Metal-to-Metal Transfer of Vinyl Ligands: Ruthenium-catalysed Synthesis of Vinylmercury Compounds *

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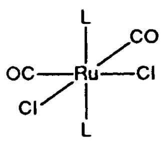
Vinyl ligands are readily transferred from ruthenium(II) to mercury(II), giving mono- or di-vinyl mercury complexes, depending on the vinyl ligand and the reaction conditions used. In conjunction with steps involving aryl ligand transfer from mercury to ruthenium and insertion of $MeO_2CC{\equiv}CCO_2Me$ into the ruthenium–aryl bond, this constitutes a ruthenium-catalysed route for the conversion of $[HgR_2]$ (R = aryl) into $[Hg\{C(CO_2Me)=C(CO_2Me)R\}R]$ and $[Hg\{C(CO_2Me)=C(CO_2Me)R\}_2]$, with alkyne insertion as the rate-limiting step. The mechanism of transfer alters according to the nature of the vinyl ligand. Reaction of $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)H\}Cl(PMe_2Ph)_2]$ with $HgCl_2$ does *not* lead to vinyl transfer: the product was characterized by X-ray crystallography as $[Ru(CO)_2\{C(CO_2Me)=C(COOMe)H\}(PMe_2Ph)_2][HgCl_3]$.

The transfer of an organic ligand from mercury to a transition metal is a common preparative route in organometallic chemistry. We have used it as a means of obtaining ruthenium complexes $[Ru(CO)_2R(Cl)(PMe_2Ph)_2]$ (R = methyl[1] or aryl[1,2]) from $[HgR_2]$ and either *trans*- or all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ {the structures of the isomers of $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ are shown, where L = PMe_2Ph}.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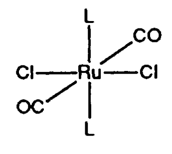
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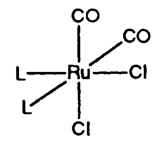
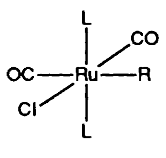

all-*cis*

An advantage of this synthetic route is that only one chloride ligand in $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ is replaced, even if an excess of $[HgR_2]$ is employed.[1] In these reactions the organic ligand is exchanged for a halide ligand, but Roper and Wright[3] have shown that $[Ru(CO)Cl(H)(PPh_3)_3]$ reacts with $[Hg(C_6H_4Me\text{-}4)_2]$ to yield $[Ru(CO)(C_6H_4Me\text{-}4)Cl(PPh_3)_2]$: here the chloride ligand is not transferred to mercury, and the co-products are methylbenzene and elemental mercury. Transfer of a phenyl ligand from mercury to ruthenium has also been proposed by Heck[4] as a preliminary step in the ruthenium-catalysed phenylation of alkenes by $[HgPh(Cl)]$.

The reverse process, in which an organic ligand moves from an organotransition-metal compound to mercury(II), is also well known. In recent years, particular attention has been focused on transfer from cobalt(III), which has been implicated as a possible route for the formation of highly toxic organomercury compounds in the environment.[5] Transfer from ruthenium(II) to mercury is certainly easy to accomplish: thus, for example, $[Ru(CO)_2Me(\eta^5\text{-}C_5H_5)]$ reacts with $HgCl_2$ to yield $[Ru(CO)_2(\eta^5\text{-}C_5H_5)Cl]$ and $[HgMe(Cl)]$.[6] The reversibility of the transfer is highlighted by the reaction between $[Ru(CO)Cl_2(PMe_2Ph)_3]$ and $[HgPh_2]$: the $[HgPh_2]$ catalyses the isomerization of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ by a two-step process in which the intermediates are $[Ru(CO)Ph(Cl)(PMe_2Ph)_3]$ and $[HgPh(Cl)]$.[1]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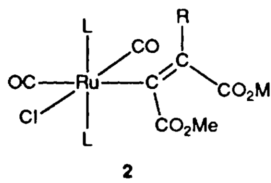
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In this paper a sequence is described in which an organic ligand is transferred from mercury to ruthenium, modified on the ruthenium, and then transferred back to mercury. It is further shown that this sequence represents a route for the ruthenium-catalysed synthesis of vinylmercury complexes. Finally, the reactions of several vinyl complexes of ruthenium(II) with $HgCl_2$ are reported, together with an investigation by X-ray crystallography of the structure of one of the products.

Results and Discussion

Details of the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of new complexes can be found in Tables 1 and 2 respectively.

(*i*) *The Catalytic Formation of Vinylmercury Complexes.*—Recently we reported[7] that aryl complexes of ruthenium $[Ru(CO)_2R(Cl)(PMe_2Ph)_2]$ (R = Ph, **1a**; $4\text{-}ClC_6H_4$, **1b**; $4\text{-}MeC_6H_4$, **1c**; or $4\text{-}MeOC_6H_4$, **1d**) reacted with $MeO_2CC{\equiv}CCO_2Me$ to yield vinyl complexes $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)R\}Cl(PMe_2Ph)_2]$ **2a**–**2d**, by insertion of the alkyne into the metal–aryl bond. The structures of **1** and **2** are shown, where L = PMe_2Ph. The complexes $[Ru(CO)_2R(Cl)(PMe_2Ph)_2]$ used for these reactions had been prepared from *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ and $[HgR_2]$ and purified by column chromatography. This removed the bulk of the organomercury compounds {$[HgR(Cl)]$ and excess of $[HgR_2]$}, but complete removal proved difficult. At the start of the work we did not anticipate that the presence of residual small quantities of organomercury compounds would affect the subsequent

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Proton NMR spectra of new complexes[a]

