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INSERTION REACTIONS OF DIMETHYL ACETYLENEDICARBOXYLATE WITH ALKENYLRUTHENIUM COMPLEXES OF THE TYPE $[\mathrm{Ru(CO)Cl(R'C{=}CHR)(PPh_3)_2}]$. THE CRYSTAL STRUCTURE OF $[\mathrm{R}\overline{\mathrm{u(CO)Cl\{MeOO}}\mathrm{C{-}C{=}C(CO_2Me){-}CH{=}CHCMe_3\}(PPh_3)_2}]$

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Summary

Reactions between alkenylruthenium complexes of the type $[\mathrm{Ru(CO)Cl(R'C{=}CHR)(PPh_3)_2}]$ ($\mathrm{R'} = \mathrm{R} =$ H, Me, Ph; $\mathrm{R'} =$ H, R = $\mathrm{C_3H_7}$, $\mathrm{CMe_3}$, $\mathrm{SiMe_3}$, Ph) with dimethylacetylenedicarboxylate give mixed bis-insertion complexes of formula $[\mathrm{R}\overline{\mathrm{u(CO)Cl\{MeOO}}\mathrm{CC{=}C(CO_2Me)CR'{=}CHR\}(PPh_3)_2}]$, which have been isolated and characterized only in the case of terminal alkyne derivatives ($\mathrm{R'} =$ H). This reaction is competitive with the simple displacement reaction of the non-activated acetylene by dimethyl acetylene-dicarboxylate. The complexes were characterized by elemental analysis and ^{1}H NMR and IR spectroscopy. The molecular structure of $[\mathrm{R}\overline{\mathrm{u(CO)Cl\{MeOO}}\mathrm{CC{=}C(CO_2Me)CH{=}CHCMe_3\}(PPh_3)_2}]$, determined by X-ray diffraction, can be regarded as a distorted octahedral species, in which the butadienyl ligand acts as bidentate through an additional C=O–Ru bond involving a carboxylate oxygen atom, the atom pairs (P,P), (Cl,C=) and (=O,C) being in *trans* positions.

Introduction

We recently described the insertion reactions of $\mathrm{Ru(CO)ClH(PPh_3)_3}$ with non-activated and activated acetylenes [1,2], which lead in all cases to formation of five-coordinated alkenyl complexes of general formula $[\mathrm{Ru(CO)Cl(R'C{=}CHR)(PPh_3)_2}]$. These compounds can be regarded as arising from a simple *cis*-insertion of one alkyne molecule into the Ru–H bond. On the other hand, the reactions with activated acetylenes of the type ROC–C≡CH (R = Me, OMe, OEt) give rise to two different bis-insertion derivatives, of general formulae $[\overline{\mathrm{Ru(CO)Cl\{HC{=}C(ROC)}}\mathrm{CH{=}CHCOR\}(PPh_3)_2}]$ (R = OMe, OEt) and $[\mathrm{R}\overline{\mathrm{u(CO)(C{\equiv}CCOR)\{RO}}\mathrm{CC{=}CHCH{=}CHCOR\}(PPh_3)_2}]$ [2]. In these compounds the insertion of the second

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alkyne molecule could in principle take place either into the Ru–C bond or into a terminal vinylic C–H bond. We consider that a study of the reactions of dimethyl acetylenedicarboxylate with a series of alkenyl complexes derived from non-activated acetylenes might contribute to elucidation of the mechanism of the bis-insertion process.

Several of the mono-insertion complexes used as starting compounds have not been previously described.

Results and discussion

The new complexes of general formula $[\mathrm{Ru(CO)Cl(R'C{=}CHR)(PPh_3)_2}]$ ($\mathrm{R = R' = H, Me; R' = H, R = CMe_3, SiMe_3}$), used as starting compounds for this study, are similar to those earlier described [1]. Details of their preparations and analytical and spectral (IR and ^{1}H NMR) data are given in the Experimental part. Noteworthy is the ^{1}H NMR spectrum of the acetylene derivative, in which the coupling with each of the remaining protons and both phosphorus is clearly observed.

