

Rapid Ring-opening Reactions of *trans*-[OsX₂(dppm-*P,P'*)₂] with [Rh₂X₂(CO)₄] (X = Cl or Br) to give Osmium–Rhodium Heterobimetals: Crystal Structure of [Cl₂Os(μ-CO)₂(μ-dppm)₂RhBr] (dppm = Ph₂PCH₂PPh₂)

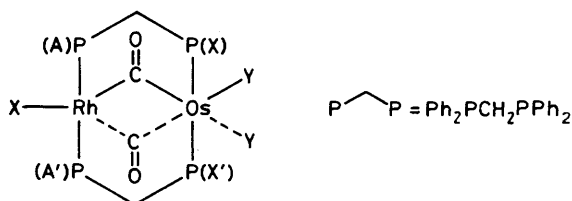
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Complexes of the type [Y₂Os(μ-CO)₂(μ-dppm)₂RhX] (Y = Cl or Br; X = Cl, Br, I, SCN, or N₃) have been made either as described in the title or by metathesis; the crystal structure and the i.r. spectrum of the title compound suggest strongly bridging CO groups.

Chelating Ph₂PCH₂PPh₂ (dppm) complexes of metals with d⁸ electron configuration, e.g. of type [M(dppm-*P,P'*)₂]Cl₂ (M = Pd or Pt) or [M(CO)(dppm-*P,P'*)₂]Cl (M = Rh or Ir) are relatively labile towards substitution and undergo ring-opening reactions with a variety of metals (M') to give heterobimetallic complexes containing M(μ-dppm)₂M' moieties.^{1–3} In contrast, octahedrally co-ordinated bis chelate dppm complexes of metals with d⁶ electron configuration are usually inert to substitution, including chelate ring opening, especially if the metal is from the 2nd or 3rd transition series. In agreement with this, complexes of type [M(CO)₂(dppm-*P,P'*)₂] (M = Mo or W) or *cis*- or *trans*-[RuCl₂(dppm-*P,P'*)₂] are unaffected by treatment with Cu^I or Ag^I halides or Rh^I or Ir^I carbonyl halides *etc.* Similarly, *trans*-[OsCl₂(dppm-*P,P'*)₂] does not react with [AuCl(PPh₃)], [IrCl(CO)₂(*p*-toluidine)], or [Ag₄I₄(PPh₃)₄]. However, we have found that a remarkably rapid and specific ring-opening reaction occurs when *trans*-[OsCl₂(dppm-*P,P'*)₂] is treated with the equivalent amount of [Rh₂Cl₂(CO)₄] in dichloromethane, to give [Cl₂Os(μ-CO)₂(μ-

dppm)₂RhCl] (**1a**). With a solution *ca.* 0.03 M in osmium complex, reaction is complete in <2 min at 20 °C, no other product being detected [³¹P{¹H} n.m.r. evidence]. The osmium–rhodium complex was isolated as large orange prisms in 75% yield and characterized by elemental analysis and by ³¹P{¹H} n.m.r. [40.25 MHz, CD₂Cl₂, AA'MM'X pattern with satellites due to coupling to ¹⁸⁷Os. δ_P(Os) –4.2 p.p.m., ¹J(OsP) 176 Hz, δ_P(Rh) + 27.0 p.p.m., ¹J(RhP) 106 Hz, 'N' = |J(A_X) + J(A_{X'})| = 79 Hz, 'M' = |J(AA') – J(XX')| = 94 Hz] and i.r. spectroscopy. The i.r. spectrum (Nujol) showed ν(CO) bands at 1800s and 1842 cm⁻¹, and ν(Rh–Cl) at 311 cm⁻¹; bands due to ν(Os–Cl) were not identified. Treatment of complex (**1a**) with LiBr (10 mol. equiv.) in acetone for 16 h gave [Cl₂Os(μ-CO)₂(μ-dppm)₂RhBr] (**1b**), characterized by elemental analysis, n.m.r., and i.r. spectroscopy [³¹P{¹H} n.m.r. (in CD₂Cl₂) δ_P(Os) –5.2 p.p.m., δ_P(Rh) + 24.8 p.p.m., ¹J(RhP) 106 Hz, 'N' doublet separation = 78 Hz; i.r. (Nujol) ν(CO) 1800s and 1705s cm⁻¹]. The crystal structure of this compound has been determined and is shown in Figure 1.† The very low values for ν(CO) suggest stronger bridging interaction of the carbonyl groups in (**1b**) than in (**1a**). Treatment of (**1a**) with NaI, NaN₃, or KSCN in



- (1) a; X = Y = Cl
 b; X = Br, Y = Cl
 c; X = I, Y = Cl
 d; X = N₃, Y = Cl
 e; X = SCN, Y = Cl
 f; X = Y = Br
 g; X = Y = I

