The Preparation and Hydridic Reduction of Dicationic Dicarbonyl Complexes of Osmium(II); The Crystal and Molecular Structure† of *trans*-Bis[1,2-bis-(diphenylphosphino)ethane-*PP'*]carbonylformylosmium(II) Hexafluoroantimonate–Dichloromethane (1/1)

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Reactions of *cis*- or *trans*-$[OsCl_2(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) or *trans*-$[OsCl_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with $AgSbF_6$ under CO give *cis*-$[Os(CO)_2(dppm)_2][SbF_6]_2$ and *trans*-$[Os(CO)_2(dppe)_2][SbF_6]_2$ respectively, the latter *via* $[OsCl_2(dppe)_2][SbF_6]_2$. Reductions of $[Os(CO)_2(P–P)_2][SbF_6]_2$ (P–P = dppm or dppe) with $K[BH(OPr^i)_3]$, $Li[BHEt_3]$, or $Li[BDEt_3]$ give $[Os(CHO)(CO)(P–P)_2][SbF_6]$, $[Os(CHO)(CO)(P–P)_2][BEt_4]$, and $[Os(CDO)(CO)(P–P)_2][SbF_6]$ respectively without change of stereochemistry. Pure *trans*-$[Os(CHO)(CO)(dppe)_2][SbF_6]$ is thermally very stable, although it decomposes rapidly to *trans*-$[OsCl(CO)(dppe)_2][SbF_6]$ if contaminated with boron residues. Impure *cis*-$[Os(CHO)(CO)(dppm)_2]^+$ is much more stable than the purified complex, which decomposes to *trans*-$[OsCl(CO)(dppm)_2]^+$, *cis*-$[OsH(CO)(dppm)_2]^+$, and an unusual dimeric complex. The complexes have been fully characterised by analytical and spectroscopic means as well as by an X-ray structure analysis of *trans*-$[Os(CHO)(CO)(dppe)_2]$-$[SbF_6]\cdot CH_2Cl_2$. Crystals of this complex are orthorhombic, space group $Pn2_1a$ ($\equiv Pna2_1$, no. 33), with $a = 22.361(4)$, $b = 20.209(2)$, $c = 11.940(2)$ Å, and $Z = 4$. The structure was obtained from 2 301 observed intensities measured on an automatic diffractometer and refined to an R value of 0.059. The main features of interest are the long Os–C bond [2.155(28) Å] and the Os–C–O angle of 130.7(27)° for the formyl ligand.

We have recently reported[1] on the first isolable formyl complexes of ruthenium, formed by hydridic reduction of $[Ru(CO)_2(P–P)_2]^{2+}$, P–P = $Ph_2P(CH_2)_nPPh_2$, $n = 1$ (dppm) or 2 (dppe).[2] Although these complexes were sufficiently stable for complete (including crystallographic) characterisation, they decomposed[3] rapidly in solution at temperatures above 0 °C so that attempts to study their reaction chemistry have largely been frustrated.

In order to confer extra stability upon similar formyl complexes, and knowing that the first step of the decomposition reaction was Ru–P bond cleavage,[3] we have attempted to prepare the analogous complexes of the congener metal, osmium, which were expected to be less labile. Other formyl complexes of osmium are known[4–9] and some are remarkably stable.[4,5]

We now report the complete results of these investigations, for which a preliminary communication has appeared.[10]

Results and Discussion

Preparation of $[Os(CO)_2(P–P)_2][SbF_6]_2$.—Compounds of the form $[Os(CO)_2(P–P)_2][SbF_6]_2$ can be synthesised by routes similar to those employed for their ruthenium analogues.[2] Thus, reactions of *cis*- or *trans*-$[OsCl_2(dppm)_2]$ with 2 molar equivalents of $AgSbF_6$ under carbon monoxide at 80 °C lead smoothly to the production of *cis*-$[Os(CO)_2(dppm)_2][SbF_6]_2$ [$v(C\equiv O)$ at 2 042 and 2 083 cm^{-1}], although the product from the *trans* isomer is sometimes contaminated with what is believed to be *trans*-$[Os(CO)_2(dppm)_2][SbF_6]_2$ [$v(C\equiv O)$ at

2 033 cm^{-1}]. Starting from the *cis* isomer, *trans*-$[OsCl(CO)-(dppm)_2][SbF_6]$ [$v(C\equiv O)$ at 1 962 cm^{-1}], which probably arises from partial oxidation by the silver followed by CO reduction (see below), contaminates the product, but this can be removed by careful recrystallisation. The observation that the *cis* isomer is the predominant product regardless of the stereochemistry of the starting material is consistent with the known *trans*–*cis* isomerism of other osmium ditertiary phosphine complexes, which have been observed at high temperatures.[11]

Treatment of *trans*-$[OsCl_2(dppe)_2]$ under similar conditions leads initially to a dark green solution together with some silver metal. Provided that excess (>3 mol) of $AgSbF_6$ is employed, the solution then pales and *trans*-$[Os(CO)_2(dppe)_2][SbF_6]_2$ [$v(C\equiv O)$ at 2 028 cm^{-1}] can be isolated in high yield.‡ By carrying out this reaction in the absence of CO, the dark green solution is again obtained and $[OsCl_2(dppe)_2][SbF_6]$ can be isolated. Oxidation by Ag^+ is clearly responsible for this osmium(III) intermediate, although this oxidation does not occur for *cis*-$[MCl_2(dppm)_2]$ (M = Ru or Os) or for *trans*-$[RuCl_2(dppe)_2]$. This ready oxidation of the *trans*-osmium species is consistent with the redox potentials for *cis*- and *trans*-$[MCl_2(dppm)_2]$, which have been measured[11] and show that *trans*-$[OsCl_2(dppm)_2]$ is much more easily oxidised [$E = 0.18$ V *vs.* saturated calomel electrode] than any of the other complexes in this series. Observed[12] redox potentials for Ag^+–Ag in non-aqueous solvents suggest that, in this series of complexes, Ag^+ should *only* be capable of oxidising *trans*-$[OsCl_2(dppm)_2]$. Presumably changing dppm for dppe does not greatly affect these redox potentials.

Carbon monoxide is evidently a sufficiently strong reducing

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† *Supplementary data available* (No. SUP 56105, 5 pp.): thermal parameters, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

‡ In the absence of excess of $AgSbF_6$, *trans*-$[OsCl(CO)(dppe)_2]$-$[SbF_6]$ contaminates the product.

agent to reduce the osmium(III) species back to Os[II] and form the dicationic dicarbonyl complex.