The alkenyl complexes $[\mathrm{Ru(CO)Cl(R'C{=}CHR)(PPh_3)_2}]$ derived from terminal non-activated acetylenes ($\mathrm{R' = H, R = C_3H_7, CMe_3, SiMe_3, Ph}$) react with dimethylacetylenedicarboxylate in $\mathrm{CH_2Cl_2}$ to give products of general formula $[\overline{\mathrm{Ru(CO)Cl\{MeO}}\mathrm{_2CC{=}C(CO_2Me)CH{=}CHR\}(PPh_3)_2}]$, which can be regarded as formed by insertion of a dimethylacetylenedicarboxylate molecule into the Ru–C bond to the alkenyl ligand. Unidentified oils were formed in the reactions with the alkenyl complexes derived from the symmetrical acetylenes ($\mathrm{R = R' = H, Me, Ph}$).

The mixed bis-insertion derivatives separate out on addition of petroleum ether or hexane to the solution obtained by addition of diethyl ether to the reaction mixture followed by filtration to remove the precipitate of $[\mathrm{Ru(CO)Cl(MeO_2CC{=}CHCO_2Me)(PPh_3)_2}]$ formed as a secondary product. The bis-insertion derivatives can be crystallized from $\mathrm{CH_2Cl_2/MeOH}$. The yield of the bis-insertion product increases in the order $\mathrm{C_3H_7}$ (15%) < Ph (30%) < $\mathrm{CMe_3}$ (40%) < $\mathrm{SiMe_3}$ (45%). The insertion of dimethyl acetylenedicarboxylate into the Ru–C= bond seems to be competitive with the simple displacement reaction of the non-activated acetylene by the activated ones, products of both reaction always being present:

$$[\mathrm{Ru(CO)Cl(HC{=}CHR)(PPh_3)_2}] + \mathrm{MeO_2CC{\equiv}CCO_2Me} \rightarrow$$
$$[\mathrm{Ru(CO)Cl(MeO_2C\text{-}C{=}CHCO_2Me)(PPh_3)_2}] + \mathrm{RC{\equiv}CH} +$$
$$[\overline{\mathrm{Ru(CO)Cl\{MeO}}\mathrm{_2C\text{-}C{=}C(CO_2Me)\text{-}CH{=}CHR\}(PPh_3)_2}]$$

All these complexes are yellow, and have similar properties. The IR spectra shows a strong ν(C≡O) band at 1910–1925 cm^{-1}. No bands assignable to ν(C≡C) absorptions were observed. Strong bands at 1720-1735 cm^{-1} were assigned to the carboxylate ν(C=O) frequency. The presence in all cases of a strong band towards 1570 cm^{-1} seems to suggest the coordination of a ketonic oxygen of a carboxylate group to ruthenium, and a ν(C=C) band is observed as a medium or weak peak near 1550 cm^{-1}.

^{1}H NMR spectra

The ^{1}H NMR spectra of all these mixed bis-insertion derivatives are very similar and show two alkenylic proton signals at approximately the same δ values. These

TABLE 1

THE MORE RELEVANT BOND LENGTHS (Å) AND ANGLES (°) FOR [$\overline{\text{Ru(CO)Cl(MeOO}}$CC=C(COOMe)CH=CH–CMe$_3$}(PPh$_3$)$_3$] (e.s.d.'s. are given in parentheses)

