Characterisation of an Unusual Heteronuclear Complex, $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$

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Summary The complex $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$, prepared from $RhCl(PPh_3)_3$ and $Ag(C{\equiv}CC_6F_5)$, contains a central rhodium atom which is octahedrally coordinated to one PPh_3 ligand and five σ-acetylide units; each PPh_3Ag group is π-bonded to three acetylenic bonds (one acetylenic linkage thereby being involved with both silver atoms); rhodium–silver distances are 3·086(1) and 3·102(1) Å.

The reaction between $RhCl(PPh_3)_3$ and $Ag(C{\equiv}CC_6F_5)$ in tetrahydrofuran affords the hexanuclear cluster $Rh_2Ag_4(C{\equiv}CC_6F_5)_8(PPh_3)_2$ (I) [which is presumed to be isostructural with $Ir_2Cu_4(C{\equiv}CPh)_8(PPh_3)_2$[1]] and the binuclear species $RhAg(C{\equiv}CC_6F_5)_4(PPh_3)_3$ (II). From 1,2-dimethoxyethane, a third, trinuclear, complex can be isolated, of stoicheiometry $RhAg_2(C{\equiv}CC_6F_5)_5(PPh_3)_3$ (III). The ^{19}F n.m.r. spectrum of (III) showed two types of C_6F_5 groups in a 1:4 ratio, well-resolved signals with the usual 2:1:2 intensity pattern being found at 134·5, 159, and 163·5 (intensity 1) and 137, 160, and 164·5 p.p.m. (intensity 4).

The detailed molecular geometry of (III) has been determined *via* a single-crystal *X*-ray structural analysis.

Crystal data: $C_{94}H_{45}Ag_2F_{25}P_3Rh$, $M = 2060{\cdot}9$, monoclinic, $a = 15{\cdot}902(2)$, $b = 21{\cdot}497(3)$, $c = 25{\cdot}041(3)$ Å, $\beta = 102{\cdot}00(1)^\circ$, $U = 8373{\cdot}5$ Å^3, $D_m = 1{\cdot}627(5)$, $D_c = 1{\cdot}635$ g cm^{-3}, $Z = 4$, space group $P2_1/n$.

Diffraction data complete to $2\theta = 40^\circ$ (Mo-K_α radiation) were collected with a Picker FACS-1 diffractometer and were corrected for Lorentz, polarization, and absorption ($\mu = 7{\cdot}95$ cm^{-1}) effects. The structure was solved *via* a combination of Patterson, Fourier, and least-squares refinement techniques. All 125 non-hydrogen atoms have been accurately located,‡ the present discrepancy index being R 6·8% for the 7820 independent reflections (no data being rejected).

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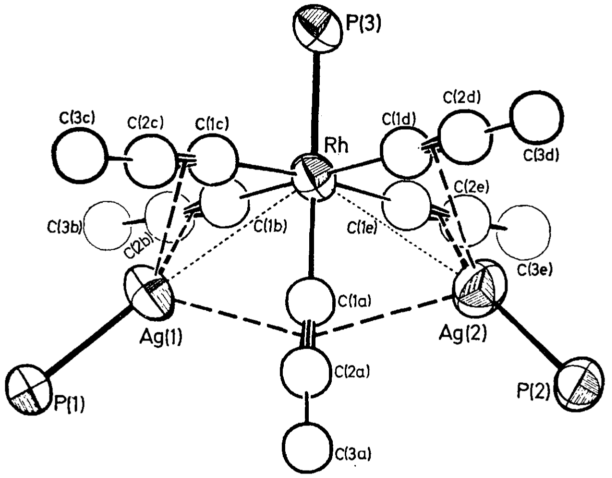
‡ Two phenyl groups are subject to disorder and have been resolved.

E.s.d.'s are *ca.* 0·001 Å for metal–metal, *ca.* 0·002 forÅ metal–phosphorus, and *ca.* 0·01 Å for (light atom)–(light atom) vectors.



The geometry of the RhAg$_2$(C≡C–C)$_5$(P)$_3$ 'core' of the molecule is illustrated in the Figure. The rhodium atom is in essentially regular octahedral co-ordination to one PPh$_3$ ligand [Rh–P(3) = 2·342 Å] and five σ-acetylides [Rh–C(1a) = 2·04, Rh–C(1b) = 2·01, Rh–C(1c) = 2·03, Rh–C(1d) = 2·02, Rh–C(1e) = 2·02 Å]. The acetylenic bonds, C(1)–C(2), are 1·19—1·22 Å in length, while the C–C$_6$F$_5$ [C(2)–C(3)] distances range from 1·43 to 1·46 Å.

The silver atoms are each in essentially tetrahedral co-ordination environments.

Atom Ag(1) is linked asymmetrically to three acetylenic bonds, with Ag(1)–C(1a) = 2·52, Ag(1)–C(2a) = 2·87, Ag(1)–C(1b) = 2·48, Ag(1)–C(2b) = 2·79, Ag(1)–C(1c) = 2·49, and Ag(1)–C(2c) = 2·69 Å. Atom Ag(2) is similarly bonded, with Ag(2)–C(1a) = 2·64, Ag(2)–C(2a) = 3·13, Ag(2)–C(1d) = 2·64, Ag(2)–C(2d) = 2·99, Ag(2)–C(1e) = 2·34, and Ag(2)–C(2e) = 2·60 Å. Silver–phosphorus distances are Ag(1)–P(1) = 2·388 and Ag(2)–P(2) = 2·389 Å.

The rhodium–silver distances, Rh–Ag(1) = 3·086 Å and Rh–Ag(2) = 3·102 Å, are longer than that expected for rhodium–silver single bonds [*ca.* 2·790 Å, based upon (Rh–Rh)$_{\mathrm{min}}$ = 2·690 Å and (Ag–Ag)$_{\mathrm{min}}$ = 2·889 Å in the pure metals[2]]. This, in conjunction with the otherwise normal octahedral and tetrahedral geometry around the rhodium and silver atoms (respectively), leads us to prefer a zwitterionic structure based upon Rh$^{\mathrm{III}}$ and Ag$^{\mathrm{I}}$ rather than the alternative metal–metal bonded structure based on Rh$^{\mathrm{V}}$ and Ag^{0}.

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[2] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, Table 4.3, pp. 278—285.