Preparation of Formyl Complexes.—(a) *dppe.* The low-temperature hydridic reduction of *trans*-[Os(CO)₂(dppe)₂]-[SbF₆]₂ in CH₂Cl₂ yields the expected formyl complexes *trans*-[Os(CXO)(CO)(dppe)₂][Y] (X = H, Y = SbF₆ or BEt₄*; X = D, Y = SbF₆), analogous to the previously reported[1] ruthenium complexes. However, it is necessary to use the stronger hydride donors Li[BHEt₃] and K[BH(OPr^i)₃] to ensure complete reaction. The reaction mixtures are usually dark brown (lithium reductions) or black (potassium reductions), although the isolated and recrystallised formyl complexes are yellow.

The osmium formyl complexes are substantially more stable to decomposition than the analogous ruthenium complexes (see below), hence several attempts to promote further hydridic reductions were made. Treatment of *trans*-[Os(CO)₂(dppe)₂]-[SbF₆]₂ or *trans*-[Os(CHO)(CO)(dppe)₂][SbF₆] in CH₂Cl₂ with large excesses (3—10 fold) of Li[BHEt₃] or K[BH(OPr^i)₃] resulted in *trans*-[Os(CHO)(CO)(dppe)₂]⁺ as the only complex containing a reduced carbon monoxide group to be recovered, together with impurities of *trans*-[OsCl-(CO)(dppe)₂]⁺ from solvent interaction (see later). This complex, *trans*-[Os(CO)₂(dppe)₂][SbF₆]₂, was then treated with NaBH₄ in tetrahydrofuran (thf), since it has been shown[13] that with this hydride source stepwise reduction of co-ordinated CO can be achieved by careful control of reaction conditions. However, the product obtained under a variety of conditions [NaBH₄:Os, 1.2 or 5:1, dry or 'wet' thf (5% water); reaction time 5, 16, or 48 h] was always the same. It had n.m.r. properties identical to those of *trans*-[Os(CHO)(CO)(dppe)₂][SbF₆] and, although its i.r. spectrum was slightly different, it was identical to that of a compound prepared from *trans*-[Os(CO)₂-(dppe)₂][SbF₆]₂ and K[BH(OPr^i)₃] in thf, or by refluxing *trans*-[Os(CHO)(CO)(dppe)₂][SbF₆] in thf. We believe the i.r. differences arise from thf of crystallisation.

Using a suspension of KH in mineral oil as the hydride source (H:Os, 2 or 10:1), only partial (40%) reduction of the dicarbonyl in thf could be achieved. The product was identical to that obtained from NaBH₄, with an impurity of unreacted dicarbonyl complex.

These results are not too surprising, since it has been shown that when using equimolar amounts of alkylborohydrides yields of [Fe(CHO)(CO)₄]⁻ from [Fe(CO)₅] are in the region of 65—100% whereas KH gives no formyl and NaBH₄ gives only 5%, even after 48 h, with a four-fold excess of hydride.[14]

(b) *dppm.* Reductions of *cis*-[Os(CO)₂(dppm)₂][SbF₆]₂ with K[BH(OPr^i)₃], Li[BHEt₃], or Li[BDEt₃] in dichloromethane at −30 °C yield the formyls *cis*-[Os(CHO)(CO)-(dppm)₂][SbF₆], *cis*-[Os(CHO)(CO)(dppm)₂][BEt₄], and *cis*-[Os(CDO)(CO)(dppm)₂][SbF₆], respectively. For the [SbF₆]⁻ salts *ca.* 30% of the total yield precipitates during the reaction, whilst the remaining 70% readily precipitates on addition of a small volume of diethyl ether. The [BEt₄]⁻ complex is slightly more soluble, with little precipitation from the reaction mixture. However, once isolated, all the formyl complexes are only sparingly soluble in CH₂Cl₂ at low temperatures, whilst at ambient temperatures they are unstable, reacting with the solvent to form *trans*-[OsCl(CO)(dppm)₂]⁺ (see later). The presence of a formyl group is confirmed by i.r. studies (see Table 3) and low-temperature ¹H and ³¹P n.m.r. spectra of *cis*-[Os(CHO)(CO)(dppm)₂][BEt₄] have been obtained.

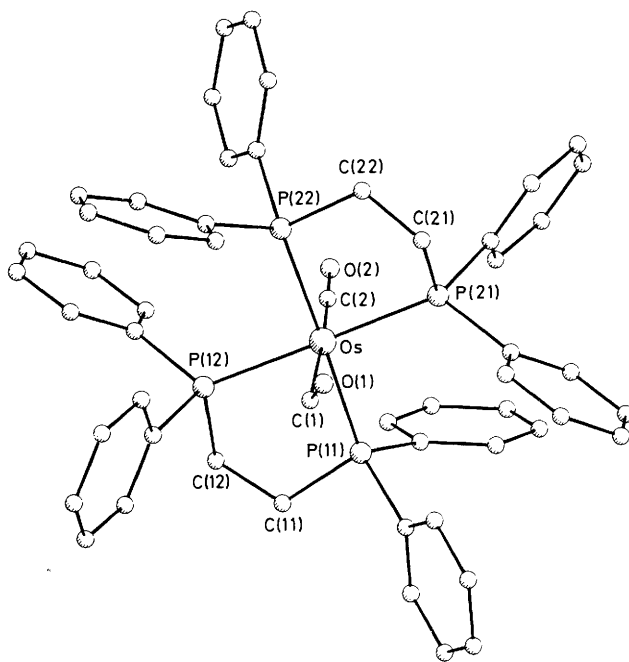When a mixture of *cis*- and *trans*-[Os(CHO)(CO)(dppm)₂]-

Figure. Solid-state structure and numbering scheme for *trans*-[Os(CHO)(CO)(dppe)₂][SbF₆]·CH₂Cl₂

