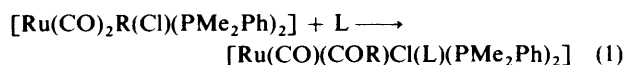


## Structure of a *cis*-Dimetalla-alkene Complex formed by the Reaction of a Ruthenium(II) Complex with Bis(phenylethynyl)mercury(II)<sup>†</sup>

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X-Ray investigation of the product of the reaction of *trans*-[Ru(CO)<sub>2</sub>Cl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] with Hg(C≡CPh)<sub>2</sub> shows it to be [Ru(CO)<sub>2</sub>{C(C≡CPh)=C(Ph)HgCl}Cl(PMe<sub>2</sub>Ph)<sub>2</sub>]. 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)<sub>2</sub>{C(C≡CCMe<sub>3</sub>)=C(CMe<sub>3</sub>)HgCl}Cl(PMe<sub>2</sub>Ph)<sub>2</sub>], prepared in the same way, decomposes slowly in solution even at room temperature, with release of Me<sub>3</sub>CC≡C–C≡CCMe<sub>3</sub> 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.<sup>1–3</sup> 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



L = CO, PMe<sub>2</sub>Ph, or CNCMe<sub>3</sub>) decreases markedly along the sequence R = Me > Ph > C(CO<sub>2</sub>Me)=C(CO<sub>2</sub>Me)Cl.<sup>2–4</sup> 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)<sub>2</sub>Cl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] with HgR<sub>2</sub> (R = Me or Ph) as a means of obtaining methyl and phenyl complexes of ruthenium(II),<sup>1</sup> we investigated the reactions of *trans*-[Ru(CO)<sub>2</sub>Cl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] with Hg(C≡CPh)<sub>2</sub> and Hg(C≡CCMe<sub>3</sub>)<sub>2</sub>. Cross and Gemmill<sup>5</sup> have shown that both chloride ligands in *cis*-[Pt(CO)Cl<sub>2</sub>(PMePh)<sub>2</sub>] can be replaced by reaction with an excess of Hg(C≡CR)<sub>2</sub> (R = Me or Ph), yielding *cis*-[Pt(CO)(C≡CR)<sub>2</sub>(PMePh)<sub>2</sub>], 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)<sub>2</sub>Cl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] and Hg(C≡CR)<sub>2</sub> (R = Ph or CMe<sub>3</sub>).—The reactions were carried out at room temperature in CHCl<sub>3</sub> 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<sub>3</sub>), did not agree with the figures expected for [Ru(CO)<sub>2</sub>(C≡CR)Cl(PMe<sub>2</sub>Ph)<sub>2</sub>] or for [Ru(CO)<sub>2</sub>(C≡CR)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>], but were close to those for simple 1:1 adducts of the reactants. From the i.r. and <sup>1</sup>H 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<sub>2</sub>Ph ligands, and that the Ru–P bonds did not lie in a plane of symmetry through the complexes,<sup>6</sup> but the spectra

Table 1. Infrared<sup>a</sup> and <sup>1</sup>H n.m.r.<sup>b</sup> spectra of complexes

Complex	$\tilde{\nu}(\text{C}=\text{O})/\text{cm}^{-1}$	$\delta/\text{p.p.m.}$	Assignment
(1)	2 055	1.96 (t, 6)	PMe <sub>2</sub> Ph
	1 980	1.93 (t, 6)	PMe <sub>2</sub> Ph
(2)	2 050	1.91 (t, 6)	PMe <sub>2</sub> Ph
		1.84 (t, 6)	PMe <sub>2</sub> Ph
	1 980	1.26 (s, 9)	CMe <sub>3</sub>
		1.21 (s, 9)	CMe <sub>3</sub>
(3) <sup>c</sup>	1 960	1.90 (t, 6)	PMe <sub>2</sub> Ph
		1.85 (t, 6)	PMe <sub>2</sub> Ph
		1.14 (s, 9)	CNCMe <sub>3</sub>

<sup>a</sup> In CHCl<sub>3</sub> solution. Only carbonyl resonances are listed. <sup>b</sup> In CDCl<sub>3</sub> solution. Resonances due to aromatic ring protons are not included. Multiplicities and relative areas are given after the chemical shift values. For PMe<sub>2</sub>Ph methyl protons, <sup>2</sup>J(P–H) + <sup>4</sup>J(P–H) = ca. 7.5 Hz. <sup>c</sup> For the nitrile group,  $\tilde{\nu}(\text{C}=\text{N})$  at 2 175 cm<sup>-1</sup>.

provided little further information. The <sup>13</sup>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)<sub>2</sub>{C(C≡CPh)=C(Ph)HgCl}Cl(PMe<sub>2</sub>Ph)<sub>2</sub>].

