Structure of a *cis*-Dimetalla-alkene Complex formed by the Reaction of a Ruthenium(II) Complex with Bis(phenylethynyl)mercury(II)†

Zbigniew Dauter, Roger J. Mawby,* Colin D. Reynolds, and David R. Saunders
Department of Chemistry, University of York, York Y01 5DD

X-Ray investigation of the product of the reaction of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with $Hg(C{\equiv}CPh)_2$ shows it to be $[Ru(CO)_2\{C(C{\equiv}CPh){=}C(Ph)HgCl\}Cl(PMe_2Ph)_2]$. The proposed mechanism involves formation on the ruthenium of 1,4-diphenylbuta-1,3-diyne, and *cis* addition of an Ru–HgCl bond across one of the triple bonds of the diyne. The mass spectrum of the complex indicates that this addition is reversed on heating, with release of the diyne. The related complex $[Ru(CO)_2\{C(C{\equiv}CCMe_3){=}C(CMe_3)HgCl\}Cl(PMe_2Ph)_2]$, prepared in the same way, decomposes slowly in solution even at room temperature, with release of $Me_3CC{\equiv}C{-}C{\equiv}CCMe_3$ and deposition of mercury.

In the course of our studies of organoruthenium chemistry, we have investigated the preparation, structure, and reactions of complexes in which ruthenium is σ-bonded to an alkyl, aryl, or alkenyl ligand.[1–3] The reactivity of the organic ligand in these complexes varies widely: thus, for example, the ease of formation of acyl complexes in reactions of the type (1) (where

$$[Ru(CO)_2R(Cl)(PMe_2Ph)_2] + L \longrightarrow [Ru(CO)(COR)Cl(L)(PMe_2Ph)_2] \quad (1)$$

L = CO, PMe_2Ph, or $CNCMe_3$) decreases markedly along the sequence R = Me > Ph > $C(CO_2Me){=}C(CO_2Me)Cl$.[2–4] We were interested in preparing alkynyl complexes of ruthenium(II) and comparing their properties with those of the complexes mentioned above. Since we had successfully used the reaction of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with HgR_2 (R = Me or Ph) as a means of obtaining methyl and phenyl complexes of ruthenium(II),[1] we investigated the reactions of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with $Hg(C{\equiv}CPh)_2$ and $Hg(C{\equiv}CCMe_3)_2$. Cross and Gemmill[5] have shown that both chloride ligands in *cis*-$[Pt(CO)Cl_2(PMePh_2)]$ can be replaced by reaction with an excess of $Hg(C{\equiv}CR)_2$ (R = Me or Ph), yielding *cis*-$[Pt(CO)(C{\equiv}CR)_2(PMePh_2)]$, and we hoped that similar replacement of one or both halide ligands would occur in the case of ruthenium.

Results and Discussion

The Reactions between trans-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ *and* $Hg(C{\equiv}CR)_2$ (R = Ph *or* CMe_3).—The reactions were carried out at room temperature in $CHCl_3$ solution, in each case using slightly more of the organomercury reagent than was required for an equimolar ratio of the reactants. Analytical data for the purified products, complexes (**1**; R = Ph) and (**2**; R = CMe_3), did not agree with the figures expected for $[Ru(CO)_2(C{\equiv}CR)Cl(PMe_2Ph)_2]$ or for $[Ru(CO)_2(C{\equiv}CR)_2(PMe_2Ph)_2]$, but were close to those for simple 1:1 adducts of the reactants. From the i.r. and ^1H n.m.r. spectra of (**1**) and (**2**) (Table 1) it was evident that in each case the ruthenium was attached to a mutually *cis* pair of carbonyl ligands and a mutually *trans* pair of PMe_2Ph ligands, and that the Ru–P bonds did not lie in a plane of symmetry through the complexes,[6] but the spectra provided little further information. The ^{13}C n.m.r. spectra (Table 2) were unexpectedly complicated and difficult to interpret, and we decided to investigate the structure of complex (**1**) by *X*-ray crystallography. The investigation revealed (see below) that the complex was $[Ru(CO)_2\{C(C{\equiv}CPh){=}C(Ph)HgCl\}Cl(PMe_2Ph)_2]$.

