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MOBILITY OF THE dppm LIGAND IN DINUCLEAR Ru–Rh COMPLEXES: FORMATION OF TRINUCLEAR $RuRh_2$ AND Ru–Rh–Cu DERIVATIVES, AND X-RAY STRUCTURE OF A NEW HETEROBIMETALLIC HYDRIDO-BRIDGED COMPLEX

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Summary

Protonation of $RuRhH_2Cl(COD)(dppm)_2$ (**1**) (COD = 1,5 cyclooctadiene, dppm = bisdiphenylphosphinomethane) with $HBF_4 \cdot Et_2O$ gives $[RuRhHCl(COD)(dppm)_2]BF_4$ (**2**), which has been shown to contain two chelating dppm ligands on ruthenium and a bridging hydride (Ru–H 2.08(7) Å; Rh–H 1.64(8) Å). Complex **2** reacts with CO to give $[RuRhHCl(CO)_3(dppm)_2]BF_4$ (**3**) containing two bridging dppm groups. Reaction of **1** with 0.5 molar equivalents of $[RhCl(COD)]_2$ at 80°C affords the trinuclear $RuRh_2H_2Cl(PhPCH_2PPh_2)(COD)_2(dppm)$ (**4**) in low yield (25%), and that with CuCl at room temperature gives $RuRhCuH_2Cl_2(COD)(dppm)_2$ (**5**) in high yield. Complex **5** is not very stable in solution and is converted into $RuCuH_2Cl(dppm)_2$ (**6**), a typical adduct between a Lewis acid and a hydride complex, which can be more easily obtained from $RuH_2(dppm)_2$ and CuCl in toluene at 80°C.

Introduction

Many studies of the synthesis of bimetallic complexes have involved the opening of the chelating bis(diphenylphosphino)methane (dppm) ligand to give a bridged species. In particular, chelated d^8 metal complexes such as $[M\text{-}\eta^2\text{-dppm}]Cl_2$ (M = Pd, Pt) or $[M(CO)(\eta^2\text{-dppm})_2]Cl$ (Rh, Ir) readily give a series of heterobimetallic complexes $M(\mu\text{-dppm})_2M'$ by this process [1–3].

This method and others allow the synthesis of heterobimetallic dppm adducts with various d^{10} metal cations, viz. Cu^I, Ag^I, Au^I, Hg^{II} and Cd^{II} as Lewis acids [1,2,4,5]. In contrast, octahedrally coordinated, bis chelated dppm d^6 metal complexes, such as *cis*- or *trans*-$RuCl_2(dppm)_2$, were considered [6] to be possibly inert with respect to the opening of the chelating ligand, especially if the metal is from the 2nd or 3rd transition series.

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In 1983, however, we showed that a typical heterobimetallic ruthenium-rhodium complex could be readily prepared by a direct reaction between $RuH_2(dppm)_2$ and $[RhCl(CO)_2]_2$ [7]. Further examples include (i) the similar preparation of $RuMo(CO)_6(dppm)_2$ [8], (ii) again starting from $RuCl_2(dppm)_2$, the more elaborate synthesis of a monobridging dppm species $Ru(CO)_2dppm(\mu\text{-dppm})AgYX_2$ [9]; and (iii) the more recent synthesis from $OsCl_2(dppm)_2$ of a series of $RhOs(\mu\text{-CO})_2(\mu\text{-dppm})_2XY_2$ compounds [6].

We recently showed that reactive heterobimetallic ruthenium-rhodium complexes could be readily prepared by the direct reaction between $RuH_2(dppm)_2$ and $[RhCl(COD)]_2$ [10]. The observation that dppm in these systems is a dynamic ligand [10,11], able to undergo facile ring opening reactions, prompted us to find out which factors influence this reaction and also whether hydrido trimetallic species could be made by this method.

We report below the reactions of $RuRh(H)_2Cl(\mu\text{-dppm})(dppm)(COD)$ (**1**) with Brønsted and Lewis acids, CuCl and excess $[RhCl(COD)]_2$. The results include the characterization of a heterobimetallic hydride (which may be semi-bridging) and the preparation of two trimetallic $RuRh_2$ and RuRhCu complexes. In contrast to the frequently observed opening of the chelating dppm to form bimetallic species, complex **1** can react with breaking of the ligand bridge with reformation of a chelated species. The previous scarcity of dppm bridges in bimetallic ruthenium compounds is probably related to the tendency of Ru^{II} to form chelates, and may be an important feature of the reactivity of dppm heterobimetallic compounds [12].

Results and Discussion

Reaction of $RuRhH_2Cl(\mu\text{-dppm})dppm(COD)$ with $HBF_4 \cdot Et_2O$. The reaction of $RuRhH_2Cl(\mu\text{-dppm})dppm(COD)$ (**1**) with $HBF_4 \cdot Et_2O$ at room temperature in CH_2Cl_2 takes place with a slight colour change, and recrystallization from CH_2Cl_2/Et_2O yields orange crystals analyzing for $[RuRhHCl(COD)(dppm)_2]BF_4 \cdot CH_2Cl_2$ (**2**). A band at 1610 cm^{-1} in the solid state infrared spectrum may be attributed to a bridging hydride [13]. Along with the phenyl protons of dppm at ca. δ 7 ppm the ^1H NMR spectrum shows a hydride as a doublet of doublets of quartets at δ -14.0 ppm (see Fig. 1 and Table 1 for coupling constants) which is transformed into a doublet on phosphorus decoupling (J(Rh–H) 22 Hz). The P–H coupling constants were determined by selective irradiation of the phosphorus, and show that the hydride is *trans* to one phosphorus and *cis* to the other three. In the 1.5–2.5 and 4–5 ppm region there are complex patterns for the cyclooctadiene protons and the methylene protons of dppm. The latter appear as two AB signals at δ 4.25 and 4.55 ppm (J(HH) 15 Hz), and 4.35 and 4.90 ppm (J(HH) 16 Hz) when the phosphorus are decoupled, showing the non equivalence of the two dppm ligands.