Compound	δ	Assignment
$[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}_2]$ **3a**	3.78 (s, 3)	CO_2Me
	3.70 (s, 3)	CO_2Me
$[Hg\{C(CO_2Me)=C(CO_2Me)(C_6H_4Cl\text{-}4)\}_2]$ **3b**	3.79 (s, 3)	CO_2Me
	3.73 (s, 3)	CO_2Me
$[Hg\{C(CO_2Me)=C(CO_2Me)(C_6H_4Me\text{-}4)\}_2]$ **3c**	3.79 (s, 3)	CO_2Me
	3.72 (s, 3)	CO_2Me
	2.35 (s, 3)	$C_6H_4\mathit{Me}$
$[Hg\{C(CO_2Me)=C(CO_2Me)(C_6H_4OMe\text{-}4)\}_2]$ **3d**	3.80 (s, 3)	CO_2Me
	3.80 (s, 3)	$C_6H_4O\mathit{Me}$
	3.73 (s, 3)	CO_2Me
$[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}Ph]$ **4a**	3.85 (s, 3)	CO_2Me
	3.81 (s, 3)	CO_2Me
$[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}Cl]$	3.86 (s, 3)	CO_2Me
	3.82 (s, 3)	CO_2Me
$[Hg\{C(CO_2Me)=C(CO_2Me)Cl\}Cl]$	3.88 (s, 3)	CO_2Me
	3.81 (s, 3)	CO_2Me
$[Hg\{C(CO_2Me)=C(CO_2Me)Cl\}_2]$	3.91 (s, 3)	CO_2Me
	3.86 (s, 3)	CO_2Me
$[Ru(CO)_2\{C(CO_2Me)=C(COOMe)H\}(PMe_2Ph)_2][HgCl_3]$ **5**	6.37 (t, 1)[b]	RuC=CH
	3.90 (s, 3)	CO_2Me
	3.42 (s, 3)	CO_2Me
	2.03 (t, 6)[c]	$P\mathit{Me}_2Ph$
	1.86 (t, 6)[c]	$P\mathit{Me}_2Ph$
$[Ru(CO)\{C(CO_2Me)=C(COOMe)H\}Cl(PMe_2Ph)_2]$ **6**[d]	6.30 (t, 1)[e]	RuC=CH
	3.49 (s, 3)	CO_2Me
	2.78 (s, 3)	CO_2Me
	1.72 (t, 6)[c]	$P\mathit{Me}_2Ph$
	1.53 (t, 6)[c]	$P\mathit{Me}_2Ph$
$[Hg\{C(CO_2Me)=C(CO_2Me)H\}_2]$	6.15 (s, 1)	HgC=CH
	3.84 (s, 3)	CO_2Me
	3.75 (s, 3)	CO_2Me
$[Hg(CH=CHCMe_3)Cl]$	5.93 (d, 1)[f]	HgC*H*=CH
	5.75 (d, 1)[f]	HgCH=C*H*
	1.05 (s, 9)	CMe_3
$[Hg(CH=CHPh)Cl]$	7.01 (d, 1)[g]	HgC*H*-CH
	6.81 (d, 1)[g]	HgCH=C*H*

[a] In $CDCl_3$ solution unless stated otherwise. Resonances due to aromatic ring protons have been omitted. [b] $|^4J(P\text{-}H)| = 2.6$ Hz. [c] $|^2J(P\text{-}H) + {}^4J(P\text{-}H)| = ca.\ 7.5$ Hz. [d] In C_6D_6 solution. [e] $|^4J(P\text{-}H)| = 1.5$ Hz. [f] $|^3J(H\text{-}H)| = 17.7$ Hz. [g] $|^3J(H\text{-}H)| = 18.0$ Hz.

reactions of complexes **1a**–**1d**, but when **2a**–**2d** were purified by column chromatography by-products **3a**–**3d** were obtained in small quantities. It was clear from their ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra that compounds **3a**–**3d** contained the vinyl group $-C(CO_2Me)=C(CO_2Me)(C_6H_4X\text{-}4)$, and elemental analysis established that they were the organomercury compounds $[Hg\{C(CO_2Me)=C(CO_2Me)R\}_2]$ (R = Ph, **3a**; $4\text{-}ClC_6H_4$, **3b**; $4\text{-}MeC_6H_4$, **3c**; or $4\text{-}MeOC_6H_4$, **3d**).

The simplest explanation for the formation of complexes **3a**–**3d** was that they resulted from direct reactions of $[HgR_2]$ with $MeO_2CC\equiv CCO_2Me$. This was, however, ruled out by showing that there was no reaction between $[HgPh_2]$ and the alkyne under the appropriate reaction conditions ($CHCl_3$ solution, 323 K). The alternative seemed to be that ligand exchange occurred between ruthenium and mercury, with vinyl ligands being transferred from ruthenium to mercury in exchange for chloride and/or aryl ligands. As a check to determine whether such ligand exchange would occur, a reaction between complex **2b** and $HgCl_2$ in a 2:1 molar ratio was carried out in $CHCl_3$ solution at 323 K in a closed flask. The products were identified by $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectroscopy as all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ and complex **3b**. A similar reaction using **2c** yielded **3c**.

Since all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ is known to react with $[HgPh_2]$ to form **1a**, we concluded that it should be possible to set up a catalytic system for the synthesis of the vinylmercury complexes **3a**–**3d**. As a test, a reaction between $[HgPh_2]$ and $MeO_2CC\equiv CCO_2Me$ was carried out, again in a closed system, at 323 K in $CDCl_3$ in the presence of a small quantity of $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$. The molar ratio of the reactants was 10:21:1, and the ruthenium complex was added in the form of the *trans* isomer, which is easier to prepare than the all-*cis* isomer that was expected to feature in the catalytic cycle. Both isomers react with $[HgPh_2]$ to form **1a** and hence initiate the cycle, so the choice between them is immaterial.

The reaction was monitored by $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectroscopy. From the resonances in the CO_2Me region of the ^1H spectrum it could be seen that the concentration of $MeO_2CC\equiv CCO_2Me$ decreased steadily, while that of a new species, **4a**, increased, reached a maximum and then declined. Resonances due to $[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}_2]$ **3a**, although not visible in the early stages of the reaction, subsequently increased steadily in area. From the $^{31}P\text{-}\{^1H\}$ NMR spectra it was evident that all the *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ was quickly consumed. In the early stages virtually all the ruthenium was present as **1a**, but two other species, $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)(C_6H_4)\}(PMe_2Ph)_2]$[8] and *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$, were slowly formed. The reason for their formation was already known: the former results from slow HCl elimination from **2a**, and the latter is a product of HCl attack on **1a**.[7] Each was tested for catalytic activity by adding it to a mixture of $[HgPh_2]$ and $MeO_2CC\equiv CCO_2Me$, and found to be inactive: thus their appearance represents a slow decrease in the amount of active catalyst present. The inactivity of *cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ is not surprising since, unlike the *trans* and all-*cis* isomers, it does not react with $[HgPh_2]$.[1] The fact that the only ruthenium species actually involved in the catalytic cycle to be detected was **1a** indicates that the slow step