[SbF₆] in CH₂Cl₂ is treated with Li[BHEt₃] (1.5 equiv.) at −30 °C, in addition to *cis*-[Os(CHO)(CO)(dppm)₂]⁺, ³¹P n.m.r. studies on the crude reaction solution show the presence of two other complexes. One of these gives rise to a singlet at δ − 46.5 p.p.m. which is tentatively assigned to *trans*-[Os(CHO)-(CO)(dppm)₂]⁺. The other shows two partially resolved multiplets at δ +0.6 and −25.9 p.p.m. which are characteristic of an AA′XX′ type spin system, and is tentatively assigned to the osmium diformyl complex *cis*-[Os(CHO)₂(dppm)₂]. This assignment is supported by two further observations: (1) further addition of hydride to the reaction mixture results in a slight increase in intensity of the AA′XX′ signals, together with a decrease in the intensity of the monoformyl resonances; and (2) the complex is also formed when a solution of pure *cis*-[Os(CHO)(CO)(dppm)₂]⁺ is treated with hydride. It has so far proved impossible to isolate this complex even though it is present in concentrations of *ca.* 30% (n.m.r. evidence). When the reaction is performed on a preparative scale the *cis*-monoformyl species is the only complex isolated and it is therefore possible that the diformyl is only present in equilibrium with the monoformyl when there is an excess of hydride present. If the above assignment as a diformyl is correct, it would represent the first neutral diformyl complex synthesised, since the few diformyl complexes so far reported have all been anionic, *e.g.* [Re(CHO)₂(η-C₅H₅)(NO)]⁻,[15,16] [Re(CHO)₂(CO)₃(PPh₃)]⁻,[15] and [Ir₄(CXO)₂(CO)₁₀]²⁻ (X = H or D).[8]

X-*Ray Structure of* *trans*-[Os(CHO)(CO)(dppe)₂][SbF₆]·CH₂Cl₂.—The greater stability of *trans*-[Os(CHO)(CO)-(dppe)₂][SbF₆] compared with its ruthenium analogue meant that crystals could be grown slowly at low temperature (−30 °C) and thus high-quality crystals for X-ray crystallography were obtained.

The cation is isostructural with its ruthenium analogue, and clearly shows (Figure 1) the presence of mutually *trans* carbonyl and formyl groups, the two being easily distinguished by an Os–C–O angle of 130.7° for the formyl ligand similar to those reported for other metal formyl complexes.[1,17-19] The formyl

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* The [BEt₄]⁻ is present as an impurity in commercial Li[BHEt₃] and its salt crystallises preferentially.[1]

Table 1. Selected bond lengths (Å) and angles for [Os(CHO)(CO)-(dppe)$_2$][SbF$_6$]·CH$_2$Cl$_2$

Os–P(11)	2.380(11)	Os–P(12)	2.414(11)
Os–P(21)	2.389(11)	Os–P(22)	2.429(11)
Os–C(1)	2.155(28)	Os–C(2)	1.983(32)
C(1)–O(1)	1.181(35)	C(2)–O(2)	1.096(35)
C(11)–C(12)	1.486(52)	C(21)–C(22)	1.468(64)
P–C(Ph)	1.820(mean)	P–C(CH$_2$)	1.873(mean)
P(11)–Os–P(12)	82.1(4)	P(21)–Os–P(22)	81.6(4)
P(11)–Os–C(1)	87.2(9)	P(11)–Os–C(2)	87.2(10)
P(21)–Os–C(1)	91.2(8)	P(21)–Os–C(2)	95.2(10)
P(12)–Os–C(1)	86.0(9)	P(12)–Os–C(2)	87.7(10)
P(22)–Os–C(1)	92.4(9)	P(22)–Os–C(2)	93.1(10)
Os–C(1)–O(1)	130.7(27)	Os–C(2)–O(2)	173.0(28)
C(1)–Os–C(2)	172.1(11)		

Table 2. I.r. and ^{31}P n.m.r. data[a] for some osmium carbonyl complexes

		^{31}P N.m.r.	
Complex	$\tilde{v}$(C≡O)/cm^{-1}	P_{trans}	P_{cis}
cis-[Os(CO)$_2$(dppm)$_2$][SbF$_6$]$_2$	2 083, 2 042	−56.5 (t)[b]	68.8 (t)[b]
trans-[Os(CO)$_2$(dppm)$_2$][SbF$_6$]$_2$	2 033	−57.3 (s)	
trans-[Os(CO)$_2$(dppe)$_2$][SbF$_6$]$_2$	2 028	10.3 (s)	
trans-[OsCl(CO)(dppm)$_2$][SbF$_6$]	1 962	−52.0 (s)	
trans-[OsCl(CO)(dppe)$_2$][SbF$_6$]	1 936	12.1 (s)	
trans-[OsH(CO)(dppe)$_2$][SbF$_6$]		30.4 (s)	
cis-[OsH(CO)(dppm)$_2$][SbF$_6$]	1 940		

[a] In CH$_2$Cl$_2$ at room temperature; δ in p.p.m. to high frequency of external 85% H$_3$PO$_4$. [b] *J*(PP) = 24.4 Hz.

Selected bond lengths and angles of *trans*-[Os(CHO)(CO)-(dppe)$_2$][SbF$_6$]·CH$_2$Cl$_2$ are given in Table 1.

Spectroscopic Properties of the Formyl Complexes.—The spectroscopic properties of the formyl complexes appear in Table 3 and confirm their identity as true formyl compounds. In general, the spectra are similar to those of their ruthenium counterparts. However, the presence[1] of two bands in the region around 2 700 cm^{-1} in the i.r. spectrum of *cis*-[Ru(CHO)(CO)(dppm)$_2$]$^+$, attributed to Fermi resonance between v(C–H) and 2δ(C–H)† is not observed for any of the osmium complexes, apparently because these absorptions are sufficiently well separated for intensity stealing by 2δ(C–H) to be insignificant. For *cis*-[Os(CDO)(CO)(dppm)$_2$]$^+$ v(C–D) is also not observed. Calculations assuming[1] v(C–H)/v(C–D) = 1.33 suggest that v(C–D) should be at 1 959 cm^{-1} and hence should be obscured by v(C≡O) at 1 958 cm^{-1}. Finally, the formyl v(C=O) of *cis*-[Os(CDO)(CO)(dppm)$_2$][SbF$_6$] is somewhat unusual as it shows four peaks in the solid state. Since one broad band is observed in solution, we attribute this fine structure to solid-state effects.