The ^{31}P NMR spectrum is first-order and shows four different phosphorus resonances at δ 12.4 (ddd, P(1)), -2.0 (ddd, P(2)), -10.6 (ddt, P(3)) and -18.9 (ddd, P(4)) ppm (See Table 2 for coupling constants). The high value of the P_2P_4 coupling constant indicates a *trans* configuration of P(2) and P(4). It is noteworthy that P(3) is the only phosphorus coupled to rhodium but with a coupling constant (5.8 Hz) which rules out a direct Rh–P bond and indicates an interaction through several bonds (see J(Rh–P) 5 Hz in **1** and J(Rh–P) 99 Hz in **4**, vide infra). Such

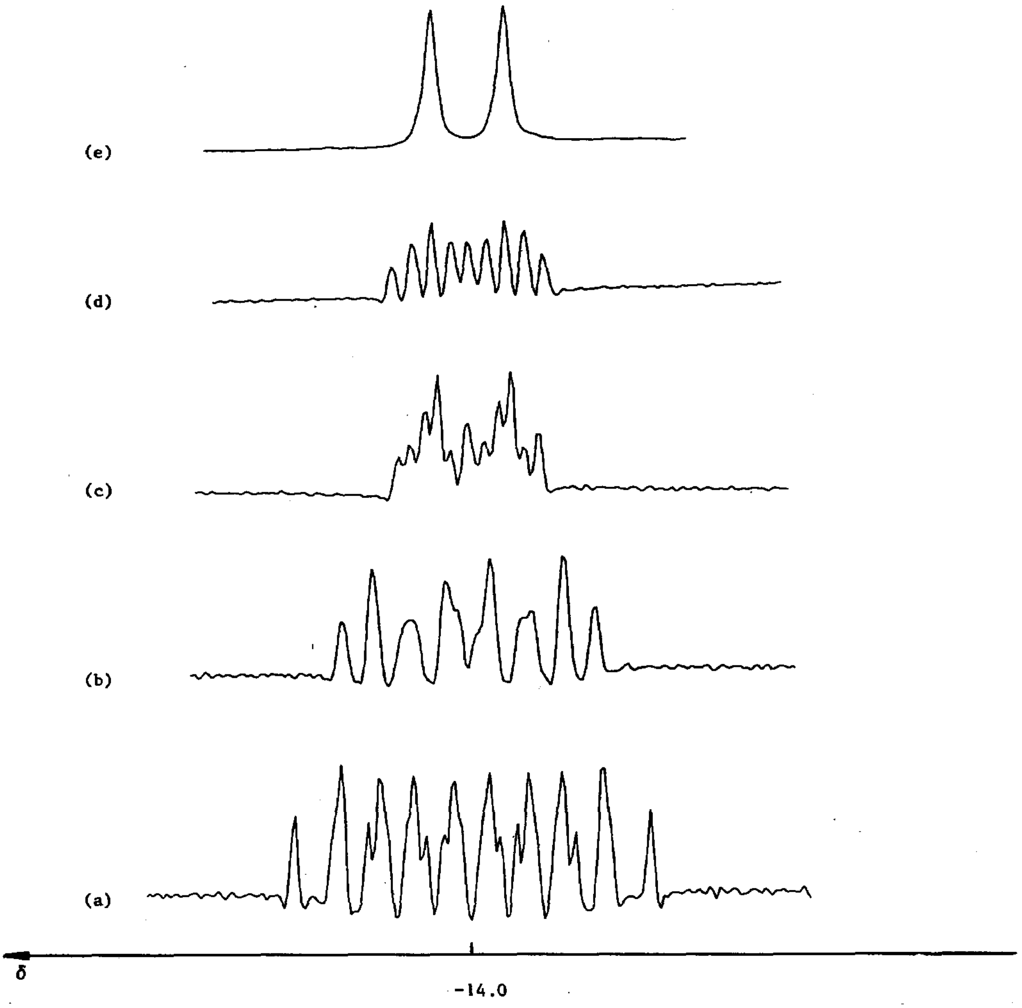


Fig. 1. Highfield ^1H NMR spectrum of **2**: (a) observed; (b) P(1) decoupled; (c) P(2)–P(3) decoupled; (d) P(4) decoupled; (e) all phosphorus decoupled.

coupling is not observed for P(1). This difference is probably related to the different ligands, hydride and chloride, in *trans* positions (see also Fig. 2) to these pair of *cis* phosphorus ligands.

The observation that all the phosphorus atoms are located on ruthenium, whereas the hydride probably occupies a bridging position seemed surprising, and led us to carry out an X-ray crystal structure determination on **2**.

The results are shown in Fig. 2 and Tables 3–5. The Ru–Rh distance (2.897(1) Å) is comparable with those for other hydrido-bridged metal–metal bonds [10], and all the other distances are in the normal range except for the two metal–hydride distances. The Rh–H bond has a length (1.64(8) Å) in the range found previously [4] for terminal Rh–H distances in $[RhHCl(dppm)_2]^+$ (1.51(7) Å), whereas the Ru–H distance (2.08(7) Å) seems to be very long and is similar to those in ruthenium complexes which involve an agostic interaction [15] (see Ru–H 2.08 Å in

TABLE 1

HIGHFIELD ^1H NMR DATA FOR THE NEW COMPLEXES (at 250 MHz) (J in Hz)

Compound	$\delta(H(1))$	$\delta(H(2))$	$^1J(H(1)P)$	$^2J(H(1)P)$	$^3J(H(1)P)$	$^4J(H(1)P)$
$RuRhHCl(COD)(dppm)_2BF_4$ (2) [c]	−14.0		13 [b]	13 [b]	41.5 [b]	13 [b]
$RuRhHCl(CO)_3(dppm)_2BF_4$ (3) [c]	−7.1		[a]	[a]	[a]	[a]
$RuRh_2H_2Cl(PhPCH_2PPh_2)$-$(COD)_2(dppm)$ (4) [d]	−10.9	−17.3	42.7	15.9	15.9	0
$RuRhCuH_2Cl(COD)(dppm)_2$ (5) [d]	−12.9	−15.6	[a]	0	32	[a]
$RuCuH_2Cl(dppm)_2$ (6) [e]	−9.1	−9.1	[a]	[a]	[a]	[a]

Compound	$J(H(1)Rh)$	$^1J(H(2)P)$	$^2J(H(2)P)$	$^3J(H(2)P)$	$^4J(H(2)P)$	$J(H(2)Rh)$
$RuRhHCl(COD)(dppm)_2BF_4$ (2) [c]	22					
$RuRhHCl(CO)_3(dppm)_2BF_4$ (3) [c]	18.6					
$RuRh_2H_2Cl(PhPCH_2PPh_2)$-$(COD)_2(dppm)$ (4) [d]	23.2	14.6	14.6	14.6	10	24
$RuRhCuH_2Cl(COD)(dppm)_2$ (5) [d]	14.2	16.3	0	16.3	16.3	0
$RuCuH_2Cl(dppm)_2$ (6) [e]	–	[a]	[a]	[a]	[a]	

[a] Coupling constant not determined precisely. [b] The notations $^iJ(H(1)P)$ and $^iJ(H(2)P)$ differentiate the different coupling constants without specific attribution to the phosphorus atoms. [c] Solvent $(CD)_3)_2CO$. [d] Solvent C_6D_6. [e] Solvent CD_2Cl_2.