Table 1. Infrared[a] and ^1H n.m.r.[b] spectra of complexes

Complex	$\tilde{\nu}$(C–O)/cm^{-1}	δ/p.p.m.	Assignment
(**1**)	2 055	1.96 (t, 6)	P*Me*$_2$Ph
	1 980	1.93 (t, 6)	P*Me*$_2$Ph
(**2**)	2 050	1.91 (t, 6)	P*Me*$_2$Ph
	1 980	1.84 (t, 6)	P*Me*$_2$Ph
		1.26 (s, 9)	CMe_3
		1.21 (s, 9)	CMe_3
(**3**)[c]	1 960	1.90 (t, 6)	P*Me*$_2$Ph
		1.85 (t, 6)	P*Me*$_2$Ph
		1.14 (s, 9)	$CNCMe_3$

[a] In $CHCl_3$ solution. Only carbonyl resonances are listed. [b] In $CDCl_3$ solution. Resonances due to aromatic ring protons are not included. Multiplicities and relative areas are given after the chemical shift values. For PMe_2Ph methyl protons, $|^2J(P{-}H) + {}^4J(P{-}H)|$ = *ca.* 7.5 Hz. [c] For the nitrile group, $\tilde{\nu}$(C–N) at 2 175 cm^{-1}.

Structure of Complex (**1**).—The structure consists of discrete molecules, with no unusually short intermolecular contacts. Atomic co-ordinates are listed in Table 3, and selected bond lengths and angles in Table 4. The stereochemistry of the molecule and the atom numbering scheme are shown in the Figure. The ruthenium is six-co-ordinate, and the ligand arrangement (not greatly distorted from regular octahedral) includes the expected pattern of carbonyl and PMe_2Ph ligands as well as a single chloride ligand. The structure of the sixth ligand was completely unexpected, and it was immediately evident that a major rearrangement of the organomercury reagent $Hg(C{\equiv}CPh)_2$ had occurred in the course of the reaction.

In terms of ruthenium–ligand bond lengths, there are marked similarities between this structure and that of $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$.[3] Thus, for example, the lengths of the bonds to the organic ligands are 2.163(16) and 2.16(2) Å respectively. Within the organic ligand in $[Ru(CO)_2\{C(C{\equiv}CPh){=}C(Ph)HgCl\}Cl(PMe_2Ph)_2]$, the length of the C=C bond is not abnormal, and the arrangement of substituents around this bond is essentially planar, with the two metal atoms mutually *cis*. The angle Ru–C(32)–C(31) [136.1(17)°] is, however, unusually large:

† *Supplementary data available* (No. SUP 56411, 2 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 2. Carbon-13 n.m.r. spectra[a] of complexes

Complex (1)	Complex (2)	Complex (3)	Assignment
195.7 (t, 11.9)	195.5 (t, 12.4)	199.4 (t, 13.3)	CO
194.0 (t, 8.2)	193.7 (t, 8.3)		CO
169.3 (t, 5.5)	181.1 (t, 5.5)	169.3 (t, 5.4)	C(C≡CR)=*C*(R)HgCl[b]
147.7 (t, 1.8)		148.8 (t)[c]	C(C≡CPh)=C(*Ph*)HgCl[d]
144.1 (t, 14.2)	155.8 (t, 13.8)	147.5 (t, 13.4)	*C*(C≡CR)=C(R)HgCl[b]
124.7 (s)		124.6 (s)	C(C≡C*Ph*)=C(Ph)HgCl[d]
99.5 (t, 2.3)	90.1 (t, 2.0)	100.5 (t)[c]	C(*C*≡CR)=C(R)HgCl[b]
98.0 (s)	111.3 (s)	97.8 (s)	C(C≡*C*R)=C(R)HgCl[b]
		57.2 (s)	C*N*C*Me*$_3$
		30.2 (s)	CNC*Me*$_3$
	41.6 (s), 34.4 (s)		C(C≡C*C*Me$_3$)=C(*C*Me$_3$)HgCl; C(C≡CC*Me*$_3$)=C(C*Me*$_3$)HgCl
	32.4 (s), 30.8 (s)		C(C≡C*C*Me$_3$)=C(*C*Me$_3$)HgCl; C(C≡CC*Me*$_3$)=C(C*Me*$_3$)HgCl
14.6 (t, 33.0)	14.4 (t, 33.0)	14.8 (t, 31.1)	P*Me*$_2$Ph[e]
14.1 (t, 33.0)	13.6 (t, 33.1)	13.8 (t, 31.8)	P*Me*$_2$Ph[e]