Stability and Decomposition Reactions of the Formyl Complexes.—As expected on the basis of crystal field stabilisation energy arguments and hence the generally much lower substitution lability of osmium complexes than of ruthenium ones, the osmium formyl complexes are very much more kinetically stable than their ruthenium counterparts.[3] However, their stability is highly dependent upon their purity. Thus, a pure sample of *trans*-[Os(CHO)(CO)(dppe)$_2$][SbF$_6$] in dichloromethane is indefinitely stable (> 2 weeks) at room

Table 3. I.r. and ^{1}H n.m.r. data for some osmium formyl complexes

	I.r.				^{1}H, CHO	
Complex	v(C–H)	v(C≡O)	v(C=O)	δ(C–H)	δ	*J*(PH)/Hz
trans-[Os(CHO)(CO)(dppe)$_2$][SbF$_6$]·CH$_2$Cl$_2$	2 558w	1 965, 1 960s[a]	1 588s	1 379[b]	14.45 (q)	4.9
trans-[Os(CHO)(CO)(dppe)$_2$][BEt$_4$]	2 559w	1 955s	1 593s			
trans-[Os(CDO)(CO)(dppe)$_2$][SbF$_6$]	1 922w[c]	1 965, 1 960s[a]	1 589s	1 053m[d]	14.4 (br)	
trans-[Os(CHO)(CO)(dppe)$_2$][SbF$_6$]·thf	2 609w	1 963s, 1 938m	1 575m[e]			
cis-[Os(CHO)(CO)(dppm)$_2$][SbF$_6$]	2 605w	1 960vs	1 588s	1 367w[f]		
cis-[Os(CHO)(CO)(dppm)$_2$][BEt$_4$]	2 599w	1 975vs	1 593s		14.66 (dd)	35[g]
cis-[Os(CDO)(CO)(dppm)$_2$][SbF$_6$]	1 959[h]	1 958vs	1 597s	1 046m[d]		

[a] 1 970 cm^{-1} in CH$_2$Cl$_2$. [b] Calculated assuming δ(C–H)/δ(C–D) = 1.31 (not identified in spectrum). [c] v(C–D). [d] δ(C–D). [e] Additional shoulders are observed at 1 590m, 1 578m, 1 570m, and 1 560 cm^{-1}. [f] Tentative assignment. [g] *J*(HP)*trans*, *J*(HP)*cis* = 12 Hz. [h] Calculated value based on v(C–H)/v(C–D) = 1.33.

C=O bond length [1.181(35) Å] is somewhat shorter than those observed for other formyls with the exception of [Rh(oep)-(CHO)] (oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate), which is unusual in many ways, including its preparation by insertion of CO into a rhodium–hydrogen bond.[17]

Similar to the ruthenium cation, the observed short C=O bond length is assumed* to arise from a lesser contribution from an oxycarbene resonance form which places a positive charge on the metal. Consistent with this, the Os–C bond length [2.155(28) Å] is comparable with those observed for Os–C single bonds (2.15 Å)[20] but much longer than Os=C as found in [Os(CO)$_2$(CC$_6$H$_5$Me)(PPh$_3$)$_2$] (1.90 Å).[21] This contrasts with the M–C bond length of, *e.g.*, [Re(CHO)(η-C$_5$H$_5$)(NO)(PPh$_3$)] which is closer to the value found for Re=C in carbene complexes.[7,18]

temperature and under an atmosphere of nitrogen. Furthermore, only 60% conversion (i.r. and ^{31}P n.m.r. evidence) into *trans*-[OsCl(CO)(dppe)$_2$]$^+$ is observed on refluxing *trans*-[Os-(CHO)(CO)(dppe)$_2$]$^+$ in CHCl$_3$ under nitrogen for 5 d, the remaining 40% being mostly unchanged formyl complex.

A crude sample of *trans*-[Os(CHO)(CO)(dppe)$_2$][SbF$_6$] (unrecrystallised) totally decomposed over a period of 24 h. The major complex isolated from these decomposed solutions was *trans*-[OsCl(CO)(dppe)$_2$]$^+$ plus traces of a complex believed to be *trans*-[OsH(CO)(dppe)$_2$]$^+$. However, since treatment of *trans*-[Os(CHO)(CO)(dppe)$_2$]$^+$ in CH$_2$Cl$_2$ with Li[BHEt$_3$]–thf or K[BH(OPr^i)$_3$]–thf leads to almost total conversion into *trans*-[OsCl(CO)(dppe)$_2$]$^+$ (90%), it seems likely that the complex formed from decomposition of the crude formyl is a result of borohydride residues interacting with the solvent and metal complex rather than the formyl reacting directly with the

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* It should be noted, however, that the high thermal parameter of the formyl oxygen atom may also be responsible for the observed short C–O bond length.

† v(C–H)′, v(C–D)′, δ(C–H)′ and δ(C–D) refer to the formyl C–H (C–D) bond.

solvent (although this does occur under certain conditions, see below). Similar effects of borohydride residues have been noted in decomposition studies of other metal formyls.[7] Refluxing the formyl in thf results in the precipitation of a pale yellow complex that has the spectral properties of trans-[Os(CHO)-(CO)(dppe)$_2$]$^+$ synthesised in thf. Remaining in solution is a further amount of this complex, plus a small amount (ca. 5%) of the chlorocarbonyl complex. Although surprising at first, the chlorocarbonyl must arise from reaction of the formyl complex with the CH$_2$Cl$_2$ solvent of crystallisation present in the initial solid. When a solid sample of the formyl is stored under nitrogen and exposed to strong sunlight for several days the colour of the bright yellow crystals darkens, and i.r. and ^{31}P n.m.r. spectra of the solid show significant conversion (ca. 55%) into trans-[OsCl(CO)(dppe)$_2$]$^+$. Again, this must be due to Cl abstraction from the CH$_2$Cl$_2$ solvent of crystallisation, which in this case presumably goes via a free-radical mechanism initiated by light. The products of these reactions have not been isolated in a pure form, but have been fully characterised spectroscopically (see Tables and Experimental section).