$[RuC_8H_{13}(P(OMe)Ph_2)_3]PF_6$ [16]; Ru–H 2.10(3) Å in $RuClC_{21}H_{25}$ [17]). Numerous examples of asymmetric bridging hydrides have been reported or postulated, and the values found in the present work are similar only to those observed for a dinuclear ruthenium complex involving what has been described as a "semi-bridging hydride" (Ru(1)–H 1.68(5) Å, Ru(2)–H 2.05(6) Å) [18]. However, the difference in Rh–H and Ru–H distance (0.44 Å) is too small in respect with the σ values to be accepted as truly indicative of asymmetry of the position of the hydride ligand. A neutron diffraction study will be necessary to locate the hydride, and we are trying to get crystals of the appropriate size for this.

Finally we note that the overall geometry of the complex is that of a typical Lewis acid–Lewis base complex, many examples of which have been described by Venanzi et al. [19]. The surprising feature is that our preparation involves the regeneration of the chelating mode of bonding of a bridging dppm group at the ruthenium atom. This behaviour is quite rare for dinuclear dppm complexes [12], although it has been shown to occur in the redistribution reaction between $RuH_2(dppm)_2$ and $[IrCl(COD)]_2$ to give $RuHCl(dppm)_2$ and an unidentified iridium hydride via the dinuclear $RuIrH_2Cl(COD)(dppm)_2$ [10]. The mechanism of these overall reactions is not completely clear, but it probably involves elimination of H_2 from ruthenium and chelation of the bridging dppm group to provide an 18-electron configuration.

Complex **2** is not very stable in CH_2Cl_2 or $(CH_3)_2CO$ and another complex appears as indicated by ^{31}P NMR (A_2B_2 pattern, δ_A 5.8 ppm, δ_B −20.3 ppm, J_{AB} 37.5 Hz) and by ^1H NMR spectroscopy, which showed the methylene protons of dppm (δ 4.2 ppm) but no signal from a new hydrido species. This is in agreement with the formation of a cationic ruthenium species, presumably $[RuCl(dppm)_2]^+$, together with decomposition of the "RhHCOD" fragment, and illustrates the strong tendency of this complex to lose the hydride remaining on rhodium.

We examined a few reactions of complex **2**. There was no reaction with molecular

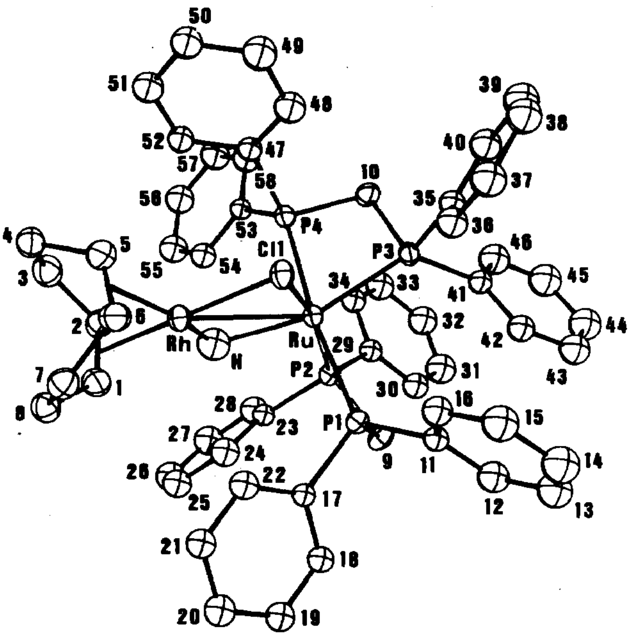


Fig. 2. Molecular structure of **2** showing the atom numbering scheme. This numbering is not the same as that used in the NMR analysis. In fact attribution of each NMR signal to each atom in the ORTEP drawing has not been attempted; it is suggested only that the pair of signals P(4) and P(2) corresponds to the pair of *trans* phosphorus atoms named P(1) and P(4) in the ORTEP drawing.

hydrogen at room temperature and pressure, but reaction did take place with carbon monoxide. A new yellow compound (3) was obtained, and was crystallized from CH_2Cl_2/Et_2O. Complex 3 shows 3 carbonyl stretching bands at 2075, 1995, and 1970 cm^{-1} and analyzes for $[RuRhHCl(CO)_3(dppm)_2]BF_4$. Its ^1H NMR spectrum in CD_2Cl_2 no longer shows cyclooctadiene protons but does show the phenyl protons, along with the methylene protons of dppm at δ 3.45 and 4.25 ppm as multiplets which are transformed into two doublets by phosphorus decoupling (*J*(HH) 13.4 Hz), and a hydride, at δ -7.1 ppm, coupled to rhodium as shown by phosphorus decoupling experiments (*J*(Rh–H) 18.6 Hz). The ^{31}P NMR spectrum is interesting since at 36.44 MHz it shows a highly degenerate AA′BB′X pattern at δ 31 and 29 ppm ($(CD_3)_2CO$) or 27.5 and 25 ppm (CD_2Cl_2). At room temperature in CD_2Cl_2 at 101.22 MHz this signal is transformed into a broad, apparently singlet, resonance at δ 27.33 ppm with broad satellites. This begins to separate at 193 K to reform an AA′BB′X pattern (δ_A 26.8 ppm, δ_B 26.2 ppm) which remains broad and poorly resolved. We were unable to analyze the spectrum and to determine the coupling constants: in particular, we could not determine a *J*(P–Rh) coupling constant, but the specific pattern for an AA′BB′X system is only compatible with two phosphorus coordinated to rhodium. The collapse of the signal observed at 101.22 MHz and room temperature is attributed to small changes of the shifts of the AA′ and BB′ parts of the second order degenerate spectrum, and has been observed previously in a quite similar form for bis-dppm bridged MoRu complexes: $MoRu(CO)_5(dppm)_2$ and $MoRuH_2(CO)_5(dppm)_2$ [8]. The data allow us to propose a structure for the complex (see Scheme 1) in which the ruthenium can

(Continued on p. 78)

TABLE 2

^{31}P NMR DATA FOR THE NEW COMPLEXES (at 101.2 MHz) (δ, ppm; J, Hz)