[a] In $CDCl_3$ solution. Chemical shift values listed are on the δ scale, and are followed by multiplicities and values for coupling constants (in Hz) to ^{31}P. [b] R = Ph for complexes (1) and (3); R = CMe_3 for complex (2). [c] Coupling constant too small for accurate measurement. [d] Resonance listed is for C^1: all other phenyl-carbon resonances have been omitted. [e] Values listed for coupling constants are for $|^1J(P–C) + {}^3J(P–C)|$.

Table 3. Fractional atomic co-ordinates (× 10^4) for $[Ru(CO)_2\{C(C{\equiv}CPh){=}C(Ph)HgCl\}Cl(PMe_2Ph)_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	2 541(1)	1 808(1)	485(1)	C(33)	2 347(19)	1 171(7)	−1 464(12)
P(1)	1 300(5)	2 631(2)	−304(3)	C(34)	2 915(21)	1 055(8)	−1 994(14)
C(11)	2 085(18)	3 091(8)	−932(13)	C(35)	3 693(21)	902(7)	−2 576(14)
C(12)	974(16)	3 125(7)	605(13)	C(36)	3 099(19)	516(9)	−3 379(15)
C(13)	−328(17)	2 515(7)	−1 221(15)	C(37)	3 910(27)	328(8)	−3 930(15)
C(14)	−1 334(27)	2 372(7)	−912(18)	C(38)	5 088(24)	539(10)	−3 676(18)
C(15)	−2 597(24)	2 289(8)	−1 670(22)	C(39)	5 589(21)	896(8)	−2 942(18)
C(16)	−2 784(23)	2 350(9)	−2 609(20)	C(40)	4 954(26)	1 089(8)	−2 372(14)
C(17)	−1 800(30)	2 466(9)	−2 939(18)	C(41)	78(19)	594(9)	−1 991(16)
C(18)	−565(22)	2 536(9)	−2 267(19)	C(42)	439(18)	29(10)	−1 874(14)
P(2)	3 586(5)	927(2)	1 235(3)	C(43)	197(21)	−361(8)	−2 684(20)
C(21)	4 406(16)	510(8)	533(12)	C(44)	−583(23)	−177(10)	−3 615(19)
C(22)	2 506(16)	395(7)	1 472(14)	C(45)	−969(21)	361(11)	−3 785(16)
C(23)	4 980(29)	1 061(7)	2 475(14)	C(46)	−720(24)	766(8)	−2 939(18)
C(24)	6 155(24)	1 090(8)	2 535(20)	Hg	−907(1)	1 061(1)	−428(1)
C(25)	7 090(22)	1 205(10)	3 536(21)	Cl(48)	−2 565(5)	1 097(2)	214(4)
C(26)	6 719(26)	1 337(9)	4 320(18)	C(51)	3 394(17)	2 242(7)	1 689(12)
C(27)	5 490(28)	1 328(11)	4 213(17)	O(52)	3 933(11)	2 531(5)	2 382(9)
C(28)	4 456(22)	1 163(6)	3 314(15)	C(61)	3 841(15)	1 957(8)	−26(13)
C(31)	383(19)	997(8)	−1 156(12)	O(62)	4 670(11)	2 101(5)	−258(9)
C(32)	1 513(20)	1 276(7)	−812(12)	Cl(7)	921(4)	1 639(2)	1 262(3)