Lengths		Angles	
Ru–P(1)	2.389(3)	P(1)–Ru–P(2)	176.3(1)
Ru–P(2)	2.403(3)	P(1)–Ru–Cl	87.8(1)
Ru–Cl	2.464(4)	P(1)–Ru–C(1)	90.9(4)
Ru–C(1)	1.80(1)	P(1)–Ru–O(2)	90.5(2)
Ru–C(3)	2.03(1)	P(1)–Ru–C(3)	91.3(4)
Ru–O(2)	2.291(9)	P(2)–Ru–Cl	88.5(1)
C(1)–O(1)	1.14(2)	P(2)–Ru–C(1)	89.7(4)
C(2)–O(2)	1.27(2)	P(2)–Ru–O(2)	90.1(2)
C(2)–C(3)	1.43(2)	P(2)–Ru–C(3)	92.2(4)
C(2)–O(3)	1.34(2)	Cl–Ru–C(1)	105.2(4)
O(3)–C(10)	1.48(2)	Cl–Ru–O(2)	93.4(2)
C(3)–C(4)	1.37(2)	Cl–Ru–C(3)	156.7(4)
C(4)–C(5)	1.46(2)	C(1)–Ru–O(2)	161.4(5)
C(4)–C(8)	1.51(2)	C(1)–Ru–C(3)	98.1(5)
C(8)–O(4)	1.18(2)	O(2)–Ru–C(3)	63.4(4)
C(8)–O(5)	1.35(2)	Ru–C(1)–O(1)	178(1)
O(5)–C(9)	1.50(2)	Ru–O(2)–C(2)	87.4(7)
C(5)–C(6)	1.32(2)	Ru–C(3)–C(2)	94.2(8)
C(6)–C(7)	1.52(2)	Ru–C(3)–C(4)	141(1)
C(7)–C(71)	1.51(3)	C(3)–C(2)–O(2)	115(1)
C(7)–C(72)	1.57(4)	C(3)–C(2)–O(3)	123(1)
C(7)–C(73)	1.38(4)	O(2)–C(2)–O(3)	121(1)
		O(2)–O(3)–C(10)	87.2(9)
Mean P–C: 1.82(1) Å		C(2)–C(3)–C(4)	125(1)
Mean C–C in phenyl groups: 1.40(2)		C(3)–C(4)–C(5)	124(1)
		C(3)–C(4)–C(8)	121(1)
		C(5)–C(4)–C(8)	115(1)
		C(4)–C(8)–O(4)	126(1)
		C(4)–C(8)–O(5)	111(1)
		O(4)–C(8)–O(5)	123(1)
		C(8)–O(5)–C(9)	115(1)
		C(4)–C(5)–C(6)	123(1)
		C(5)–C(6)–C(7)	125(1)
		C(6)–C(7)–C(71)	111(2)
		C(6)–C(7)–C(72)	112(2)
		C(6)–C(7)–C(73)	112(2)
		C(71)–C(7)–C(72)	98(2)
		C(71)–C(7)–C(73)	116(3)
		C(72)–C(7)–C(73)	106(3)
		Mean C–C–C in phenyl groups: 120(2)°	

signals are shifted towards higher fields relative to those of the corresponding starting compounds, and this is indoubtedly due to the insertion of the activated acetylene into the Ru–C bond of the alkenyl complex. Except for the complex with R = C_3H_7, both signals are doublets, with δ values corresponding to a relative *trans*-disposition of the alkenylic protons. In the complex with R = C_3H_7 the alkenyl proton signal appearing at the higher δ value is a doublet of triplets and thus corresponds to the alkenylic proton geminal to the C_3H_7 group. This behaviour is general for the remaining complexes, and can be attributed to a combined effect of the conjugation in the butadienyl system and the probable coordination through both C and O atoms.

This ^1H NMR study leads to conclude that the activated acetylene inserts into the Ru–C bond of the starting alkenyl complex $[Ru(CO)Cl(HC{=}CHR)(PPh_3)_2]$ to give butadienyl complexes of general formula $[Ru(CO)Cl\{MeOOCC{=}C(CO_2Me)CH{=}CHR\}(PPh_3)_2]$ ($R = C_3H_7$, CMe_3, $SiMe_3$, Ph).

The possible presence of an additional C=O–Ru bond involving the ketonic oxygen of the carboxylate group present as substituent at the carbon atom directly bonded to ruthenium prompted us to determine the crystal structure of one of these complexes, the compound with $R = CMe_3$ was selected because of its good crystallinity.

The structure of $[\overline{Ru(CO)Cl\{MeOO}C{-}C{=}C(CO_2Me){-}CH{=}CHCMe_3\}(PPh_3)_2]$

The crystal is made up of discrete molecules. The molecule, shown in Fig. 1, has the Ru atom at the center of a distorted octahedron in which the equatorial plane contains the Cl, O(2), C(1) and C(3) atoms whereas the two P atoms occupy the axial positions. Table 1 lists the more relevant bond lengths and angles which agree well with those obtained for $[\overline{Ru(CO)C{\equiv}CCOOMe)(MeOO}CC{=}CHCH{=}CHCOOMe)(PPh_3)_2]$ [2]. The angles in the equatorial plane around the Ru atom range from 105.2(4)° for Cl–Ru–C(1) to 63.4(4)° for O(2)–Ru–C(3), as a consequence of the geometry of the carboxylate ligand in which the angle C(3)–C(2)–O(2) has a value of 115(1)°.