Compound	δ(P(1))	δ(P(2))	δ(P(3))	δ(P(4))	J(P(1)–P(2))	J(P(1)–P(3))	J(P(1)–P(4))
RuRhHCl(COD)(dppm)$_2$BF$_4$ (**2**) ^{c,f}	12.4	−2.0	−10.6	−18.9	28.0	23.5	51.5
RuRhHCl(CO)$_3$(dppm)$_2$BF$_4$ (**3**) ^{e}	26.8	26.8	26.2	26.2	^{a}	^{a}	^{a}
RuRh$_2$H$_2$Cl(PhPCH$_2$PPh$_2$)(COD)$_2$(dppm) (**4**) ^{h}	212.2	56.6	20.3	17.2	22	30	19
RuRhCuH$_2$Cl(COD)(dppm)$_2$ (**5**) ^{g}	41.8	29.4	8.1	−12.6	63	31	308
RuCuH$_2$Cl(dppm)$_2$ (**6**) ^{f}	6.45	6.45	4.3	4.3	^{b}	^{b}	^{b}

Compound	(J(P(2)–P(3))	J(P(2)–P(4))	J(P(3)–P(4))	J(P(1)–Rh)	J(P(2)–Rh)	J(P(3)–Rh)	J(P(4)–Rh)
RuRhHCl(COD)(dppm)$_2$BF$_4$ (**2**) ^{c,f}	41.2	294.1	23.5	0	0	5.8	0
RuRhHCl(CO)$_3$(dppm)$_2$BF$_4$ (**3**) ^{e}	^{a}	^{a}	^{a}	0	0	^{a}	^{a}
RuRh$_2$H$_2$Cl(PhPCH$_2$PPh$_2$)(COD)$_2$(dppm) (**4**) ^{h}	320	110	12	134	0	0	99
RuRhCuH$_2$Cl(COD)(dppm)$_2$ (**5**) ^{g}	0	0	65				
RuCuH$_2$Cl(dppm)$_2$ (**6**) ^{f}	^{b}	^{b}	^{b}	–	–	–	–

[a] Coupling constant not determined precisely. [b] A_2B_2 spin system, J_{AB} 37 Hz. [c] The labelling of the phosphorus signals used in this table is not identical to that retained in the ORTEP diagram (Fig. 2, Tables 3, 4)), especially the pair of P(2)P(3) signals is to be attributed to the pair of P(2) and P(3) atoms but without knowing which is which. [e] Solvent CD_2Cl_2. [f] Solvent CD_2Cl_2/CH_2Cl_2. [g] Solvent C_6D_6/C_7H_8. [h] Solvent C_7D_8/C_7H_8.

TABLE 3

FRACTIONAL ATOMIC COORDINATES WITH e.s.d.'s IN PARENTHESES

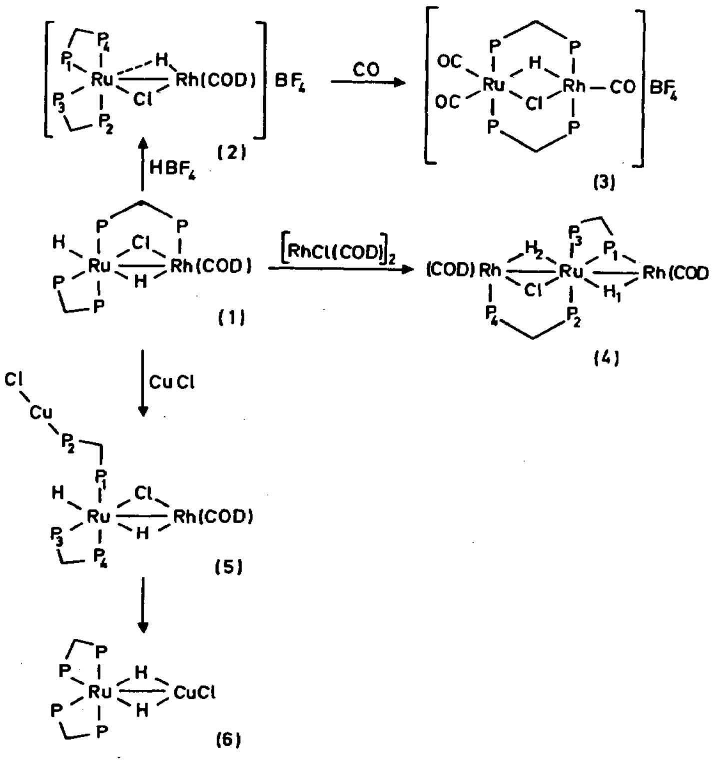
Atom	*x*	*y*	*z*
Rh	0.86152(4)	0.30895(3)	0.43472(3)
Ru	0.86217(4)	0.25836(3)	0.55712(3)
Cl(1)	0.99963(13)	0.27156(10)	0.50313(8)
H	0.779(5)	0.300(4)	0.479(3)
C(1)	0.7508(6)	0.3727(4)	0.3827(4)
C(2)	0.7236(6)	0.3045(5)	0.3739(4)
C(3)	0.7473(6)	0.2750(5)	0.3158(4)
C(4)	0.8443(5)	0.2804(4)	0.2939(4)
C(5)	0.9188(6)	0.2907(4)	0.3524(4)
C(6)	0.9483(6)	0.3538(4)	0.3748(4)
C(7)	0.9030(6)	0.4201(4)	0.3487(4)
C(8)	0.7936(6)	0.4230(4)	0.3433(4)
P(1)	0.88802(13)	0.36025(10)	0.61362(9)
P(2)	0.73097(13)	0.27643(10)	0.60425(9)
C(9)	0.7897(5)	0.3429(4)	0.6572(3)
P(3)	0.93391(14)	0.17774(10)	0.62881(8)
P(4)	0.82870(14)	0.15015(10)	0.51624(9)
C(10)	0.8685(6)	0.1043(4)	0.5891(3)
C(11)	0.9989(3)	0.3806(3)	0.6697(2)
C(12)	0.9989(3)	0.4001(3)	0.7295(2)
C(13)	1.0857(3)	0.4163(4)	0.7677(2)
C(14)	1.1725(3)	0.4130(3)	0.7460(2)
C(15)	1.1725(3)	0.3936(3)	0.6861(2)
C(16)	1.0857(3)	0.3774(3)	0.6480(2)
C(17)	0.8608(3)	0.4443(2)	0.5790(2)
C(18)	0.8246(3)	0.4953(2)	0.6112(2)
C(19)	0.8077(3)	0.5589(2)	0.5855(2)
C(20)	0.8271(3)	0.5715(2)	0.5276(2)
C(21)	0.8633(3)	0.5205(2)	0.4953(2)
C(22)	0.8801(3)	0.4570(2)	0.5210(2)
C(23)	0.6215(3)	0.3174(3)	0.5595(2)
C(24)	0.6334(3)	0.3752(3)	0.5265(2)
C(25)	0.5527(3)	0.4083(3)	0.4943(2)
C(26)	0.4601(3)	0.3836(3)	0.4951(2)
C(27)	0.4482(3)	0.3259(3)	0.5281(2)
C(28)	0.5289(3)	0.2928(3)	0.5603(2)
C(29)	0.6771(4)	0.2175(2)	0.6522(2)
C(30)	0.6643(4)	0.2363(2)	0.7103(2)
C(31)	0.6199(4)	0.1924(2)	0.7453(2)
C(32)	0.5884(4)	0.1297(2)	0.7222(2)
C(33)	0.6012(4)	0.1109(2)	0.6641(2)
C(34)	0.6455(4)	0.1548(2)	0.6291(2)
C(35)	1.0646(4)	0.1555(2)	0.6379(2)
C(36)	1.1321(4)	0.2028(2)	0.6263(2)
C(37)	1.2294(4)	0.1853(2)	0.6326(2)
C(38)	1.2593(4)	0.1205(2)	0.6504(2)
C(39)	1.1919(4)	0.0732(2)	0.6620(2)
C(40)	1.0945(4)	0.0907(2)	0.6558(2)
C(41)	0.9195(4)	0.1738(2)	0.7089(2)
C(42)	0.9640(4)	0.2242(2)	0.7474(2)
C(43)	0.9580(4)	0.2234(2)	0.8089(2)
C(44)	0.9075(4)	0.1724(2)	0.8320(2)