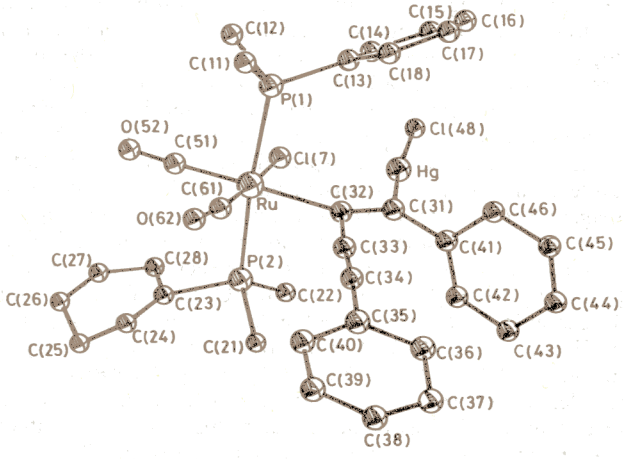


Figure. Structure of complex (1) in the solid state

inspection of the Figure reveals that the deviation from the expected angle of 120° is due to repulsion between the mercury atom and the chloride ligand on the ruthenium. Even with this opening out of the Ru–C(32)–C(31) angle, the 'non-bonded' distance Hg · · · Cl(7) is rather short [2.850(4) Å]. As in the case of $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$, the plane of the alkene grouping is roughly perpendicular to the Ru–P bonds. This allows maximum overlap between the π system of the C=C bond and the one *d* orbital on the metal with which the carbonyl ligand *cis* to the organic ligand cannot interact, but the avoidance of steric interactions with the PMe_2Ph ligands may also be a factor in determining the orientation of the organic ligand. The phenyl ring directly attached to the C=C group is almost at right angles to it, presumably because adoption of the coplanar arrangement which would maximise delocalisation between the two is prevented by the mercury atom. The co-ordination of the mercury [excluding the interaction with Cl(7)] is approximately linear [Cl(48)–Hg–C(31) 173.0(5)°]. The geometry of the

Table 4. Selected bond lengths (Å) and angles (°) for $[Ru(CO)_2\{C(C{\equiv}CPh){=}C(Ph)HgCl\}Cl(PMe_2Ph)_2]$

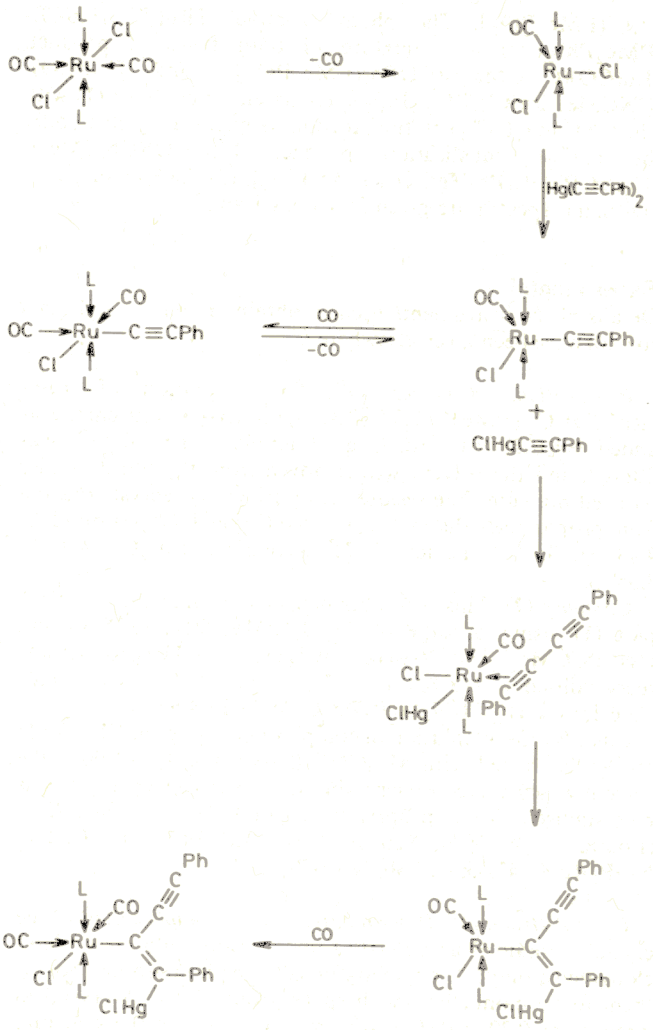
Ru–P(1)	2.374(5)	Hg–C(31)	2.045(23)
Ru–P(2)	2.390(4)	Hg–Cl(48)	2.325(7)
Ru–C(32)	2.163(16)	C(32)–C(33)	1.541(32)
Ru–C(51)	1.909(16)	C(33)–C(34)	1.171(33)
Ru–C(61)	1.860(20)	C(34)–C(35)	1.433(35)
Ru–Cl(7)	2.449(5)	C(51)–O(52)	1.159(19)
C(31)–C(32)	1.332(27)	C(61)–O(62)	1.130(25)
C(31)–C(41)	1.448(27)	Hg · · · Cl(7)	2.850(4)