Solutions of cis-[Os(CHO)(CO)(dppm)$_2$]$^+$ made in situ by the addition of K[BH(OPr^i)$_3$]–thf or Li[BHEt$_3$]–thf to cis-[Os(CO)$_2$(dppm)$_2$][SbF$_6$]$_2$ in CH$_2$Cl$_2$ are stable at room temperature for a period of up to 24 h (n.m.r. evidence) whereas the isolated formyl complexes rapidly decompose on addition of solvent (CH$_2$Cl$_2$ or thf), even at low temperature (-30 °C). Stirring a suspension of cis-[Os(CHO)(CO)(dppm)$_2$]$^+$ in CH$_2$Cl$_2$ at room temperature for 5 d results in total decomposition to give almost exclusively (> 90%) trans-[OsCl(CO)(dppm)$_2$]$^+$. Attempts to isolate pure samples of the minor products, in a sufficient amount, have so far proven unsuccessful but spectroscopic studies (hydride resonance) show that one is cis-[OsH(CO)(dppm)$_2$][SbF$_6$]. Another of the minor decomposition products of cis-[Os(CHO)(CO)-(dppm)$_2$][SbF$_6$] has two v(C≡O) at 2 052 and 1 992 cm^{-1} in its
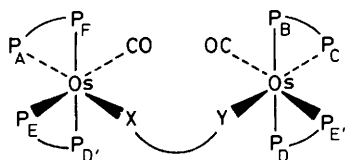
i.r. spectrum and a complex ^{31}P n.m.r. spectrum which can be analysed as having resonances from eight different phosphorus atoms. The complex is clearly a dimer with an unsymmetrical bridge. The chemical shift of P$_A$ is considerably higher than that of P$_C$, hence X must have a low trans influence[22,23] and is possibly an O donor. It is tempting to formulate this compound as a dimeric metallo-ester complex (X–Y = $-O-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-$) similar to those obtained in decomposition reactions of rhenium formyls.[15] However, since no v(C=O) between 1 500 and 1 700 cm^{-1} is observed in the i.r. spectrum, and since the ^{1}H n.m.r. spectrum is uninformative, the exact nature of this bridging species is unknown.

Experimental

Microanalyses were by Elemental Microanalysis Ltd. Infrared spectra were recorded on Nujol mulls between CsI plates on a Perkin-Elmer 577 grating spectrometer and ^{1}H n.m.r. spectra on a Perkin-Elmer R34 220-MHz spectrometer; chemical shifts are relative to SiMe$_4$. Phosphorus-31 and ^{1}H n.m.r. spectra were recorded at ambient temperature in CH$_2$Cl$_2$–CD$_2$Cl$_2$(5:1) on a JOEL FX90Q spectrometer (City of London Polytechnic), or a Bruker WM 250 multinuclear spectrometer (University of

Liverpool) operating in the Fourier-transform mode with proton noise decoupling (^{31}P). Fast atom bombardment (f.a.b.) mass spectra were recorded on glycerol suspensions on a modified MM9 mass spectrometer (ICI Pharmaceuticals Division). All solvents were dried before use by (a) distillation from sodium diphenylketyl [diethyl ether, tetrahydrofuran, and light petroleum (b.p. 40—60 °C)], (b) distillation from calcium hydride (dichloromethane), or (c) standing over molecular sieves (nitromethane). They were thoroughly degassed prior to use, and manipulations were carried out under an atmosphere of nitrogen using standard Schlenk-line and catheter-tubing techniques. All preparations and purifications of formyl complexes were performed at -35 ± 5 °C in a methanol–solid CO$_2$ bath.

Lithium triethylhydroborate, Li[BHEt$_3$], and potassium hydrotri(isopropoxy)borate, K[BH(OPr^i)$_3$], were purchased from Aldrich Chemicals as 1 mol dm^{-3} solutions in thf and were stored under nitrogen prior to use. The complexes cis- and trans-[OsCl$_2$(P–P)$_2$] were prepared by standard literature methods.[24]

cis-Bis[bis(diphenylphosphino)methane]dicarbonylosmium(II) Hexafluoroantimonate.—(a) The salt AgSbF$_6$ (1.03 g, 3.0 mmol) was added to a carbon monoxide saturated solution of cis-[OsCl$_2$(dppm)$_2$] (1.4 g, 1.36 mmol) in dichloromethane (80 cm^3). The solution was pressurised to 3 atm (ca. 3.0 × 10^5 Pa) with carbon monoxide in a Fisher–Porter bottle and stirred at 60 °C for 48 h. The resulting pale suspension was filtered to remove AgCl. The AgCl was washed with CH$_2$Cl$_2$ (2 × 5 cm^3) and the washings combined with the mother-liquors. After evaporation to half volume, diethyl ether was added until incipient crystallisation and the solution cooled. The white microcrystals were collected and recrystallised from CH$_2$Cl$_2$–diethyl ether. Yield 1.4 g, 70% (Found: C, 41.3; H, 3.1; P, 8.0. C$_{52}$H$_{44}$F$_{12}$O$_2$OsP$_4$Sb$_2$ requires C, 42.0; H, 3.0; P, 8.3%).

(b) As in (a) above but using trans-[OsCl$_2$(dppm)$_2$] (1.4 g, 1.36 mmol) and AgSbF$_6$ (1.45 g, 4.2 mmol) at 80 °C. The reaction proceeded via a turquoise intermediate and gave 1.27 g (63%) of product contaminated with ca. 3% (^{31}P n.m.r. evidence) trans-[Os(CO)$_2$(dppm)$_2$][SbF$_6$]$_2$. Silver metal deposited along with AgCl during the reaction.

trans-Bis[1,2-bis(diphenylphosphino)ethane]dicarbonyl-osmium(II) Hexafluoroantimonate.—This was prepared as in (b) above from trans-[OsCl$_2$(dppe)$_2$] (1.4 g, 1.33 mmol) and AgSbF$_6$ (1.41 g, 4.11 mmol) as white microcrystals (1.49 g, 74%) (Found: C, 42.1; H, 2.9; P, 7.9. C$_{54}$H$_{48}$F$_{12}$O$_2$OsP$_4$Sb$_2$ requires C, 42.8; H, 3.1; P, 8.2%).