† Crystal data: orange solvent dependent parallelepipeds, [Cl₂Os(μ-CO)₂(μ-dppm)₂RhBr]·CH₂Cl₂, M = 1353.7. Orthorhombic, space group *Pna*2₁ (no. 33), a = 1199.0(3), b = 1563.7(6), c = 2926.7(5) pm, U = 5.487(3) nm³, Z = 4, Mo-K_α radiation, λ = 71.069 pm, μ(Mo-K_α) = 34.8 cm⁻¹, F(000) = 2587.9, 4.0 < 2θ < 45°. Final R and R_w values 0.057 and 0.051 respectively for 2955 unique reflections [I > 2σ(I)]. The inverted structure gave significantly higher R values. 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.

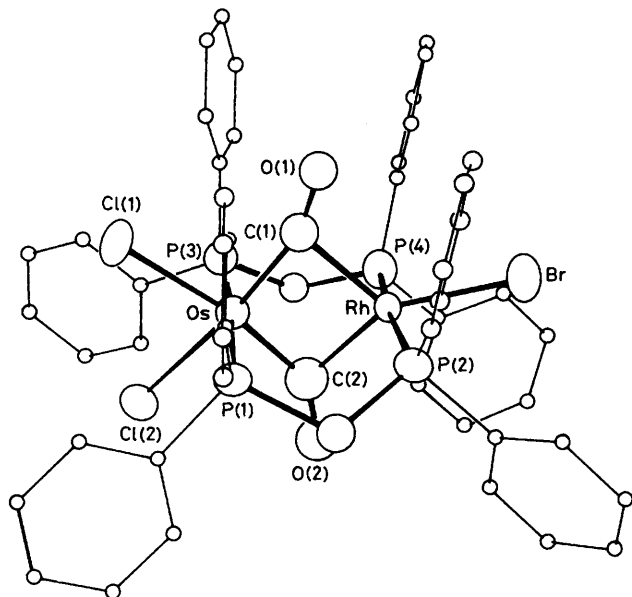


Figure 1. Molecular structure of $[\text{Cl}_2\text{Os}(\mu\text{-CO})_2(\mu\text{-dppm})_2\text{RhBr}]$ (**1b**). Selected bond lengths: Os–Cl(1) 244.3(8), Os–Cl(2) 244.7(9), Os–C(1) 192.6(26), Os–C(2) 191.0(31), Rh–Br 244.7(5), Rh–C(1) 200.8(38), Rh–C(2) 218.4(27), Os–Rh 275.8(5) pm. Selected bond angles: Os–C(1)–O(1) 145.8(28), Rh–C(1)–O(1) 124.8(22), Os–C(2)–O(2) 157.5(22), Rh–C(2)–O(2) 118.1(21)°.

acetone gave the corresponding complexes (**1c**), (**1d**), or (**1e**) respectively, all in good yield and fully characterized. Treatment of (**1a**) with a large excess (30-fold) of LiBr or NaI in boiling methyl ethyl ketone gave the corresponding complexes

(**1f**) or (**1g**) respectively. Treatment of $\text{trans-}[\text{OsBr}_2(\text{dppm-}P,P')_2]$ with $[\text{Rh}_2\text{Br}_2(\text{CO})_4]$ in CH_2Cl_2 at 20 °C also gave (**1f**).

We have also detected an intermediate in the conversion of mixtures of $\text{trans-}[\text{OsCl}_2(\text{dppm-}P,P')_2]$ and $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ into (**1a**) using $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectroscopy. On mixing the reactants in CH_2Cl_2 solution at –10 °C a new Os–Rh heterobimetallic complex, with a similar AA'MM'X pattern to that in the spectrum of (**1a**), was produced gradually, $\delta_{\text{P}}(\text{Os}) +3.2$ p.p.m., $\delta_{\text{P}}(\text{Rh}) 27.5$ p.p.m., $^1J(\text{RhP}) = 102$ Hz, $^2N = 83$ Hz (recorded at –30 °C) but over a period of several hours with gradual warming to room temperature this complex was transformed into (**1a**). This intermediate and other (minor) products possibly have bridging Cl group(s) rather than two bridging CO groups. We cannot suggest a mechanism to explain the formation of (**1a**) from $[\text{OsCl}_2(\text{dppm-}P,P')_2]$ and $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ or the intermediate but the formation of bridging carbonyls is probably important in promoting the ring-opening reaction. Preliminary results show that (**1a**) is readily protonated by HBF_4 and also reacts with NaBH_4 ; in either case the $\text{Os}(\mu\text{-dppm})_2\text{Rh}$ moiety is preserved [$^{31}\text{P}\{^1\text{H}\}$ n.m.r. evidence]. These and other reactions are being investigated.

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