continued

TABLE 3 (continued)

Atom	*x*	*y*	*z*
C(45)	0.8629(4)	0.1220(2)	0.7936(2)
C(46)	0.8689(4)	0.1227(2)	0.7321(2)
C(47)	0.9020(4)	0.1182(3)	0.4620(2)
C(48)	0.9963(4)	0.0952(3)	0.4810(2)
C(49)	1.0519(4)	0.0762(3)	0.4382(2)
C(50)	1.0133(4)	0.0803(3)	0.3764(2)
C(51)	0.9190(4)	0.1033(3)	0.3573(2)
C(52)	0.8634(4)	0.1223(3)	0.4001(2)
C(53)	0.7086(4)	0.1181(2)	0.4843(2)
C(54)	0.6335(4)	0.1626(2)	0.4633(2)
C(55)	0.5418(4)	0.1382(2)	0.4387(2)
C(56)	0.5252(4)	0.0693(2)	0.4350(2)
C(57)	0.6004(4)	0.0247(2)	0.4560(2)
C(58)	0.6921(4)	0.0491(2)	0.4806(2)
B	0.7564(10)	0.4381(7)	0.8036(6)
F(1)	0.7639(4)	0.4777(3)	0.7550(3)
F(2)	0.7376(3)	0.4751(2)	0.8516(2)
F(3)	0.6866(4)	0.3901(3)	0.7869(3)
F(4)	0.8447(5)	0.4044(3)	0.8222(3)
C(59) [a]	0.7458(16)	0.3176(12)	0.9226(10)
Cl(2) [a]	0.7124(4)	0.2401(3)	0.9199(2)
Cl(3) [a]	0.8029(4)	0.3463(3)	0.9921(2)
C(60) [a]	1.0023(11)	0.0805(8)	0.1764(7)
Cl(4) [a]	0.9461(3)	0.1502(3)	0.1951(2)
Cl(5) [a]	0.9324(4)	0.0109(3)	0.1549(2)

[a] Atom with occupancy factor 0.5.



SCHEME 1. Reactions of $RuRhH_2Cl(COD)(dppm)_2$, and proposed structures for the new complexes.

TABLE 4

SELECTED BOND LENGTHS (Å) AND ANGLES (deg) WITH e.s.d.'s IN PARENTHESES (M(12) and M(56) are the midpoints of the C(1)–C(2) and C(5)–C(6) bonds.)

Rh–Ru	2.897(1)		
Rh–Cl(1)	2.348(2)	Ru–Cl(1)	2.455(2)
Rh–H	1.64(8)	Ru–H	2.08(7)
Rh–M(12)	2.034(8)	Ru–P(1)	2.370(2)
Rh–M(56)	2.039(9)	Ru–P(2)	2.297(2)
Rh–C(1)	2.161(8)	Ru–P(3)	2.348(2)
Rh–C(2)	2.144(7)	Ru–P(4)	2.342(2)
Rh–C(3)	2.905(8)	P(1)–C(9)	1.850(8)
Rh–C(4)	3.145(8)	P(2)–C(9)	1.854(7)
Rh–C(5)	2.156(9)	P(3)–C(10)	1.854(7)
Rh–C(6)	2.149(9)	P(4)–C(10)	1.852(7)
Rh–C(7)	3.039(9)		
Rh–C(8)	3.071(8)		
C(1)–C(2)	1.407(12)		
C(2)–C(3)	1.506(12)		
C(3)–C(4)	1.522(12)		
C(4)–C(5)	1.524(10)		
C(5)–C(6)	1.381(12)		
C(6)–C(7)	1.525(11)		
C(7)–C(8)	1.511(11)		
C(8)–C(1)	1.518(12)		
Ru–Rh–Cl(1)	54.61(5)	Rh–Ru–Cl(1)	51.23(4)
Ru–Rh–H	45.(2)	Rh–Cl(1)–Ru	74.16(6)
Cl(1)–Rh–H	99.(2)	Rh–H–Ru	101.(3)
Cl(1)–Rh–M(12)	176.8(3)	Rh–Ru–H	34.(2)
Cl(1)–Rh–M(56)	94.6(2)	Cl(1)–Ru–H	85.(2)
M(12)–Rh–H	78.(2)	Rh–Ru–P(1)	100.18(6)
M(56)–Rh–H	166.(2)	Rh–Ru–P(2)	120.48(5)
M(12)–Rh–M(56)	88.3(3)	Rh–Ru–P(3)	143.18(6)
Ru–Rh–M(12)	122.4(3)	Rh–Ru–P(4)	89.22(6)
Ru–Rh–M(56)	148.7(2)	Cl(1)–Ru–P(1)	96.36(7)
		Cl(1)–Ru–P(2)	164.80(8)
		Cl(1)–Ru–P(3)	97.41(7)
		Cl(1)–Ru–P(4)	91.53(7)
		H–Ru–P(1)	96.(2)
		H–Ru–P(2)	87.(2)
		H–Ru–P(3)	161.(2)
		H–Ru–P(4)	90.(2)
P(1)–Ru–P(2)	71.52(7)	P(1)–C(9)–P(2)	94.9(4)
P(1)–Ru–P(3)	102.41(7)	Ru–P(2)–C(9)	95.9(2)
P(1)–Ru–P(4)	170.26(8)	Ru–P(3)–C(10)	95.7(2)
P(2)–Ru–P(3)	94.24(7)	P(3)–C(10)–P(4)	94.3(3)
P(2)–Ru–P(4)	101.54(7)	Ru–P(4)–C(10)	95.9(2)
P(3)–Ru–P(4)	70.78(7)		
Ru–P(1)–C(9)	93.6(2)		