*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<sub>2</sub>Ph 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≡CPh)<sub>2</sub> 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)<sub>2</sub>{C(CO<sub>2</sub>Me)=C(CO<sub>2</sub>Me)Cl}Cl(PMe<sub>2</sub>Ph)<sub>2</sub>].<sup>3</sup> 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)<sub>2</sub>{C(C≡CPh)=C(Ph)HgCl}Cl(PMe<sub>2</sub>Ph)<sub>2</sub>], 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:

<sup>†</sup> 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.

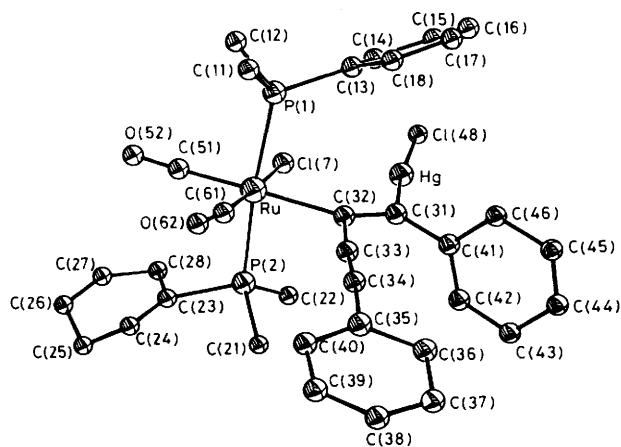
**Table 2.** Carbon-13 n.m.r. spectra<sup>a</sup> of complexes

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 <sup>b</sup>
147.7 (t, 1.8)		148.8 (t) <sup>c</sup>	C(C≡CPh)=C(Ph)HgCl <sup>d</sup>
144.1 (t, 14.2)	155.8 (t, 13.8)	147.5 (t, 13.4)	C(C≡CR)=C(R)HgCl <sup>b</sup>
124.7 (s)		124.6 (s)	C(C≡CPh)=C(Ph)HgCl <sup>d</sup>
99.5 (t, 2.3)	90.1 (t, 2.0)	100.5 (t) <sup>c</sup>	C(C≡CR)=C(R)HgCl <sup>b</sup>
98.0 (s)	111.3 (s)	97.8 (s)	C(C≡CR)=C(R)HgCl <sup>b</sup>
		57.2 (s)	CNCMe <sub>3</sub>
		30.2 (s)	CNCMe <sub>3</sub>
	41.6 (s)		C(C≡CCMe <sub>3</sub> )=C(CMe <sub>3</sub> )HgCl
	34.4 (s)		
	32.4 (s)		
	30.8 (s)		
14.6 (t, 33.0)	14.4 (t, 33.0)	14.8 (t, 31.1)	C(C≡CCMe <sub>3</sub> )=C(CMe <sub>3</sub> )HgCl
14.1 (t, 33.0)	13.6 (t, 33.1)	13.8 (t, 31.8)	C(C≡CCMe <sub>3</sub> )=C(CMe <sub>3</sub> )HgCl
			PMe <sub>2</sub> Ph <sup>e</sup>
			PMe <sub>2</sub> Ph <sup>e</sup>

<sup>a</sup> In CDCl<sub>3</sub> solution. Chemical shift values listed are on the δ scale, and are followed by multiplicities and values for coupling constants (in Hz) to <sup>31</sup>P. <sup>b</sup> R = Ph for complexes (1) and (3); R = CMe<sub>3</sub> for complex (2). <sup>c</sup> Coupling constant too small for accurate measurement. <sup>d</sup> Resonance listed is for C<sup>1</sup>; all other phenyl-carbon resonances have been omitted. <sup>e</sup> Values listed for coupling constants are for <sup>1</sup>J(P-C) + <sup>3</sup>J(P-C).