Table 2 ^{13}C-$\{^1H\}$ NMR spectra of new complexes[a]

				Aryl group					
Compound	C=C	$\mathit{C}\mathrm{O_2Me}$	$\mathrm{CO_2}\mathit{Me}$	C^1	$C^{2,6}$	$C^{3,5}$	C^4	X	Others
$[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}_2]$ **3a**	162.4	170.1	52.5	138.7	127.4	129.1	129.5		
	152.2	169.4	52.3						
$[Hg\{C(CO_2Me)=C(CO_2Me)(C_6H_4Cl\text{-}4)\}_2]$ **3b**	163.3	169.8	52.7	136.9	128.7	128.9	135.7		
	150.6	168.8	52.4						
$[Hg\{C(CO_2Me)=C(CO_2Me)(C_6H_4Me\text{-}4)\}_2]$ **3c**	161.4	170.3	52.6	135.7	127.2	129.7	139.8	21.3	
	152.5	169.7	52.3						
$[Hg\{C(CO_2Me)=C(CO_2Me)(C_6H_4OMe\text{-}4)\}_2]$ **3d**	160.3	170.3	52.5	130.8	128.7	114.4	160.8	55.3	
	152.6	170.0	52.3						
$[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}Ph]$ **4a**	168.9	172.0	52.6	139.4	128.0	129.1	129.3		
	163.7	171.5	52.3	148.5	137.2	128.8	128.8		
$[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}Cl]$	154.3	168.3	53.1	138.0	127.4	129.6	130.7		
	147.1	166.5	53.0						
$[Hg\{C(CO_2Me)=C(CO_2Me)Cl\}Cl]$	150.6	165.4	53.8						
	139.3	162.6	53.3						
$[Hg\{C(CO_2Me)=C(CO_2Me)Cl\}_2]$	165.6	169.6	54.5						
	131.5	166.0	52.5						
$[Ru(CO)_2\{C(CO_2Me)=C(COOMe)H\}(PMe_2Ph)_2]$-$[HgCl_3]$ **5**	203.1 (t)[b]	182.5	55.6						196.4 (t)[d]
	127.9 (t)[c]	171.4	52.4						191.8 (t)[d]
									16.1 (t)[e]
									13.4 (t)[e]
$[Ru(CO)\{C(CO_2Me)=C(COOMe)H\}Cl(PMe_2Ph)_2]$ **6**[f]	204.7 (t)[g]	179.2	52.7						217.1 (t)[d]
	119.6 (t)[h]	174.6	51.0						13.6 (t)[e]
									13.1 (t)[e]
$[Hg\{C(CO_2Me)=C(CO_2Me)H\}_2]$	173.1	172.4	52.4						
	131.3	164.2	52.1						
$[Hg(CH=CHCMe_3)Cl]$	160.7								36.4[i]
	127.9								29.0[j]
$[Hg(CH=CHPh)Cl]$[k]	147.0			138.7	127.1	129.5	129.0		
	136.9								

[a] In $CDCl_3$ solution unless stated otherwise. Resonances due to phenyl groups in PMe_2Ph ligands have been omitted. Unless otherwise indicated, resonances were singlets. [b] $|^2J(P\text{–}C)| = 11.9$ Hz. [c] $|^3J(P\text{–}C)| = 3.6$ Hz. [d] RuCO, $|^2J(P\text{–}C)| =$ *ca.* 10 Hz. [e] PMe_2Ph, $|^1J(P\text{–}C) + {}^3J(P\text{–}C)| =$ *ca.* 32 Hz. [f] In C_6D_6 solution. [g] $|^2J(P\text{–}C)| = 15.0$ Hz. [h] $|^3J(P\text{–}C)| = 2.0$ Hz. [i] $\mathit{C}\mathrm{Me_3}$. [j] $\mathrm{C}\mathit{Me_3}$. [k] In CD_3COCD_3 solution.

in the cycle is the insertion of $MeO_2CC\equiv CCO_2Me$ into the ruthenium–phenyl bond of **1a**.

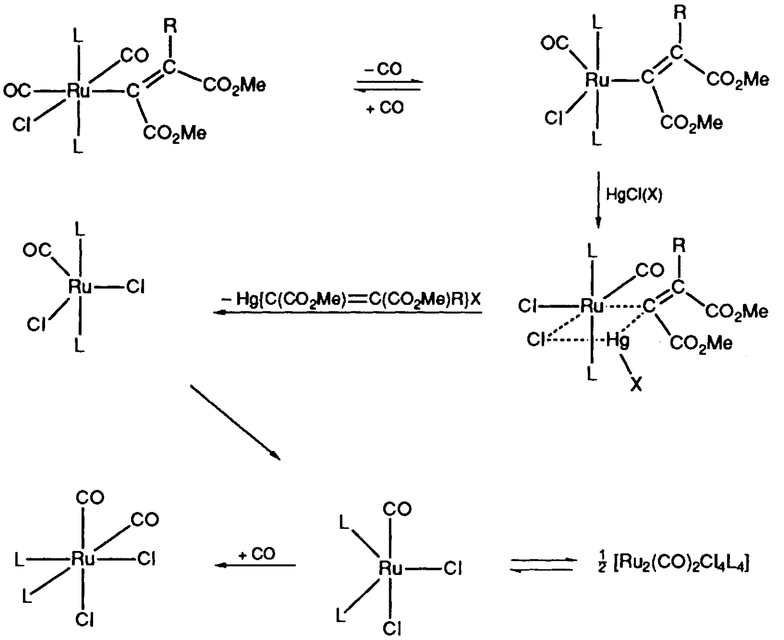
Complex **4a** (see above) was isolated from a similar reaction, halted at the point where the concentration of **4a** was at its maximum. After purification by column chromatography it was identified by elemental analysis and NMR spectroscopy as $[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}Ph]$, a logical intermediate in the conversion of $[HgPh_2]$ into $[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}_2]$. Thus the catalytic cycle appears to consist of two successive sequences, in each of which an aryl ligand is transferred from mercury to ruthenium, a molecule of $MeO_2CC\equiv CCO_2Me$ is inserted into the ruthenium–aryl bond, and the resulting ligand is transferred back to mercury. We have discussed the mechanisms of the first two steps in previous papers,[1,7] and the following section describes studies of the final step, the transfer of the vinyl ligand from ruthenium to mercury.