Bis[1,2-bis(diphenylphosphino)ethane]dichloro-osmium(III) Hexafluoroantimonate–Dichloromethane (1/1).—This was prepared as immediately above, but omitting the carbon monoxide. Silver metal was precipitated and the complex was isolated as green microcrystals. Yield ca. 60% (Found: C, 44.0; H, 3.7; Cl, 10.3; P, 8.4. C$_{53}$H$_{50}$Cl$_4$F$_6$OsP$_4$Sb requires C, 46.1, H, 3.6; Cl, 10.3; P, 9.0%). All ^{31}P n.m.r. signals were broad.

trans-Bis[1,2-bis(diphenylphosphino)ethane]carbonylformyl-osmium(II) Hexafluoroantimonate–Dichloromethane (1/1).—(a) To a solution of trans-[Os(CO)$_2$(dppe)$_2$][SbF$_6$]$_2$ (0.60 g, 0.4 mmol) in CH$_2$Cl$_2$ (30 cm^3) at -35 °C was added K[BH(OPr^i)$_3$] in thf (0.8 cm^3, 0.8 mmol) and the solution stirred for 4 h. The black solution was filtered into diethyl ether (200 cm^3) pre-cooled to -35 °C and allowed to stand at -30 °C for 16 h. The resulting pale brown solid was collected and dried in vacuo. Analytically pure samples of the complex were obtained by dissolving the crude material in CH$_2$Cl$_2$ (20

cm^3) at −35 °C, filtering, adding diethyl ether pre-cooled to −35 °C to the filtrate until incipient crystallisation, and allowing the resulting solution to stand at −30 °C for several days. The bright yellow oval-shaped crystals were collected and dried in vacuo. Yield 0.23 g (42%) (Found: C, 47.8; H, 3.7; Cl, 5.6; P, 9.0. $C_{55}H_{51}Cl_2F_6O_2OsP_4Sb$ requires C, 48.4; H, 3.7; Cl, 5.2; P, 9.1%). N.m.r.: ^{1}H, δ 5.32 (s) (CH_2Cl_2); 14.45 (q), J = 4.9 Hz (CHO). ^{31}P, δ 17.85 (s).

trans-Bis[1,2-bis(diphenylphosphino)ethane]carbonylformyl-osmium(II) Tetraethylborate–Dichloromethane (1/1).—As above but using Li[BHEt$_3$]–thf (1.4 cm^3, 1.0 mol dm^{-3}, 1.4 mmol). Yield of the dark yellow complex: 0.17 g (34%).

trans-Bis[1,2-bis(diphenylphosphino)ethane]carbonyl-(deuterioformyl)osmium(II) Hexafluoroantimonate–Dichloromethane (1/1).—As for trans-[Os(CHO)(CO)(dppe)$_2$][SbF$_6$]·CH$_2$Cl$_2$ but using Li[BDEt$_3$]–thf (0.8 cm^3, 1.0 mol dm^{-3}, 0.80 mmol) and stirring for 16 h. Yield of the bright yellow complex: 0.2 g (37%).

trans-Bis[1,2-bis(diphenylphosphino)ethane]carbonylformyl-osmium(II) Hexafluoroantimonate–Tetrahydrofuran (1/1).—(a) The complex was prepared as for trans-[Os(CHO)(CO)-(dppe)$_2$][SbF$_6$]·CH$_2$Cl$_2$ from trans-[Os(CO)$_2$(dppe)$_2$][SbF$_6$]$_2$ (0.55 g, 0.36 mmol) and K[BH(OPr^i)$_3$]–thf (0.7 cm^3, 1.0 mol dm^{-3}, 0.7 mmol) in thf (50 cm^3) to give the pale brown impure complex (0.31 g, 64%). ^{31}P N.m.r.: δ 17.85 (s).

(b) As in (a) but using NaBH$_4$ (0.03 g, 0.72 mmol).

(c) As in (a) but using KH (0.3 g, 50% in mineral oil, 3.6 mmol). The product consisted mainly of unreacted starting material containing the required complex (40%, i.r. evidence).

cis-Bis[bis(diphenylphosphino)methane]carbonylformyl-osmium(II) Hexafluoroantimonate.—To a solution of cis-[Os(CO)$_2$(dppm)$_2$][SbF$_6$]$_2$ (0.56 g, 0.38 mmol) in CH$_2$Cl$_2$ (50 cm^3) at −35 °C, K[BH(OPr^i)$_3$]–thf (0.8 cm^3, 1.0 mol dm^{-3}, 0.8 mmol) was added, and the solution stirred for 6 h. The resultant black solution was then filtered, diethyl ether (at −35 °C) was added to the pale brown filtrate until incipient precipitation, and the solution left to stand at −30 °C for several days. The white, air-stable complex was then collected and dried in vacuo (0.18 g, 38%). Similar to the analogous ruthenium complex,[1] analytical figures suggested contamination with LiSbF$_6$ and/or boron-containing residues. A further crop of the formyl complex could be obtained from the black residue of the reaction mixture, by washing with light petroleum (3 × 20 cm^3) and drying in vacuo. Yield of the grey, impure complex: 0.08 g (17%).

cis-Bis[bis(diphenylphosphino)methane]carbonylformyl-osmium(II) Tetraethylborate.—The complex was prepared as above, but using Li[BHEt$_3$]–thf (1.5 cm^3, 1.0 mol dm^{-3}, 1.5 mmol) as the hydride source. Work up of the resultant dark brown solution as above yielded the complex as white microcrystals (0.21 g, 51%) with no precipitation of formyl from the reaction mixture. N.m.r.: ^{1}H (CD$_2$Cl$_2$, −35 °C), δ 0.73 (tq, 1:1:1:1), J(HB) = 3, J(HH) = 7 (CH$_3$CH$_2$B); −0.03 (qq,

X = H or CHO

1:1:1:1), J(HB) = 4.5 (CH$_3$CH$_2$B); 14.66, J(HP$_D$) = 35, J(HP) = 12 Hz (CHO); ^{31}P (−35 °C), δ −44.4 (ddd, P$_A$), −52.5 (dd, P$_B$), 53.8 (ddd, P$_C$), and −58.9 (dd, P$_D$); J(P$_A$P$_B$) = 197, J (P$_A$P$_C$) = 40, J(P$_A$P$_D$) = 19, J(P$_B$P$_C$) = 26.7, J(P$_B$P$_D$) = 0, and J(P$_C$P$_D$) = 15 Hz; ^{11}B, δ − 16.1 (s).

cis-Bis[bis(diphenylphosphino)methane]carbonyl(deuterio-formyl)osmium(II) Hexafluoroantimonate.—The complex was prepared as for cis-[Os(CHO)(CO)(dppm)$_2$][SbF$_6$] but using Li[BDEt$_3$]–thf (0.8 cm^3, 1.0 mol dm^{-3}, 0.8 mmol) over a period of 16 h. Total yield of the complex: 0.25 g (53%).