There are significant differences in the carbon–carbon distances in the butadienyl ligand. Thus, double bonds C(3)–C(4) and C(5)–C(6) (1.37(2) Å and 1.32(2) Å, respectively) alternate with single bonds C(4)–C(5) and C(6)–C(7) (1.46(2) Å and 1.52(2) Å, respectively). The calculated bond lengths in the t-butyl group are as expected; the rather shorter distance is found for the C(7)–C(73) bond (1.38(4) Å)

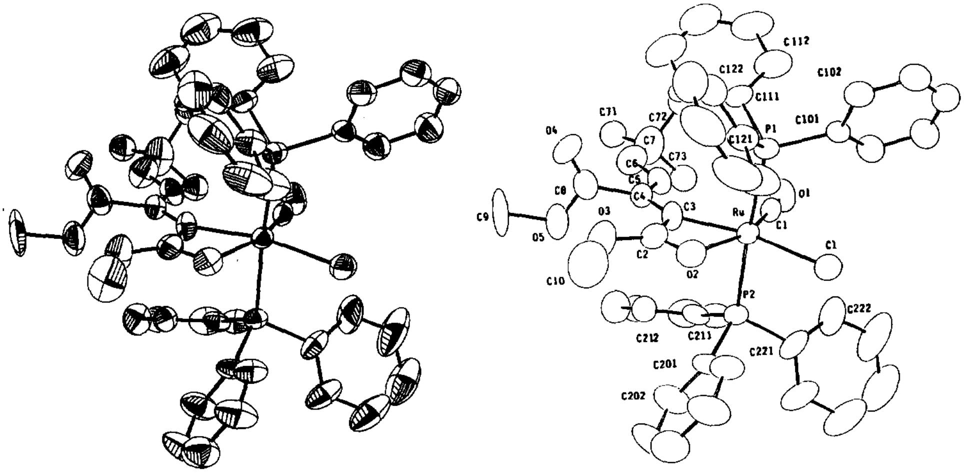

Fig. 1. ORTEP (5) drawing of the molecular structure (with hydrogen atoms omitted) of $[\overline{Ru(CO)Cl\{MeOO}CC{=}C(CO_2Me)CH{=}CHCMe_3\}(PPh_3)_2]$ showing the octahedral coordination at Ru. The atom numbering is the same as in Table 2.

can be attributed as uncertainty in the refinement arising from the large thermal vibrations of the terminal methyl groups (see Table 2).

It is noteworthy that the two metal–carbon distances are different. The Ru–C(1) bond length (1.80(1) Å) is shorter as a consequence of back bonding, since for Ru–C(3) (2.03(1) Å) only σ bonding is to be expected.

Experimental

The ^{1}H NMR spectra were recorded on a Bruker WM 360 spectrometer at 360 MHz; shifts are relative to TMS (0.00 ppm). IR spectra were recorded on a Perkin–Elmer 325 instrument, using KBr or polyethylene disks. Solvents were dried and distilled under nitrogen, and all operations were conducted under dry, oxygen-free nitrogen.

The $[Ru(CO)Cl(R'C{=}CHR)(PPh_3)_2]$ compounds with $R = C_3H_7$, Ph; $R' = H$ and $R = R' = Ph$ were prepared as described earlier [1].

[Ru(CO)Cl(CH=CH₂)(PPh₃)₂]

Acetylene was bubbled through a solution of $Ru(CO)ClH(PPh_3)_3$ (0.3 g, 0.315 mmol) in CH_2Cl_2 (15 ml) for 30 min with stirring and mild heating. The resulting solution was chromatographed on a Florisil column; elution with CH_2Cl_2 gave an orange solution, from which an orange solid was isolated by concentration and precipitation with petroleum ether. The yellow substance retained on the Florisil column was eluted with acetone, and appeared to be a mixture of products of polyinsertion of acetylene. (Yield 55%) (Found: C, 65.3; H, 4.68. $C_{39}H_{33}ClOP_2Ru$ calcd.: 65.39; H, 4.64%). Infrared: ν(CO) 1925 vs, ν(C=C) 1575 m, ν(Ru–Cl) 285 cm^{-1}. ^{1}H NMR (ppm): δ 4.475 (ddd, J 13.7, 1.8, 1.6 Hz, 1H, =CH), 5.075 (dtd, J 5.97, 2.56, 1.60 Hz, 1H, =CH), 7.3–7.4 (m, 20H, 4 Ph), 7.4–7.6 (m, 10H, 2 Ph), 7.787 (ddt, J 13.7 Hz, 5.97 Hz, 1.80 Hz, 1H, HC=) (in $CDCl_3$).