All phenyl rings treated as rigid groups: C–C 1.385 Å, C–H 0.95 Å, C–C–C 120°

TABLE 5

SUMMARY OF CRYSTAL AND INTENSITY COLLECTION DATA FOR **2**

Formula	$BC_{59}Cl_3F_4H_{59}P_4RhRu$
Formula wt	1288.2
a, Å	13.960(3)
b, Å	19.812(4)
c, Å	22.218(4)
β, deg	100.46(2)
V, Å^3	6043
Z	4
$F(000)$	2616
D_c, g cm^{-3}	1.416
Crystal system	monoclinic
Space group	C_2^5h; $P2_1/n$
Radiatn	λ 0.71073 Å (Mo-K_α graphite monochromatized)
Linear abs coef, cm^{-1}	μ 7.99
Temperature, °C	20
Receiving aperture, mm	4.0×4.0
Take-off angle, deg	3.4
Scan mode	$\theta-2\theta$
Scan range, deg	$0.90+0.35\tan\theta$
2θ limits, deg	43

accomodate two *cis* CO groups whereas only one would be coordinated on rhodium, with the hydride and the chloride remaining in the bridging position. The only reasonable alternative possibility would involve two chelating dppm ligands on ruthenium, one bridging hydride, one bridging chloride, and three CO on rhodium. This would give $^{31}P\ \{^1H\}$NMR spectra similar to that of **2**. Moreover, since one of the phosphorus atoms would be necessarily *trans* to the bridging hydride such a disposition would give an observable *trans* J(P–H) coupling, and this is not observed.

The mechanism of this reaction probably involves the initial displacement of the cyclooctadiene ligand, since when the reaction was monitored by infrared, after 2 h, 2 bands were observed, at 2080 and 2020 cm^{-1}, which could be attributed to a *cis* dicarbonyl rhodium moiety. This reaction is another rare example of intramolecular ring opening of the chelated dppm ligands, and confirms their great mobility in the Ru–Rh systems.

Reaction of $RuRhH_2Cl(COD)(dppm)_2$ *with* $[RhCl(COD)]_2$. Since $RuRhH_2Cl(COD)(dppm)_2$ (**1**) is obtained by ring opening of one dppm ligand of $RuH_2(dppm)_2$, we thought that it should be possible to prepare trimetallic complexes by ring

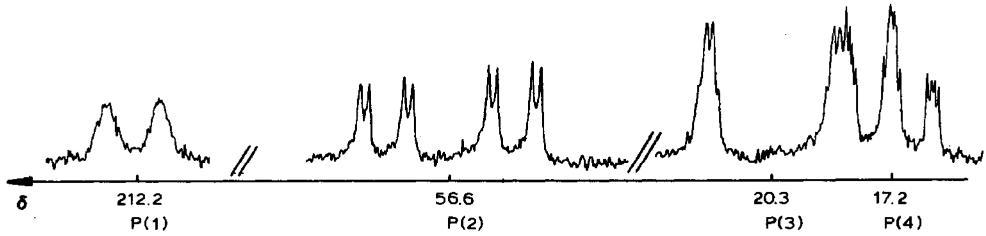


Fig. 3. ^{31}P NMR spectrum of **4**.

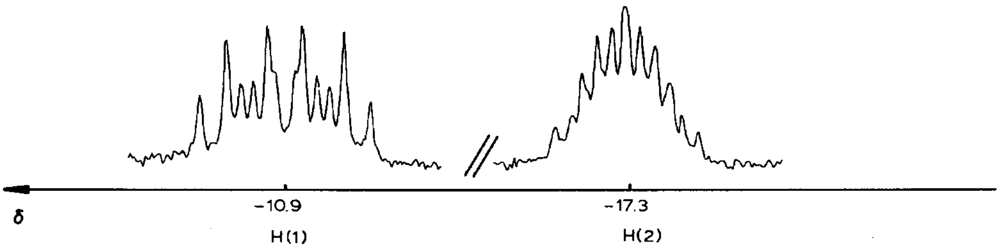


Fig. Highfield ^{1}H NMR spectrum of **4**.

opening of a second chelating dppm ligand. Thus **1** was treated with 0.5 molar equivalent of $[RhCl(COD)]_2$ at room temperature but no reaction was observed. However, when the reaction was carried out at 80°C the initially orange solution darkens, and after 3 days a deep red solution is obtained. NMR studies on the solution show the system to be complicated, and to contain 3 products: $RuHCl(dppm)_2$ [20] (minor product) and two complexes containing phosphido bridges. Although separation of the products by crystallization proved difficult, we obtained one of the two phosphido derivatives pure (as deep red needles) by recrystallization from toluene/hexane. The yield was low (ca. 25%) and the complex analyzed for $RuRh_2H_2Cl(PhPCH_2PPh_2)(COD)_2(dppm)$ (**4**). The ^{31}P NMR spectrum shows four phosphorus resonances at δ 212.2 (d, br, P(1)), 56.6 (ddd, P(2)), 20.3 (ddd, P(3)) and 17.2 ppm (dddd, P(4)) (Fig. 3 and Table 2). The P(1) and P(4) signals show a Rh–P coupling of 134 and 99 Hz, respectively. The study of the other coupling constants show that P(2) and P(3) are *trans* to each other (J(P(2)P(3)) 320 Hz), and that P(2) and P(4) probably belong to the same dppm group (J(P(2)P(4)) 110 Hz).

The ^{1}H NMR spectrum is also very interesting. It shows the phenyl protons of dppm (δ 7 ppm), the protons of cyclooctadiene (δ 1.5–2.5 and 4–5 ppm) and the methylene protons of dppm near δ 4.5 and 2.4 ppm, but the more informative peaks are two hydride signals which appear in 1/1 ratio at δ −10.9 and −17.3 ppm as complicated multiplets (Fig. 4). It is of interest to compare these values with those found for the bridging hydrides of $RuRhHPh(PhPCH_2PPh_2)(COD)(dppm)$ [10] (−10.95 ppm) and of **4** (−15.6 ppm), respectively. Noise decoupling of the phosphorus shows that both hydrides are coupled to rhodium, with coupling constants of 23.2 and 24 Hz, respectively. The signal for H(1) can be interpreted as a doublet of doublets of triplets with J(H(2)P(1)) 42.7 Hz, J(H(2)P(2)) = J(H(2)P(3)) = 15.9 Hz and J(H(2)Rh) 23.2 Hz. No J(H(2)P(4)) coupling was observed. Similarly, the signal for H(2) can be interpreted as a doublet of doublet of quartets with J(H(2)P(1)) = J(H(2)P(2)) = J(H(2)P(3)) = 14.6 Hz, J(H(2)P(4)) 10 Hz and J(H(2)Rh) 24 Hz. The proposed structure (Scheme 1) fits all our data. In particular, H(1) is in a chemical environment very similar to that of the bridging hydride of $RuRhH(Ph)(PhPCH_2PPh_2)(COD)(dppm)$, and has a very similar chemical shift, while H(2) is in a chemical environment very similar to that of the bridging hydride of **1** and has a similar chemical shift. The coupling constants are all in the normal range except for J(H(1)P(1)), which is high for a *cis*-H–P coupling constant.