(*ii*) *The Stereochemistry and Mechanism of Transfer of Vinyl Ligands from Ruthenium to Mercury.*—A series of reactions between ruthenium(II) vinyl complexes $[Ru(CO)_2(CR=CRR')Cl(PMe_2Ph)_2]$ and $HgCl_2$ was carried out in propanone solution. Propanone was used as it is a better solvent for $HgCl_2$ and complexes $[Hg(CR=CRR')Cl]$ than is $CHCl_3$. The reaction between **2c** and $HgCl_2$ in a 2:1 molar ratio in a closed system at 323 K yielded **3c** and all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$, as expected. A similar reaction carried out under CO instead of N_2 was much slower, indicating severe inhibition by CO. A reaction between **2a** and $HgCl_2$ in an open system under N_2 yielded **3a** and a mixture of two isomers of the dimeric species $[Ru_2(CO)_2Cl_4(PMe_2Ph)_4]$,[9] both of which were converted into all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$ on treatment with CO. From these results we inferred that the transfer of the vinyl ligand was preceded by loss of a carbonyl ligand from $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)R\}Cl(PMe_2Ph)_2]$ (R = Ph or $4\text{-}MeC_6H_4$).

When the reaction between complex **2a** and $HgCl_2$ was repeated with a 1:1 molar ratio of the reactants the same ruthenium products were obtained: the mercury product was isolated and shown by elemental analysis and NMR spectroscopy to be $[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}Cl]$. Similar experiments were carried out using the complex $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$.[10] In an open system under N_2 the complex was converted by $HgCl_2$ into $[Ru_2(CO)_2Cl_4(PMe_2Ph)_4]$. Using equimolar quantities of the reactants the other product was $[Hg\{C(CO_2Me)=C(CO_2Me)Cl\}Cl]$; with a 1:2 Hg:Ru ratio, $[Hg\{C(CO_2Me)=C(CO_2Me)Cl\}_2]$ was obtained. Both mercury complexes were fully characterized.

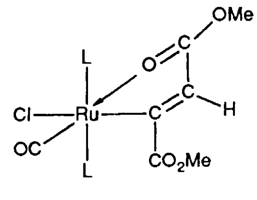
A possible mechanism for these reactions is shown in Scheme 1, where L = PMe_2Ph, R = Ph, $4\text{-}ClC_6H_4$, $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$ or Cl, and X = Cl, R or $C(CO_2Me)=C(CO_2Me)R$. The change in the ligand arrangement around the ruthenium which accompanies the reaction is attributable to the rearrangement of the five-co-ordinate $[Ru(CO)Cl_2(PMe_2Ph)_2]$, a step proposed in our earlier study[9] of the isomerization of $[Ru(CO)_2Cl_2(PMe_2Ph)_2]$.

From X-ray work,[10] the CO_2Me groups in the vinyl ligand of $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$ are known to be mutually *cis*, and the geometry of complexes **2a**–**2d** is believed to be the same.[7,8] In the case of $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)H\}Cl(PMe_2Ph)_2]$, however, the magnitude of the coupling constant between the β-hydrogen and the carbonyl carbon in the α-CO_2Me group [$|^3J(C\text{–}H)| = 9.5$ Hz][11] indicates that the CO_2Me groups are mutually *trans*.[12] Interestingly, this complex reacted with $HgCl_2$ quite differently from those discussed above. Addition of $HgCl_2$ to a



Scheme 1

CD$_3$COCD$_3$ solution of [Ru(CO)$_2${C(CO$_2$Me)=C(CO$_2$Me)H}Cl(PMe$_2$Ph)$_2$] at room temperature resulted in immediate changes in the ^{31}P-{^{1}H} and ^{1}H NMR spectra of the solution, and from a solution containing equimolar amounts of the reactants a complex **5** was obtained which analysed as a 1:1 adduct of the two reactants. Adduct formation had virtually no effect on the resonance for the β-hydrogen in the vinyl ligand, which retained a triplet splitting due to coupling to the ^{31}P nuclei in the PMe$_2$Ph ligands, implying that the ligand had *not* been transferred from ruthenium to mercury. The most marked difference between the ^{1}H NMR spectra of **5** and the parent ruthenium complex [Ru(CO)$_2${C(CO$_2$Me)=C(CO$_2$Me)H}Cl(PMe$_2$Ph)$_2$] was in the chemical shift for the methyl protons in one of the CO$_2$Me groups. The reason for this was revealed by an X-ray investigation of the structure of **5** (see below), which showed it to be an ionic species [Ru(CO)$_2${C(CO$_2$Me)=C(COOMe)H}(PMe$_2$Ph)$_2$][HgCl$_3$] resulting from the transfer of a *chloride* ligand from ruthenium to mercury and the occupation of the vacated co-ordination site on the ruthenium by the carbonyl oxygen atom of the β-CO$_2$Me substituent in the vinyl ligand. The link between the change in reaction pathway and the stereochemistry of the vinyl ligand seems clear: only in this complex is the β-CO$_2$Me substituent *cis* to the ruthenium, allowing ring closure to occur on loss of the chloride ligand. Even when the propanone solution of **5** was heated the vinyl ligand was not transferred to mercury: the ruthenium product isolated from the reaction gave elemental analysis results and NMR spectra consistent with the formula [Ru(CO){C(CO$_2$Me)=C(COOMe)H}Cl(PMe$_2$Ph)$_2$] and the structure shown as **6**, where L = PMe$_2$Ph, or a similar structure with the positions of the carbonyl and chloride ligands reversed. Conversion of **5** into **6** involves the replacement of a carbonyl ligand by the chloride ligand returned from mercury to ruthenium.



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The case for a link between the course of the reaction and the position of the carboxylate groups was strengthened by a study of the reaction between HgCl$_2$ and [Ru(CO){C(CO$_2$Me)=C(CO$_2$Me)H}Cl(PMe$_2$Ph)$_3$], for which the value for $|^3J$(C–H)$|$ (see above) is 14.8 Hz,[11] indicating that the CO$_2$Me groups are mutually *cis*.[12] There was no evidence of reaction when the two compounds were mixed in propanone solution at room temperature, but when the two (Hg:Ru molar ratio 1:2) were heated in propanone solution the vinyl complex [Hg{C(CO$_2$Me)=C(CO$_2$Me)H}$_2$] was obtained and fully characterized. The value for $|^3J$(C–H)$|$, obtained from a proton-coupled ^{13}C NMR spectrum of the complex, was 14.7 Hz, implying that the vinyl group had retained its stereochemistry in the transfer from ruthenium to mercury.