P(1)–Ru–P(2)	174.2(2)	C(51)–Ru–Cl(7)	83.6(6)
P(1)–Ru–C(32)	90.9(4)	C(61)–Ru–Cl(7)	176.3(5)
P(2)–Ru–C(32)	85.3(4)	Ru–C(51)–O(52)	175.7(16)
P(1)–Ru–C(51)	91.0(5)	Ru–C(61)–O(62)	171.9(16)
P(2)–Ru–C(51)	92.5(5)	Ru–C(32)–C(31)	136.1(17)
C(32)–Ru–C(51)	175.7(8)	Ru–C(32)–C(33)	110.7(12)
P(1)–Ru–C(61)	93.7(6)	C(31)–C(32)–C(33)	113.1(15)
P(2)–Ru–C(61)	90.8(6)	C(32)–C(31)–C(41)	121.4(21)
C(32)–Ru–C(61)	91.0(8)	C(32)–C(33)–C(34)	174.5(18)
C(51)–Ru–C(61)	92.7(8)	C(33)–C(34)–C(35)	175.7(18)
P(1)–Ru–Cl(7)	87.0(2)	Hg–C(31)–C(32)	121.0(14)
P(2)–Ru–Cl(7)	88.8(2)	Hg–C(31)–C(41)	117.4(15)
C(32)–Ru–Cl(7)	92.7(6)	Cl(48)–Hg–C(31)	173.0(5)

–C≡CPh group appears to be normal, with angles at the alkyne carbon atoms [174.5(18) and 175.7(18)°] not far from 180°. The phenyl ring in this group is roughly coplanar with the C=C bond and its substituents, allowing delocalisation throughout the Ru–C(C≡CPh)=C system.

With the structure of complex (**1**) established, and with the aid of a spectrum recorded under conditions of weak noise decoupling, it was possible to interpret the ^{13}C n.m.r. spectrum (Table 2). The resonances for both carbon atoms in the C=C group exhibited triplet splittings due to coupling to the ^{31}P nuclei, as did one of the alkyne-carbon resonances (presumably that for the carbon atom nearer the ruthenium) and the C^1 resonance for one of the phenyl groups (assumed to be the one directly attached to the C=C group). The similarities between the spectra of complexes (**1**) and (**2**) left little doubt that complex (**2**) was $[Ru(CO)_2\{C(C{\equiv}CCMe_3){=}C(CMe_3)HgCl\}Cl(PMe_2Ph)_2]$.

Mechanism of Formation of Complexes (**1**) *and* (**2**).—In the reaction of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ with the alkyne $MeO_2CC{\equiv}CCO_2Me$ the mechanism appears to involve initial dissociation of a carbonyl ligand, formation of an alkyne complex $[Ru(CO)(MeO_2CC{\equiv}CCO_2Me)Cl_2(PMe_2Ph)_2]$, *cis* addition of an Ru–Cl bond across the triple bond of the alkyne, and finally re-association of the CO to give $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$.[3] The geometry of complex (**1**) suggests (see Scheme, where L = PMe_2Ph) a similar *cis* addition of an Ru–HgCl bond across a triple bond in the diyne ligand in $[Ru(CO)(PhC{\equiv}C{-}C{\equiv}CPh)Cl(HgCl)(PMe_2Ph)_2]$. This raises the question of how the diyne ligand is formed. We have shown[1] that *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ reacts with compounds HgR_2 (R = Me or Ph) to form $[Ru(CO)_2R(Cl)(PMe_2Ph)_2]$ and HgR(Cl) by initial loss of a carbonyl ligand, conversion of $[Ru(CO)Cl_2(PMe_2Ph)_2]$ into $[Ru(CO)R(Cl)(PMe_2Ph)_2]$, and re-association of CO. Assuming that the initial stages of the reaction between *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ and $Hg(C{\equiv}CPh)_2$ follow a similar path, it is possible (see Scheme) that the five-co-ordinate species $[Ru(CO)(C{\equiv}CPh)Cl(PMe_2Ph)_2]$ is formed and then reacts further with its co-product, Hg(C≡CPh)Cl, to yield the diyne complex $[Ru(CO)(PhC{\equiv}C{-}C{\equiv}CPh)Cl(HgCl)(PMe_2Ph)_2]$. This reaction could involve either a single-step four-centre rearrangement or a two-step oxidative addition–reduction sequence *via* the intermediate $[Ru(CO)(C{\equiv}CPh)_2Cl(HgCl)(PMe_2Ph)_2]$.