The ^{31}P NMR spectra, suggest that the other phosphido-bridged species formed in the reaction have a similar structure, but it has not been isolated pure and has not been fully characterized.

Finally, the mechanism of formation of these species presents a problem. Since the formation of the phosphido species is always accompanied by the appearance of $RuHCl(dppm)_2$, we suggest that in the first step there is a redistribution similar to that observed between $RuH_2(dppm)_2$ and $[IrCl(COD)]_2$ [10]:

$$RuH_2(dppm)_2 + 1/2[RhCl(COD)]_2 \xrightarrow{i} RuRhH_2Cl(COD)(dppm)_2 \xrightarrow{ii}$$

$$RuHCl(dppm)_2 + \text{“RhH(COD)”}$$

The decomposition (ii) would explain the darkening of the solution, which is also observed during the reaction of $RuH_2(dppm)_2$ with $[IrCl(COD)]_2$. Then the very reactive "RhH(COD)", which could be either a dimer or the recently isolated cluster $[RhH(COD)]_4$ [21], would react with excess **1** to give **4** with elimination of benzene. This trinuclear product is of interest, but a study of its reactivity has been restricted by the experimental conditions for its preparation.

Reactions of $RuRhH_2Cl(COD)(dppm)_2$ with CuCl. With the usual idea of bringing about ring opening of the chelated dppm group on ruthenium, we treated **1** with the reactive Lewis acid CuCl at room temperature in toluene. An orange solution was obtained, from which orange crystals deposited on addition of hexane in ca. 50% yield. They analyzed for $RuRhCuH_2Cl_2(COD)(dppm)_2$ (**5**). The ^1H NMR spectrum showed two rigid hydrides at δ −12.9 and −15.6 ppm. The signal at δ −12.9 ppm is a complex multiplet with a large P–H coupling of 32 Hz and a Rh–H coupling of 14 Hz (detected by phosphorus decoupling). An additional 4 Hz H–H coupling is also present (as shown by double resonance experiments), and may be indicative of a mutual *trans* configuration. The signal at δ −15.6 ppm is a quartet which is transformed into a broad singlet by phosphorus decoupling, indicating that it is coupled to three equivalent phosphorus atoms in a *cis* position (J(PH) 16.3 Hz). The ^{31}P NMR spectrum is fairly simple, and shows four different phosphorus P(1) (ddd), P(2) (br), P(3) (dd) and P(4) (dd). These results enabled us to conclude that P(4) is *trans* to P(1) and *cis* to P(3), while P(1) is *cis* to P(3) and shows an additional coupling of 63 Hz, compatible with a ^2J(PP) coupling between the two phosphorus atoms of one dppm ligand, and was attributed to J(P(1)P(2)). We attribute the width of P(2) to a direct coordination to copper, which possesses a high quadrupolar moment [22]. None of the phosphorus resonances shows Rh–P coupling. The data are again consistent with the formation of an acid–base ruthenium-rhodium complex such as **2**, bridged by a hydride and a chloride group. The difference is that the ruthenium now accomodates only three phosphorus atoms, the fourth being attached to CuCl. This reaction shows once again that the weaker M–P linkage in this system is the Rh–P bond. It has not been possible to achieve simple ring opening of the chelating dppm group by this method.

As before, the compound is not stable in solution, since the appearance of a second compound (**6**) is observed; this shows an A_2B_2 signal around δ 5.2 ppm in CD_2Cl_2/CH_2Cl_2 at 36.44 MHz (J_{AB} 28 Hz) and a hydride signal that we interpret as a doublet of doublet of triplets $(J(PH)_{cis}$ 14 Hz, $J(PH)_{cis}$ 5 Hz, $J(PH)_{trans}$ 42 Hz) at δ −9.1 ppm. This compound was obtained more readily and crystalline by treating $RuH_2(dppm)_2$ with CuCl in toluene at 80°C. The product analyzes for $RuCuH_2Cl(dppm)_2$, and in addition to signals described above it shows the methylene protons of dppm as two multiplets which are converted into two doublets by phosphorus decoupling (δ 4.27 and 4.11 ppm; J(HH) 13.9 Hz). This suggested a structure containing two chelating dppm ligands on ruthenium and two hydride bridges between Ru and Cu (Scheme 1). However, compound **6** could alternatively be a tetrametallic dimer. It is a typical example of a Lewis acid–Lewis base adduct between metal hydrides and copper(I) complexes, many examples of which have been prepared by Caulton et al. [23]. The complex is air-sensitive but otherwise has a low reactivity. It does not react with H_2, CO or an olefin, and on treatment with one equivalent of methyllithium is reconverted to $RuH_2(dppm)_2$.

Conclusion

This study confirms that dppm in this system is a versatile ligand. The regeneration of the chelating position of a bridging dppm group in a dinuclear complex observed during the reaction of $RuRhH_2Cl(COD)(dppm)_2$ with HBF_4 and CuCl is rare. Ring opening of the chelating dppm ligand can be achieved by addition of CO.

The study also shows that trimetallic complexes can be obtained, although the dppm remaining chelated on ruthenium in $RuRhH_2Cl(COD)(dppm)_2$ is reluctant to undergo ring opening.

The possible asymmetry of the Ru–H–Rh moiety, if confirmed by neutron diffraction, will provide a unique example of a semi-bridging hydride in a heterobimetallic complex.

Experimental

Microanalyses were performed by the "Centre de Microanalyse du CNRS" or in this laboratory. Infrared spectra were obtained as Nujol mulls or in solution in CH_2Cl with Perkin–Elmer PE 557 or PE 225 grating diffractometers. NMR spectra were recorded with a Bruker WH 90 (90 MHz) or WM 250 (250 MHz) spectrometer, these were operated in the Fourier transform mode with proton noise decoupling for recording of the ^{31}P NMR spectra unless otherwise stated. All solvents were thoroughly degassed before use and all operations were carried out under nitrogen or argon. $RuRhH_2Cl(COD)(dppm)_2$ [10], $RuH_2(dppm)_2$ [20] and $\{RhCl(COD)]_2$ [24] were prepared by published methods.