Other vinyl ligands may also be transferred from ruthenium to mercury. Reactions between equimolar quantities of [Ru(CO)$_2$(CH=CHR)Cl(PMe$_2$Ph)$_2$] (R = CMe$_3$ or Ph)[13] and HgCl$_2$ in propanone solution at 323 K in a closed flask yielded the mercury complexes [Hg(CH=CHR)Cl] which were isolated and fully characterized. In the ^{1}H NMR spectra of the complexes the values for the coupling constant $|^3J$(H–H)$|$ between the two vinyl protons were 17.7 (R = CMe$_3$) and 18.0 Hz (R = Ph). These values are similar to those for the starting materials [Ru(CO)$_2$(CH=CHR)Cl(PMe$_2$Ph)$_2$],[13] and indicate that the vinyl protons are mutually *trans*[14,15] and that the vinyl groups have retained their stereochemistry in the transfer.

There were, however, clear differences between the reactions involving the complexes [Ru(CO)$_2${C(CO$_2$Me)=C(CO$_2$Me)R}Cl(PMe$_2$Ph)$_2$] and those with [Ru(CO)$_2$(CH=CHR)Cl(PMe$_2$Ph)$_2$]. First, the ruthenium product of the reactions with the latter complexes was *cis*-[Ru(CO)$_2$Cl$_2$(PMe$_2$Ph)$_2$], not the all-*cis* isomer. Secondly, a study of the reaction of [Ru(CO)$_2$(CH=CHCMe$_3$)Cl(PMe$_2$Ph)$_2$] with HgCl$_2$ showed that it was *not* inhibited by CO. Finally, the use of an excess of the complexes [Ru(CO)$_2$(CH=CHR)Cl(PMe$_2$Ph)$_2$] did not lead to the formation of [Hg(CH=CHR)$_2$]: only one vinyl group was transferred to the mercury. Both the absence of inhibition by CO and the formation of the *cis* rather than the all-*cis* isomer of [Ru(CO)$_2$Cl$_2$(PMe$_2$Ph)$_2$] imply a change in reaction mechanism, suggesting that a carbonyl ligand is not lost from the ruthenium complex prior to the exchange of vinyl and

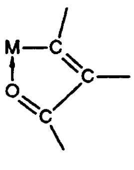
Table 3 Fractional atomic coordinates for complex **5**

Atom	*x*	*y*	*z*
Hg	−0.284 97(7)	0.000 14(6)	0.270 45(7)
Ru	0.165 0(1)	0.205 91(8)	0.155 0(1)
Cl(1)	−0.151 5(5)	−0.003 1(4)	0.174 5(4)
Cl(2)	−0.304 1(6)	−0.102 2(5)	0.374 8(6)
Cl(3)	−0.401 0(6)	0.102 3(4)	0.268 7(6)
P(1)	0.067 2(4)	0.199 4(3)	0.284 0(4)
P(2)	0.270 1(4)	0.208 1(3)	0.029 7(4)
O(1)	0.253 3(8)	0.296 6(6)	0.228 9(8)
O(2)	0.401(1)	0.322 4(7)	0.346(1)
O(3)	0.358(1)	0.055 8(7)	0.359(1)
O(4)	0.285(1)	0.029 6(7)	0.199(1)
O(5)	0.005(1)	0.313(1)	0.033(1)
O(6)	0.056(1)	0.069 3(8)	0.060(1)
C(1)	−0.076(1)	0.200(1)	0.239(2)
C(2)	0.092(2)	0.118(1)	0.361(2)
C(3)	0.092(2)	0.278(1)	0.367(2)
C(4)	0.052(2)	0.345(1)	0.333(2)
C(5)	0.075(2)	0.406(1)	0.392(2)
C(6)	0.138(3)	0.404(2)	0.485(2)
C(7)	0.175(2)	0.338(2)	0.520(2)
C(8)	0.157(2)	0.274(1)	0.464(2)
C(9)	0.194(2)	0.212(1)	−0.097(2)
C(10)	0.357(2)	0.131(1)	0.027(2)
C(11)	0.353(1)	0.289(1)	0.046(1)
C(12)	0.315(2)	0.357(1)	0.010(2)
C(13)	0.377(2)	0.419(1)	0.033(2)
C(14)	0.476(2)	0.415(1)	0.089(2)
C(15)	0.518(2)	0.348(2)	0.125(2)
C(16)	0.458(2)	0.285(1)	0.101(2)
C(17)	0.334(1)	0.279(1)	0.290(1)
C(18)	0.356(1)	0.199(1)	0.309(1)
C(19)	0.288(1)	0.154(1)	0.253(1)
C(20)	0.308(2)	0.073(1)	0.266(2)
C(21)	0.384(2)	−0.020(1)	0.380(2)
C(22)	0.372(2)	0.401(1)	0.336(2)
C(23)	0.061(2)	0.273(1)	0.074(1)
C(24)	0.097(1)	0.122(1)	0.095(1)

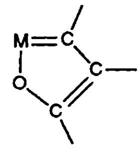
Table 4 Selected bond lengths (Å) and angles (°) for complex **5**