Scheme.

Reactions of Complexes (**1**) *and* (**2**).—The mechanism proposed above for formation of the complexes envisages the addition of an Ru–HgCl bond across a triple bond of the diyne. The mass spectrum of complex (**1**) was dominated by a peak at $m/z = 202$, corresponding to $[PhC{\equiv}C{-}C{\equiv}CPh]^+$, and also contained clusters of peaks corresponding to $[Ru(CO)_2Cl(HgCl)(PMe_2Ph)_2]^+$ and to fragments derived from this ion. This appeared to indicate that the addition was reversed on heating, releasing the diyne and reforming the metal–metal bond. Proton n.m.r. spectra of a $CDCl_3$ solution of complex (**2**) showed that $Me_3CC{\equiv}C{-}C{\equiv}CCMe_3$ was very slowly formed even at ambient temperature, and there was also some deposition of mercury, possibly as a result of the breakdown of the co-product of the diyne, $[Ru(CO)_2Cl(HgCl)(PMe_2Ph)_2]$.

We have found[4] that organoruthenium complexes $[Ru(CO)_2R(Cl)(PMe_2Ph)_2]$ react with Me_3CNC in two quite different ways. Thus $[Ru(CO)_2Me(Cl)(PMe_2Ph)_2]$ forms $[Ru(CO)(CNCMe_3)_2(COMe)(PMe_2Ph)_2]^+$ by combination of methyl and carbonyl ligands and substitution of the chloride ligand, whereas $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$ undergoes carbonyl substitution to yield the compound $[Ru(CO)(CNCMe_3)\{C(CO_2Me){=}C(CO_2Me)$-

$Cl\}Cl(PMe_2Ph)_2]$. The phenyl complex $[Ru(CO)_2Ph(Cl)(PMe_2Ph)_2]$ gives a mixture of both types of product, $[Ru(CO)(CNCMe_3)_2(COPh)(PMe_2Ph)_2]^+$ and $[Ru(CO)(CNCMe_3)Ph(Cl)(PMe_2Ph)_2]$. Treatment of complex (**1**) with Me_3CNC in $CHCl_3$ solution at room temperature yielded only the carbonyl-substitution product, $[Ru(CO)(CNCMe_3)\{C(C{\equiv}CPh){=}C(Ph)HgCl\}Cl(PMe_2Ph)_2]$, (**3**). Details of its i.r. and n.m.r. spectra are given in Tables 1 and 2.

Experimental

Details of the instruments used to obtain i.r., n.m.r., and mass spectra have been given elsewhere.[7,8]

Preparations.—Complex (**1**). To a solution of *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$[9] (0.37 g) in $CHCl_3$ (50 cm^3) was added $Hg(C{\equiv}CPh)_2$[10] (0.33 g). After 96 h the solution was filtered, and the solvent was removed from the filtrate under reduced pressure. The residue was purified by recrystallisation from propanone–ethanol (1:1) at 280 K (yield 44%) (Found: C, 45.3; H, 3.70. Calc. for $C_{34}H_{32}Cl_2HgO_2P_2Ru$: C, 45.0; H, 3.55%).