**Table 3.** Fractional atomic co-ordinates (× 10<sup>4</sup>) for [Ru(CO)<sub>2</sub>{C(C≡CPh)=C(Ph)HgCl}Cl(PMe<sub>2</sub>Ph)<sub>2</sub>]

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)<sub>2</sub>{C(CO<sub>2</sub>Me)=C(CO<sub>2</sub>Me)Cl}Cl(PMe<sub>2</sub>Ph)<sub>2</sub>], 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<sub>2</sub>Ph 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



Cl}Cl(PMe<sub>2</sub>Ph)<sub>2</sub>]. The phenyl complex [Ru(CO)<sub>2</sub>Ph(Cl)-(PMe<sub>2</sub>Ph)<sub>2</sub>] gives a mixture of both types of product, [Ru(CO)(CNCMe<sub>3</sub>)<sub>2</sub>(COPh)(PMe<sub>2</sub>Ph)<sub>2</sub>]<sup>+</sup> and [Ru(CO)-(CNCMe<sub>3</sub>)Ph(Cl)(PMe<sub>2</sub>Ph)<sub>2</sub>]. Treatment of complex (1) with Me<sub>3</sub>CNC in CHCl<sub>3</sub> solution at room temperature yielded only the carbonyl-substitution product, [Ru(CO)(CNCMe<sub>3</sub>)-{C(C≡CPh)=C(Ph)HgCl}Cl(PMe<sub>2</sub>Ph)<sub>2</sub>], (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.<sup>7,8</sup>

**Preparations.**—**Complex (1).** To a solution of *trans*-[Ru(CO)<sub>2</sub>Cl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]<sup>9</sup> (0.37 g) in CHCl<sub>3</sub> (50 cm<sup>3</sup>) was added Hg(C≡CPh)<sub>2</sub><sup>10</sup> (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<sub>34</sub>H<sub>32</sub>Cl<sub>2</sub>HgO<sub>2</sub>P<sub>2</sub>Ru: C, 45.0; H, 3.55%).

**Complex (2).** This was obtained in the same way as complex (1), using *trans*-[Ru(CO)<sub>2</sub>Cl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (0.25 g) and Hg(C≡CMe)<sub>2</sub><sup>10</sup> (0.20 g) in CHCl<sub>3</sub> (15 cm<sup>3</sup>). The product was recrystallised at 243 K (yield 53%) (Found: C, 41.25; H, 4.50. Calc. for C<sub>30</sub>H<sub>40</sub>Cl<sub>2</sub>HgO<sub>2</sub>P<sub>2</sub>Ru: C, 41.55; H, 4.65%).

**Complex (3).** A solution of complex (1) (0.16 g) in CHCl<sub>3</sub> (25 cm<sup>3</sup>) was treated with Me<sub>3</sub>CNC (0.03 cm<sup>3</sup>). 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<sub>38</sub>H<sub>41</sub>Cl<sub>2</sub>HgNOP<sub>2</sub>Ru: 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 *P*2<sub>1</sub>/*c*. A crystal of dimensions 0.20 × 0.20 × 0.15 mm was used in the structure determination.

**Crystal data.** C<sub>34</sub>H<sub>32</sub>Cl<sub>2</sub>HgO<sub>2</sub>P<sub>2</sub>Ru, *M* = 907.20, *a* = 11.057(2), *b* = 23.076(5), *c* = 14.167(3) Å, β = 111.11(2)°, *U* = 3 374.4 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.786 g cm<sup>-3</sup>, *F*(000) = 1 760, μ(Cu-*K*<sub>α</sub>) = 150.2 cm<sup>-1</sup>, λ = 1.5418 Å.

Intensity data were collected on a Hilger and Watts Y290 computer-controlled four-circle diffractometer. Integrated intensities were collected up to θ = 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* < 2σ(*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.<sup>11</sup>

The ruthenium and mercury positions were determined by direct methods,<sup>12</sup> 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*.<sup>13</sup> 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/[σ<sup>2</sup>(*F*<sub>o</sub>) + 0.002|*F*<sub>o</sub>|<sup>2</sup>].

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