Hg–Cl(1)	2.367(6)	O(1)–C(17)	1.23(2)
Hg–Cl(2)	2.391(7)	O(2)–C(17)	1.29(2)
Hg–Cl(3)	2.380(7)	O(3)–C(20)	1.34(2)
Ru–P(1)	2.371(5)	O(4)–C(20)	1.20(2)
Ru–P(2)	2.393(5)	O(5)–C(23)	1.08(2)
Ru–O(1)	2.13(1)	O(6)–C(24)	1.14(2)
Ru–C(19)	2.07(2)	C(17)–C(18)	1.49(3)
Ru–C(23)	1.97(2)	C(18)–C(19)	1.31(2)
Ru–C(24)	1.86(2)	C(19)–C(20)	1.50(2)
Cl(1)–Hg–Cl(2)	119.2(3)	C(19)–Ru–C(24)	97.7(7)
Cl(1)–Hg–Cl(3)	122.6(3)	C(23)–Ru–C(24)	93.9(8)
Cl(2)–Hg–Cl(3)	118.3(3)	Ru–O(1)–C(17)	114(1)
P(1)–Ru–P(2)	177.0(2)	O(1)–C(17)–O(2)	127(2)
P(1)–Ru–O(1)	89.9(3)	O(1)–C(17)–C(18)	118(2)
P(1)–Ru–C(19)	86.9(5)	O(2)–C(17)–C(18)	115(2)
P(1)–Ru–C(23)	92.7(5)	C(17)–C(18)–C(19)	116(2)
P(1)–Ru–C(24)	90.8(6)	Ru–C(19)–C(18)	114(1)
P(2)–Ru–O(1)	90.1(3)	Ru–C(19)–C(20)	127(1)
P(2)–Ru–C(19)	90.2(5)	C(18)–C(19)–C(20)	119(2)
P(2)–Ru–C(23)	90.3(5)	O(3)–C(20)–O(4)	124(2)
P(2)–Ru–C(24)	89.0(6)	O(3)–C(20)–C(19)	112(2)
O(1)–Ru–C(19)	77.8(5)	O(4)–C(20)–C(19)	124(2)
O(1)–Ru–C(23)	90.7(6)	Ru–C(23)–O(5)	176(2)
O(1)–Ru–C(24)	175.4(6)	Ru–C(24)–O(6)	178(2)
C(19)–Ru–C(23)	168.4(7)		

chloride ligands between the two metals. It may be that there is a direct attack on the vinyl ligand in $[Ru(CO)_2(CH{=}CHR)Cl(PMe_2Ph)_2]$ by mercury(II), and that the resulting cation $[Ru(CO)_2Cl(PMe_2Ph)_2]^+$ then accepts a chloride ligand from the mercury.



A



B

(*iii*) *Structure of Complex* **5**.—The structure consists of an assembly of $[Ru(CO)_2\{C(CO_2Me){=}C(COOMe)H\}(PMe_2Ph)_2]^+$ cations and planar $[HgCl_3]^-$ anions only slightly distorted from regular trigonal geometry. Atomic coordinates are listed in Table 3, and selected bond lengths and angles in Table 4. The atom numbering scheme is shown in Fig. 1.

The only major deviation from regular octahedral geometry around the ruthenium lies in the angle O(1)–Ru–C(19) [77.8(5)°], which is contained within the five-membered metallacycle. The remaining angles in the ring range from 114(1)° for both Ru–C(19)–C(18) and Ru–O(1)–C(17) to 118(2)° for O(1)–C(17)–C(18). The ring is almost exactly planar, and O(2) and C(22) in the β-CO_2Me substituent also lie close to the plane, as does C(20) in the α-CO_2Me group. In contrast, the O–C–O skeleton of the α-CO_2Me substituent is twisted out of the plane by *ca.* 30°, presumably for steric reasons.

The bonding within a metallacycle of this type can be represented as shown in **A**. An alternative canonical structure, **B**, is also possible, however, and as the contribution made by **B** increases the effect will be to make the lengths of the two carbon–carbon bonds more similar and to increase the carbon–oxygen bond length. At the same time the α-carbon in the vinyl ligand becomes more carbene-like, which should increase its chemical shift. Thus, for example, in $[W(CO)_2(\eta^5\text{-}C_5Me_5)\{C(Me){=}C(Me){-}C(O)Me\}]$, the two C–C bond lengths are 1.36(2) and 1.39(2) Å, C–O is 1.29(2) Å, and the chemical shift of the α-carbon is δ 253.5.[16] Similarly, for $[Mo(CO)_2(\eta^5\text{-}C_5H_5)\{C(Me){=}C(Me){-}C(O)CMe{=}CHMe\}]$, the C–C bond lengths are 1.380(4) and 1.416(4) Å, C–O is 1.292(4) Å, and the α-carbon chemical shift is δ 261.0.[17] In sharp contrast, for complex **5** the C–C bond lengths are 1.31(2) and 1.49(3) Å, C–O is 1.23(2) Å, and the α-carbon chemical shift is only δ 203.1. Evidently any contribution by canonical structure **B** must be relatively small.

The lengths of the Ru–C bonds to the two carbonyl ligands, Ru–C(23) and Ru–C(24), are 1.97(2) and 1.86(2) Å respectively. The rather large value for the former bond presumably reflects the *trans* effect of the vinyl ligand.[18]

Experimental

Complexes were prepared and purified using dry, oxygen-free solvents. Except where indicated otherwise, reactions were carried out under an atmosphere of dry nitrogen. The NMR spectra were recorded on JEOL FX90Q and Bruker MSL300 instruments. Elemental analysis figures for new complexes are collected in Table 5. Complex **6** was yellow: all others were colourless. A sample of $[Ru(CO)\{C(CO_2Me){=}C(CO_2Me)H\}Cl(PMe_2Ph)_3]$ was kindly provided by Dr. J. D. Vessey.

Syntheses.—Complexes **3a**–**3d**. These were originally obtained in small quantities during the purification by column chromatography on alumina, using $CHCl_3$–Et_2O mixtures as eluent, of complexes **2a**–**2d**. These had been prepared[7] by the reaction of $MeO_2CC{\equiv}CCO_2Me$ with complexes $[Ru(CO)_2R(Cl)(PMe_2Ph)_2]$ (R = Ph, **1a**; 4-ClC_6H_4, **1b**; 4-MeC_6H_4, **1c**; or 4-$MeOC_6H_4$, **1d**) contaminated (as a result of their method of preparation[2]) with small amounts of [HgR(Cl)] and/or $[HgR_2]$. Solvent was removed from the appropriate fractions, and complexes **3a**–**3d** were further purified by recrystallization from EtOH.