[RuRhHCl(COD)(dppm)$_2$]BF$_4$ (2). $RuRhH_2Cl(COD)(dppm)_2$ (0.25 g, 0.22 mmol) was dissolved in dichloromethane (20 ml) and $HBF_4 \cdot Et_2O$ (35 μl, 0.25 mmol) was added. The mixture was stirred for 30 min, during which its colour changed from orange to red, and was then concentrated. Hexane was added (to the point of floculation) and the solution was then filtered and cooled to −18°C, to give orange crystals of complex **2** (yield 71%). Anal. Found: C, 54.1; H, 4.6; Cl, 8.4; P, 9.2. $RuRhC_{58}ClH_{57}P_4BF_4$ calcd.: C, 54.95; H, 4.6; Cl, 8.3; P, 9.6%.

[RuRhHCl(CO)$_3$(dppm)$_2$]BF$_4$ (3). $RuRhHCl(COD)(dppm)_2BF_4$ (0.15 g, 0.12 mmol) was dissolved in CH_2Cl_2 (20 ml). CO was passed through the solution for 10 min and the solution then kept under a CO atmosphere for 2 days. Hexane was then added, and the resulting yellow solution was filtered and cooled to −18°C, to give yellow crystals of complex **3** (yield 80%). Anal. Found: C, 53.1; H, 3.8; P, 9.9; Cl, 3.6. $RuRhC_{53}ClH_{45}O_3P_4BF_4$ calcd.: C, 53.9; H, 3.8; P, 10.5; Cl, 3.0%.

RuRh$_2$H$_2$Cl(PhPCH$_2$PPh$_2$)(COD)$_2$(dppm) (4). $[RhCl(COD)]_2$ (0.24 g, 0.49 mmol) was dissolved in 30 ml toluene and $RuH_2(dppm)_2$ (0.42 g, 0.49 mmol) was added. The solution was left at room temperature for a few minutes to produce a

2/1 mixture of $RuRhH_2Cl(COD)(dppm)_2$ and $[RhCl(COD)]_2$, and then warmed at 80°C for 3 days, during which the colour changed from orange to deep brown. After concentration, and addition of pentane, yellow crystals of $RuHCl(dppm)_2$ and red crystals of complex **4** were successively obtained (yield ca. 25%). Anal. Found: C, 57.2; H, 5.2; P, 9.1. $RuRh_2C_{60}ClH_{65}P_4$ calcd.: C, 57.5; H, 5.2; P, 9.9%.

$RuRhCuH_2Cl_2(COD)(dppm)_2$ (5). $RuRhH_2Cl(COD)(dppm)_2$ (0.4 g, 0.36 mmol) and then CuCl (0.0355 g, 0.36 mmol) were added to 70 ml toluene, and the solution was kept at room temperature for 1 day, then filtered. The filtrate was concentrated and pentane was added, resulting in the slow formation of orange crystals of complex **5** at room temperature (yield ca. 50%). Anal. Found: C, 57.0; H, 4.8; P, 10.0; Cl, 6.1; Cu, 5.9. $RuRhCuC_{58}Cl_2H_{58}P_4$ calcd.: C, 57.2; H, 4.8; P, 10.2; Cl, 5.8; Cu, 5.2%.

$RuCuH_2Cl(dppm)_2$ (6). $RuH_2(dppm)_2$ (0.8 g, 0.92 mmol) and CuCl (0.092 g, 0.92 mmol) were added to 75 ml toluene. The mixture was stirred at room temperature for 1 h during which the $RuH_2(dppm)_2$ dissolved to give a yellow solution while the CuCl remained insoluble. The mixture was then warmed to 80°C for 8 h, during which an off-white precipitate formed, and was found to consist of pure **6** (yield ca. 90%). It was recrystallized from CH_2Cl_2/Et_2O to give white crystals. Anal. Found: C, 61.7; H, 4.9; P, 12.8; Cl, 3.7; Cu, 6.5. $RuCuC_{50}ClH_{46}P_4$ calcd.: C, 61.9; H, 4.7; P, 12.8; Cl, 3.7; Cu, 6.5%.

Collection and reduction of X-ray data. The crystals are monoclinic, space group $P2_1/n$. An orange rhomb of 0.30 × 0.30 × 0.15 mm was sealed in a Lindeman glass capillary under argon and mounted on an Enraf–Nonius CAD4 diffractometer. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections. Details of crystal data and of the diffraction data collection are given in Table 5. 6916 independent reflections were recorded to a 2θ(Mo) maximum of 43° by procedures described elsewhere [25]. Standard reflections examined periodically showed only random, statistical fluctuations. Lorentz and polarization corrections [26] were applied to intensity data. Absorption corrections were judged not to be necessary.

Structure solution and refinement. The structure was solved [27] by the heavy-atom method. Successive difference Fourier maps and least-squares refinement cycles processes revealed the positions of all non-hydrogen atoms. Important residual peaks on a ΔF synthesis were attributed to molecules of dichloromethane. Two CH_2Cl_2 molecules were introduced in calculations, without H atoms, with 0.5 occupancy factors. Rh, Ru, Cl, P, F, B and methylenic C atoms were refined anisotropically. Phenyl groups were refined as isotropic rigid groups (C–C 1.385 Å). Hydrogen atoms were located from a ΔF synthesis and introduced in constrained geometry (C–H 0.97 Å) with an fixed isotropic temperatur factor U_H 0.07 Å^2, but the hydride atom was isotropically refined.

The atomic scattering factors used were those listed by Cromer and Waber [28] with anomalous dispersion effects [29]. Scattering factors for the hydrogen atoms were taken from Stewart et al. [30].

The final full-matrix least-squares refinement converged to $R = \Sigma[\,|F_0| - |F_c|\,]/\Sigma|F_0| = 0.026$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2} = 0.031$ with unit weights. The standard in an observation of unit weight was $S = \Sigma w(|F_0| - |F_c|)^2/(n-m)^{1/2} = 2.8$ with $n = 3517$ observations ($F_0^2 > 3\sigma(F_0^2)$) and $m = 343$ variables. An analysis of variance showed no unusual trends. The maximum shift for all parameters was 0.1 σ (mean value 0.06 σ). A final difference Fourier map showed a residual electron density of 0.2 e/Å^3.

Supplementary material available. Tables of structure factors, thermal parameters, hydrogen parameters and least-squares planes equations are available from the authors.

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