Complex (**2**). This was obtained in the same way as complex (**1**), using *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ (0.25 g) and $Hg(C{\equiv}CCMe_3)_2$[10] (0.20 g) in $CHCl_3$ (15 cm^3). The product was recrystallised at 243 K (yield 53%) (Found: C, 41.25; H, 4.50. Calc. for $C_{30}H_{40}Cl_2HgO_2P_2Ru$: C, 41.55; H, 4.65%).

Complex (**3**). A solution of complex (**1**) (0.16 g) in $CHCl_3$ (25 cm^3) was treated with Me_3CNC (0.03 cm^3). After 600 h the solvent was removed under reduced pressure. The product was recrystallised from propanone–ethanol (1:1) (yield 72%) (Found: C, 48.35; H, 4.60; N, 1.50. Calc. for $C_{38}H_{41}Cl_2HgNOP_2Ru$: C, 47.45; H, 4.30; N, 1.45%).

Crystal-structure Determination of Complex (**1**).—The crystals, obtained as described above, were colourless plates elongated along *a*. Preliminary precession photographs showed them to be monoclinic, with space group $P2_1/c$. A crystal of dimensions 0.20 × 0.20 × 0.15 mm was used in the structure determination.

Crystal data. $C_{34}H_{32}Cl_2HgO_2P_2Ru$, $M = 907.20$, $a = 11.057(2)$, $b = 23.076(5)$, $c = 14.167(3)$ Å, $\beta = 111.11(2)°$, $U = 3\,374.4$ Å^3, $Z = 4$, $D_c = 1.786$ g cm^{-3}, $F(000) = 1\,760$, $\mu(Cu\text{-}K_\alpha) = 150.2$ cm^{-1}, $\lambda = 1.5418$ Å.

Intensity data were collected on a Hilger and Watts Y290 computer-controlled four-circle diffractometer. Integrated intensities were collected up to $\theta = 51°$ using the ω scanning technique, with 30 steps of 0.02° and a count time per step of 1 s. 3 796 Reflections were recorded, of which 3 275 were unique, and 1 096 with $I < 2\sigma(I)$ were classified as unobserved. The intensities of three reference reflections showed no significant variation over the period of data collection. A semiempirical absorption correction was applied.[11]

The ruthenium and mercury positions were determined by direct methods,[12] and a subsequent Fourier difference synthesis revealed the positions of the other non-hydrogen atoms. The structure was refined by full-matrix least-squares refinement on F.[13] Atomic scattering factors and f' and f'' values were taken from ref. 14. Anisotropic thermal parameters for non-hydrogen atoms were included in the final cycles. Hydrogen positions were estimated geometrically using C–H 1.08 Å. Refinement converged at $R = 0.064$, $R' = 0.066$ for 2 179 observed reflections; $w = 1.0193/[\sigma^2(F_o) + 0.002|F_o|^2]$.

Acknowledgements

We thank the S.E.R.C. for a maintenance grant (to D. R. S.).

References

1 C. F. J. Barnard, J. A. Daniels, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1976, 961.
2 C. F. J. Barnard, J. A. Daniels, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1979, 1331.
3 P. R. Holland, B. Howard, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1983, 231.
4 E. J. Probitts and D. R. Saunders, unpublished work.
5 R. J. Cross and J. Gemmill, *J. Chem. Soc., Dalton Trans.*, 1984, 199.
6 J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc. A*, 1966, 1787.
7 D. R. Saunders, M. Stephenson, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1983, 2473.
8 D. R. Saunders and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1984, 2133.
9 C. F. J. Barnard, J. A. Daniels, J. Jeffery, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1976, 953.
10 J. R. Johnson and W. L. McEwen, *J. Am. Chem. Soc.*, 1926, **48**, 469.
11 A. C. T. North, D. C. Phillips, and F. A. Mathews, *Acta Crystallogr., Sect A.*, 1968, **24**, 35.
12 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J-P. Declercq, and M. M. Woolfson, MULTAN 80, a system of computer programs for the automatic solution of crystal structures from *X*-ray diffraction data, Universities of York and Louvain, 1980.
13 G. M. Sheldrick, SHELX 76, a program system for crystal structure determination, University of Cambridge, 1976.
14 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974.

Received 28*th May* 1985; *Paper* 5/898