Table 5 Analytical data (%) for new complexes

Compound	Found C	Found H	Calc. C	Calc. H
$[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}_2]$ **3a**	45.75	3.75	45.10	3.45
$[Hg\{C(CO_2Me)=C(CO_2Me)(C_6H_4Cl\text{-}4)\}_2]$ **3b**	41.05	2.85	40.70	2.85
$[Hg\{C(CO_2Me)=C(CO_2Me)(C_6H_4Me\text{-}4)\}_2]$ **3c**	46.95	4.00	46.80	3.95
$[Hg\{C(CO_2Me)=C(CO_2Me)(C_6H_4OMe\text{-}4)\}_2]$ **3d**	45.00	3.75	44.65	3.75
$[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}Ph]$ **4a**	43.75	3.35	43.50	3.25
$[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}Cl]$	31.75	2.45	31.65	2.45
$[Hg\{C(CO_2Me)=C(CO_2Me)Cl\}Cl]$	17.65	1.35	17.40	1.45
$[Hg\{C(CO_2Me)=C(CO_2Me)Cl\}_2]$	25.45	1.90	25.95	2.20
$[Ru(CO)_2\{C(CO_2Me)=C(COOMe)H\}(PMe_2Ph)_2][HgCl_3]$ **5**	32.65	3.25	32.65	3.30
$[Ru(CO)\{C(CO_2Me)=C(COOMe)H\}Cl(PMe_2Ph)_2]$ **6**	47.60	4.95	47.30	5.00
$[Hg\{C(CO_2Me)=C(CO_2Me)H\}_2]$	29.10	3.00	29.60	2.90
$[Hg(CH=CHCMe_3)Cl]$	22.80	3.40	22.60	3.45
$[Hg(CH=CHPh)Cl]$	28.60	2.05	28.35	2.10

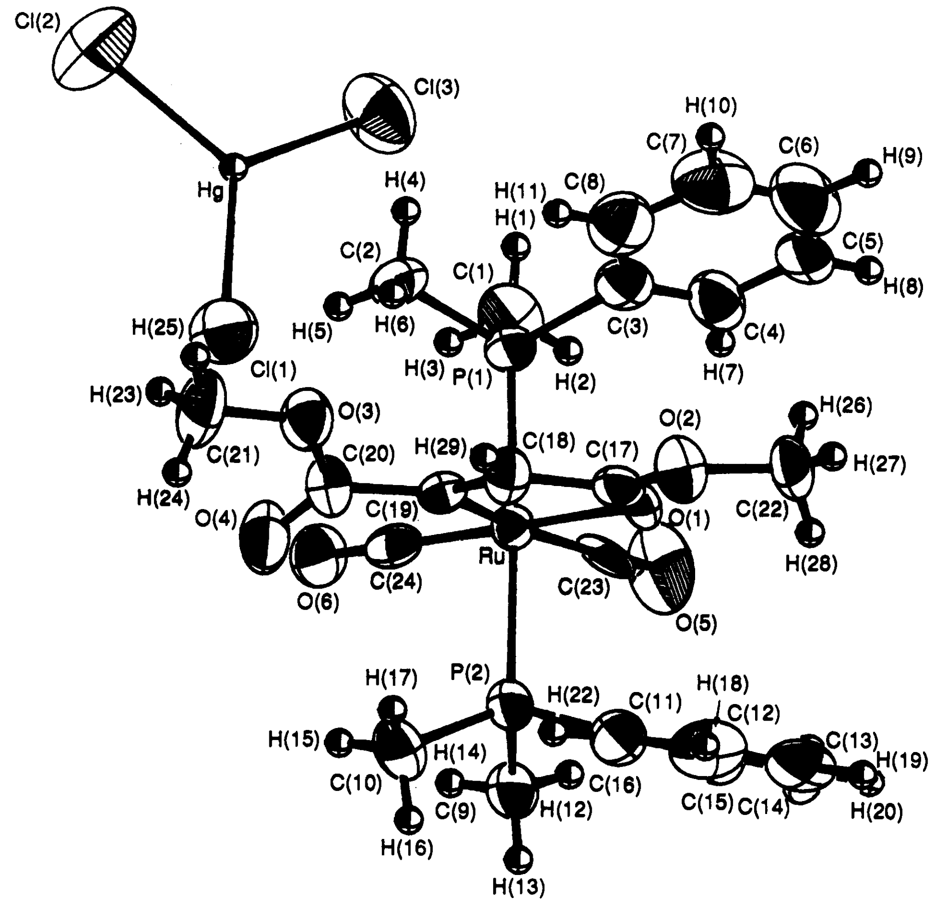


Fig. 1 Structure of complex **5** in the solid state

The complexes could also be obtained by reaction of $HgCl_2$ with **2a**–**2d** in $CHCl_3$ or Me_2CO. Thus, for example, **2c** (0.140 g) and $HgCl_2$ (0.025 g) were warmed in Me_2CO (15 cm^3) at 323 K in a closed flask. After 36 h the solvent was removed under reduced pressure, and crystallization of the residue from ethanol yielded **3c**.

Catalytic synthesis of **3a** *and* **4a**. The compounds *trans*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$[9] (0.019 g), $[HgPh_2]$ (0.134 g) and $MeO_2CC{\equiv}CCO_2Me$ (0.10 cm^3) were warmed in $CDCl_3$ (2 cm^3) in a closed flask at 323 K. The reaction was monitored by NMR spectroscopy, as the concentration of **4a** rose and then declined. After 19 d, conversion into **3a** was essentially complete. In a repeat experiment the reaction was halted after 9 d and the solvent removed under reduced pressure. The residue, dissolved in the minimum volume of $CHCl_3$, was subjected to chromatography on an alumina column packed under Et_2O, using $CHCl_3$ as eluent. Fractions were examined by IR and NMR spectroscopy. Solvent was removed from the fraction containing **4a**, and the resulting solid was washed with small portions of ethanol.

$[Hg\{C(CO_2Me)=C(CO_2Me)Ph\}Cl]$. Complex **2a** (0.170 g) and $HgCl_2$ (0.067 g) were heated under reflux in Me_2CO (50 cm^3). After 6 h, the solvent was removed under reduced pressure. The residue, dissolved in the minimum volume of

$CHCl_3$, was subjected to chromatography on an alumina column packed under Et_2O, using $CHCl_3$ as eluent. Solvent was removed from the fraction containing $[Hg\{C(CO_2Me){=}C(CO_2Me)Ph\}Cl]$, and the residue was recrystallized from ethanol–light petroleum (b.p. 40–60 °C).