^{31}P N.M.R. Studies.—(a) Of the reaction of cis-[Os(CO)$_2$-(dppm)$_2$][SbF$_6$]$_2$ with Li[BHEt$_3$]. To a solution of cis-[Os(CO)$_2$(dppm)$_2$][SbF$_6$]$_2$ (0.1 g, 0.07 mmol) in dichloromethane (2 cm^3) containing CD$_2$Cl$_2$ (0.5 cm^3) at −30 °C was added Li[BHEt$_3$] (0.1 cm^3, 0.1 mmol) and the ^{31}P n.m.r. spectrum was measured immediately. This showed resonances attributable to cis-[Os(CHO)(CO)(dppm)$_2$]$^+$, trans-[Os-(CHO)(CO)(dppm)$_2$]$^+$, and the AA'XX' resonances of cis-[Os(CHO)$_2$(dppm)$_2$] [δ +0.6 and −25.9, J(PP) = 39, J(PP') = 32 Hz]. Addition of more K[BH(OPr^i)$_3$] (0.1 cm^3) to this solution after warming to room temperature caused an increase in the intensity of the signals attributable to cis-[Os(CHO)$_2$-(dppm)$_2$], loss of the signals of [Os(CHO)(CO)(dppm)$_2$]$^+$, and the appearance of other signals from decomposition products.

(b) Of the reaction of cis-[Os(CHO)(CO)(dppm)$_2$][BEt$_4$] with Li[BHEt$_3$]. A sample of cis-[Os(CHO)(CO)(dppm)$_2$]-[BEt$_4$] (0.08 g, 0.07 mmol) was suspended in CH$_2$Cl$_2$ (2 cm^3) containing CD$_2$Cl$_2$ (0.5 cm^3) at −35 °C. The ^{31}P n.m.r. spectrum showed only resonances from cis-[Os(CHO)(CO)-(dppm)$_2$]$^+$. The salt Li[BHEt$_3$] (0.1 cm^3, 0.1 mmol) was then added and the ^{31}P n.m.r. spectrum recorded at −30 °C. The resonances from the starting material were replaced by those attributed to cis-[Os(CHO)$_2$(dppm)$_2$] and some decomposition products.

Decomposition Studies of Osmium Formyl Complexes.—(a) Preparation of trans-bis[1,2-bis(diphenylphosphino)ethane]car-bonylchloro-osmium(II) hexafluoroantimonate–dichloromethane (1/1). A solution of unrecrystallised trans-[Os(CXO)(CO)-(dppe)$_2$][SbF$_6$] (X = H or D) in CH$_2$Cl$_2$ was stirred for 48 h at room temperature. Filtration of the black solution followed by addition of diethyl ether to the pale filtrate gave the product as a pale brown powder. Recrystallisation of the solid from CH$_2$Cl$_2$–diethyl ether afforded the complex as an off-white crystalline solid, contaminated with trans-[OsX(CO)(dppe)$_2$]$^+$ (X = H or D) [n.m.r.: ^{1}H, (CDCl$_3$) δ −8.1 (q), J(PH) =19.0 Hz; ^{2}D, δ −7.95 (br m)]. It has not been possible to obtain a pure sample of the chlorocarbonyl complex, but the assignment was confirmed by f.a.b. mass spectroscopy: m/e 1 051, M$^+$; 1 016, M$^+$ − Cl; 998, M$^+$ − (Cl, CO). The peaks show typical Os and Cl isotope patterns; masses were calculated using ^{192}Os and ^{35}Cl as the most abundant isotopes.

An alternative method of preparation was to reflux a CHCl$_3$ solution of pure trans-[Os(CHO)(CO)(dppe)$_2$][SbF$_6$] (0.2 g, 0.15 mmol) for 5 d under an atmosphere of nitrogen. Filtration of the resultant pale yellow solution, addition of diethyl ether until incipient precipitation, followed by standing at −30 °C for 16 h afforded the complex as cream coloured crystals (0.04 g, 20%) contaminated with unreacted formyl complex.

(b) Preparation of trans-bis[bis(diphenylphosphino)methane]-carbonylchloro-osmium(II) hexafluoroantimonate–dichloro-methane (1/1). A suspension of cis-[Os(CHO)(CO)(dppm)$_2$]-[SbF$_6$] (0.35 g, 0.28 mmol) in CH$_2$Cl$_2$ (50 cm^3) was stirred for 7 d. The solution was then filtered, diethyl ether added until incipient precipitation, and the solution allowed to stand at −30 °C for 48 h. The resultant crystalline solid was collected
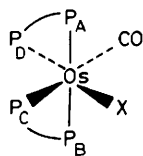
Table 4. Atom co-ordinates ($\times 10^4$) for [Os(CHO)(CO)(dppe)$_2$][SbF$_6$]·CH$_2$Cl$_2$