$[Hg\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl]$. The complex $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$[10] (0.098 g) was heated under reflux with $HgCl_2$ (0.041 g) in Me_2CO (35 cm^3) for 24 h. The Me_2CO was removed under reduced pressure and the residual oil was dissolved in $CDCl_3$ (0.5 cm^3) and treated with CO. When a ^{31}P NMR spectrum indicated that the two isomers of $[Ru_2(CO)_2Cl_4(PMe_2Ph)_4]$ formed in the reaction had been converted into all-*cis*-$[Ru(CO)_2Cl_2(PMe_2Ph)_2]$, the solution was subjected to chromatography on a silica column packed under hexane, using $CHCl_3$ as eluent. Solvent was removed from the fraction containing $[Hg\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl]$ under reduced pressure, and the residue recrystallized from a mixture of $CHCl_3$, EtOH and hexane.

A similar procedure was used to obtain $[Hg\{C(CO_2Me){=}C(CO_2Me)Cl\}_2]$ from $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$ (0.136 g) and $HgCl_2$ (0.029 g), with a reaction time of 72 h. After the treatment with CO, the residue was applied to the silica column as a solution in a mixture of $CHCl_3$ and hexane. Initial elution with a mixture of $CHCl_3$ and hexane was followed by removal of the $[Hg\{C(CO_2Me){=}C(CO_2Me)Cl\}_2]$ with pure $CHCl_3$. The complex was recrystallized from a mixture of $CHCl_3$ and EtOH.

Complex **5**. To a solution of $[Ru(CO)_2\{C(CO_2Me){=}C(CO_2Me)H\}Cl(PMe_2Ph)_2]$[13] (0.140 g) in Me_2CO was added $HgCl_2$ (0.063 g). When dissolution was complete the solvent was removed under reduced pressure and the product recrystallized from a mixture of $CHCl_3$ and EtOH.

Conversion of **5** *into* **6**. A solution of complex **5** in Me_2CO was heated under reflux for 100 h. The solvent was then removed under reduced pressure, the residue dissolved in the minimum of $CHCl_3$ and applied to an alumina column packed under Et_2O. Elution with mixtures of $CHCl_3$ and Et_2O removed by-products, and subsequent elution with $CHCl_3$ caused very slow movement of a yellow band down the column. Elution was halted, the yellow band was removed, and the product extracted from the alumina with warm $CHCl_3$ (10 cm^3) followed by warm Me_2CO (3 × 10 cm^3). Solvent was removed from the combined extracts under reduced pressure, and the residue was recrystallized from EtOH.

$[Hg\{C(CO_2Me){=}C(CO_2Me)H\}_2]$. A solution of $[Ru(CO)\{C(CO_2Me){=}C(CO_2Me)H\}Cl(PMe_2Ph)_3]$ (0.148 g) and $HgCl_2$ (0.028 g) in Me_2CO (35 cm^3) was heated under reflux for 12 h. The solvent was removed under reduced pressure, and the residue dissolved in a mixture of EtOH and Me_2CO. Slow evaporation of the solution under a stream of N_2 yielded crystals of the product. The mother-liquor was removed and the crystals washed with hexane.

$[Hg(CH{=}CHCMe_3)Cl]$. A solution of $[Ru(CO)_2(CH{=}CHCMe_3)Cl(PMe_2Ph)_2]$[13] (0.110 g) and $HgCl_2$ (0.054 g) in Me_2CO (15 cm^3) was warmed at 323 K in a closed flask. After 3 h the solvent was removed under reduced pressure. The $[Hg(CH{=}CHCMe_3)Cl]$ was isolated from the residue by sublimation at 323 K and 1 mmHg (*ca.* 133 Pa).

The same procedure was used to obtain $[Hg(CH{=}CHPh)Cl]$ from $[Ru(CO)_2(CH{=}CHPh)Cl(PMe_2Ph)_2]$[13] (0.180 g) and $HgCl_2$ (0.084 g), except that the residue was extracted with several small portions of $CHCl_3$ and Me_2CO, leaving $[Hg(CH{=}CHPh)Cl]$, which is only sparingly soluble in both solvents.

Crystal-structure Determination of Complex **5**.—The crystal used in the structure determination, of dimensions 0.30 × 0.05 × 0.20 mm, was obtained by slow evaporation of a solution of complex **5** in a mixture of $CHCl_3$ and EtOH.

Crystal data. $C_{24}H_{29}Cl_3HgO_6P_2Ru$, $M = 883.46$, monoclinic, space group $P2_1/n$ (no. 14) (from systematic absences: $h0l$, $h + l \neq 2n$, $0k0$, $k \neq 2n$), $a = 12.826(2)$, $b = 18.224(2)$, $c = 13.656(2)$ Å, $\beta = 102.19(2)°$, $U = 3119.8(9)$ Å^3, $Z = 4$, $D_c = 1.881$ g cm^{-3}, $F(000) = 1704$, μ(Mo-Kα) = 57.83 cm^{-1}, $\lambda = 0.710\,69$ Å.

X-Ray diffraction data were measured at 295 K on a Rigaku AFC6S diffractometer equipped with a graphite monochromator. Unit-cell dimensions and an orientation matrix for data collection were determined by least-squares refinement using the setting angles for 20 carefully centred reflections in the range $34.09 < 2\theta < 35.43°$. Intensity data were collected in the ω–2θ mode with a scan width of $1.20 + 0.30 \tan\theta$ to a maximum 2θ value of 55°. The ω-scan rate was 4.0° min^{-1}. Scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.32° with a take-off angle of 2.8°. Weak reflections $[I < 10.0\sigma(I)]$ were rescanned (maximum of two rescans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak-to-background counting time was 2:1. The intensities of three representative reflections, measured after every ten reflections, declined by 1.80%. A linear correction factor was applied to the data to allow for this. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.73 to 1.00. Intensities were corrected for Lorentz and polarization effects. Of the 10 337 reflections recorded, 5493 were unique ($R_{int} = 0.081$).

The structure was solved by direct methods.[19,20] Non-hydrogen atoms were refined anisotropically. The final cycle of least-squares refinement was based on 3109 observed reflections $[I > 3\sigma(I)]$ and 334 variable parameters, and converged (largest parameter shift/e.s.d. = 0.01) with $R = 0.057$, $R' = 0.072$. The standard deviation of an observation of unit weight, $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, was 6.53. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final Fourier difference map corresponded to 1.83 and −1.43 e Å^{-3} respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[21] Anomalous dispersion effects were included in F_c;[22] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[21] All calculations were performed using the TEXSAN[23] crystallographic software package.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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