Atom	x	y	z	Atom	x	y	z
Os	1 678	2 500	2 446(1)	C(214)	2 330(12)	−315(14)	2 586(20)
P(11)	1 238(4)	1 887(5)	957(8)	C(215)	2 445(12)	361(14)	2 486(20)
P(12)	944(4)	3 309(5)	1 880(8)	C(216)	2 215(12)	802(14)	3 274(20)
C(11)	651(16)	2 365(17)	298(31)	C(221)	3 114(9)	1 672(12)	2 536(24)
C(12)	691(19)	3 098(20)	382(37)	C(222)	3 193(9)	1 742(12)	1 383(24)
C(111)	826(10)	1 114(9)	1 117(18)	C(223)	3 759(9)	1 659(12)	912(24)
C(112)	822(10)	744(9)	2 103(18)	C(224)	4 246(9)	1 506(12)	1 594(24)
C(113)	497(10)	155(9)	2 158(18)	C(225)	4 168(9)	1 436(12)	2 747(24)
C(114)	176(10)	−63(9)	1 227(18)	C(226)	3 602(9)	1 519(12)	3 218(24)
C(115)	179(10)	307(9)	241(18)	C(231)	1 658(12)	3 577(13)	4 985(22)
C(116)	504(10)	896(9)	186(18)	C(232)	1 576(12)	4 257(13)	4 857(22)
C(121)	1 754(10)	1 669(14)	−145(20)	C(233)	1 244(12)	4 610(13)	5 645(22)
C(122)	1 907(10)	2 165(14)	−906(20)	C(234)	995(12)	4 283(13)	6 563(22)
C(123)	2 348(10)	2 050(14)	−1 707(20)	C(235)	1 078(12)	3 603(13)	6 691(22)
C(124)	2 638(10)	1 439(14)	−1 749(20)	C(236)	1 409(12)	3 250(13)	5 902(22)
C(125)	2 486(10)	943(14)	−988(20)	C(241)	2 645(10)	3 790(11)	3 719(22)
C(126)	2 044(10)	1 058(14)	−186(20)	C(242)	3 084(10)	3 912(11)	4 524(22)
C(131)	234(8)	3 317(11)	2 663(17)	C(243)	3 521(10)	4 391(11)	4 328(22)
C(132)	−317(8)	3 273(11)	2 121(17)	C(244)	3 519(10)	4 747(11)	3 328(22)
C(133)	−845(8)	3 298(11)	2 741(17)	C(245)	3 080(10)	4 625(11)	2 523(22)
C(134)	−822(8)	3 365(11)	3 903(17)	C(246)	2 643(10)	4 146(11)	2 719(22)
C(135)	−271(8)	3 409(11)	4 445(17)	C(1)	988(12)	2 103(14)	3 511(23)
C(136)	257(8)	3 384(11)	3 825(17)	O(1)	1 007(16)	1 915(18)	4 446(24)
C(141)	1 133(12)	4 183(9)	1 664(22)	C(2)	2 224(13)	2 888(16)	1 314(24)
C(142)	895(12)	4 665(9)	2 371(22)	O(2)	2 559(12)	3 124(13)	775(22)
C(143)	1 018(12)	5 332(9)	2 178(22)	Sb	−803(1)	2 696(2)	8 038(2)
C(144)	1 379(12)	5 517(9)	1 278(22)	F(1)	−45(17)	2 436(24)	7 956(28)
C(145)	1 618(12)	5 035(9)	571(22)	F(2)	−872(20)	2 326(23)	6 709(33)
C(146)	1 495(12)	4 367(9)	764(22)	F(3)	−683(17)	3 125(18)	9 258(31)
P(21)	2 380(4)	1 703(5)	3 120(8)	F(4)	−1 515(20)	3 009(22)	8 091(36)
P(22)	2 105(4)	3 146(4)	3 963(8)	F(5)	−695(20)	3 374(23)	7 144(39)
C(21)	2 464(20)	1 839(22)	4 670(35)	F(6)	−1 227(29)	2 124(35)	8 570(58)
C(22)	2 581(16)	2 552(27)	4 776(28)	C(3)	395(29)	1 254(33)	6 350(50)
C(211)	1 869(12)	568(14)	4 162(20)	Cl(1)	1 039(8)	1 351(9)	6 996(15)
C(212)	1 754(12)	−108(14)	4 262(20)	Cl(2)	291(9)	449(10)	5 812(16)
C(213)	1 984(12)	−550(14)	3 474(20)				

and recrystallised from CH$_2$Cl$_2$–diethyl ether to give the complex as gold coloured crystals (0.21 g, 56%) (Found: 46.6; H, 3.4; Cl, 7.6; P, 9.2. C$_{52}$H$_{46}$Cl$_3$F$_6$OOsP$_4$Sb requires C, 46.5; H, 3.4; Cl, 7.9; P, 9.2%).

Addition of diethyl ether until incipient precipitation, followed by cooling, to the filtrate obtained when the above chlorocarbonyl complex was first collected, gave a mixture of trans-[OsCl(CO)(dppm)$_2$][SbF$_6$] and cis-[OsH(CO)(dppm)$_2$]-[SbF$_6$]. ^{1}H N.m.r. (CD$_2$Cl$_2$): δ −8.7 (ddt), J(HP$_A$) = 12.5, J(HP$_B$) = 12.5, J(HP$_C$) = 21, and J(HP$_D$) = 51 Hz {cis-[OsH(CO)(dppm)$_2$][SbF$_6$], see p. 391 for assignments (X = H): those of J(HP$_A$) and J(HP$_B$) are arbitrary}. Total yield < 0.02 g. I.r.: v(C≡O) at 2 050m, 1 988m, 1 960m, and 1 950m cm^{-1}.

Further addition of diethyl ether, followed by cooling, to the above solution yielded an almost pure sample of the 'dimer' (p. 390) as white microcrystals. Yield < 0.015 g. I.r.: v(C≡O) at 2 052m and 1 992m cm^{-1}. ^{31}P N.m.r.: 22.63 (dd, P$_A$), 12.35 (ddd, P$_B$), −29.4 (dd, P$_C$), −41.73 (ddd, P$_D$), −42.08 (ddd, P$_D$), −60.61 (dd, P$_E$), −61.19 (dd, P$_{E'}$), and −15.97 (dt, P$_F$); J(P$_A$P$_D$) = 7.5, J(P$_A$P$_F$) = 23.2, J(P$_B$P$_C$) = 51.3, J(P$_B$P$_D$) = 224, J(P$_B$P$_E$) = 24.4, J(P$_C$P$_D$) = 8.5, J(P$_D$P$_{E'}$) = J(P$_D$P$_E$) = 24.4, J(P$_D$P$_F$) = 232, J(P$_E$P$_F$) = 23.2, and J(P$_A$P$_{E'}$) = J(P$_C$P$_{F'}$) = 0 Hz.

Crystallographic Studies.—Crystal data. [Os(CHO)(CO)-(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$][SbF$_6$]·CH$_2$Cl$_2$, M = 1 363.9, orthorhombic, a = 22.361(4), b = 20.209(2), c = 11.940(2) Å, U = 5 369 Å^3, space group $Pn2_1a$ ($\equiv Pna2_1$, no. 33), Z = 4, D_c = 1.65 cm^{-3}, μ(Mo-K_α) = 29.64 cm^{-1}, λ = 0.710 69 Å.

Data collection.[25] CAD4 diffractometer using graphite monochromated Mo-K_α radiation; ω—2θ scan mode, ω scan width = 0.85 +0.15 tanθ, ω scan speed = 1.35—6.77° min^{-1}, 1.5 < θ < 23.0°. 3 861 Unique reflections were measured of which 2 301 were observed [I > 1.5σ(I)]. The data were corrected for absorption empirically.[26]

Structure solution and refinement. Standard heavy-atom method. Only Ru, Sb, and P atoms refined anisotropically, all others were isotropic; phenyl rings were refined as idealised hexagons with C–C distances of 1.395 Å. Final R value = 0.059. Final atomic co-ordinates are given in Table 4. Programs and computers used and sources of scattering factor data were as in ref. 25.

Acknowledgements

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