[Ru(CO)Cl(CH₃C=CHCH₃(PPh₃)₂]

An excess of but-2-yne was added to a solution of $HRu(CO)Cl(PPh_3)_3$ (0.3 g, 0.315 mmol) in CH_2Cl_2 (15 ml) until a red colour developed. After 15 min stirring the solution was concentrated and chromatographed on a Florisil column. Elution with CH_2Cl_2 gave an orange solution, from which, after concentration, a reddish-orange solid was precipitated with diethyl ether. The compound was recrystallized from a very concentrated solution in CH_2Cl_2/Et_2O at −12°C. (Yield 60–70%). (Found: C, 66.08; H, 5.11, $C_{41}H_{37}ClOP_2Ru$ calcd.: C, 66.17; H, 5.01%). Infrared: ν(CO) 1925 vs, ν(C=C) 1625 m, ν(Ru–Cl) 280 w cm^{-1}). ^{1}H NMR (ppm): δ 1.46 (d, 3H, Me), 1.56 (s, 3H, Me), 4.23 (qq, J 6.6, 1.3 Hz, 1H, =CH), 7.26–7.49 (m, 20H, 4 Ph), 7.50–7.72 (m, 10H, 2 Ph).

[Ru(CO)Cl(trans-HC=CHCMe₃)(PPh₃)₂]

An excess of $Me_3CC{\equiv}CH$ was added to a solution of $HRu(CO)Cl(PPh_3)_3$ (0.3 g, 0.315 mmol) in CH_2Cl_2 (15 ml) until a red colour persisted. After 15 min stirring the solution was concentrated and Et_2O was added. The orange solid which separated was recrystallized from CH_2Cl_2/Et_2O at −12°C. (Yield 65–70%). (Found: C, 66.4; H, 5.6. $C_{43}H_{41}ClOP_2Ru$ calcd.: C, 66.88; H, 5.35%). Infrared: ν(CO) 1920 vs, ν(C=C) 1620 m, ν(Ru–Cl) 285 w cm^{-1}. ^{1}H NMR (ppm): δ 1.465 (s, 9H, 3 Me), 4.698 (dt, *J* 14.00 Hz, 2.56 Hz, 1H, =CH), 6.939 (dt, *J* 14.00 Hz, 2.56 Hz, 1H, HC=), 7.2–7.7 (m, 30H, 6 Ph).

$[Ru(CO)Cl(trans\text{-}H\text{-}C{=}CHSiMe_3)(PPh_3)_2]$

An excess of Me$_2$SiC≡CH was added to a solution of Ru(CO)ClH(PPh$_3$)$_3$ (0.3 g, 0.315 mmol) in CH$_2$Cl$_2$ (15 ml) until a yellow colour persisted. After 15 min stirring the solution was concentrated and Et$_2$O was added to precipitate a yellow powder, which was recrystallized from CH$_2$Cl$_2$/Et$_2$O at −12°C. (Yield 70%). (Found: C, 64.3; H, 5.5. C$_{42}$H$_{41}$ClOP$_2$RuSi calcd.: C, 63.99; H, 5.24%). Infrared: ν(CO) 1925 vs, ν(C=C) 1525 m, ν(Ru–Cl) 280 w cm^{-1}. ^{1}H NMR (ppm): δ 1.765 (s, 9H, 3 Me), 5.36 (dt, *J* 14.00, 2.56 Hz, 1H, =CH), 8.45 (dt, *J* 14.00, 2.56 Hz, 1H, HC=).

$[R\overline{u(CO)Cl\{MeOO}CC{=}C(CO_2Me)CH{=}CHC_3H_7\}(PPh_3)_2]$

An excess of dimethyl acetylenedicarboxylate was added to a solution of [Ru(CO)Cl(HC=CHC$_3$H$_7$)(PPh$_3$)$_2$] in CH$_2$Cl$_2$ (15 ml). After 1 h stirring, the solution was concentrated and [Ru(CO)Cl(MeO$_2$CC=CHCO$_2$Me)] was precipitated by addition of Et$_2$O and filtered off. The yellow solution was diluted with hexane, and the impure yellow solid which separated, was purified by recrystallisation from CH$_2$Cl$_2$/MeOH. (Yield 15%) (Found: C, 63.99; H, 5.29. C$_{48}$H$_{45}$ClO$_5$P$_2$Ru calcd.: C, 64.03; H, 5.04%). Infrared: ν(C≡O) 1920 vs, ν(C=O) 1730 s, ν(C=O–Ru) 1570 s, ν(C=C) 1545 w, ν(COC) 1190 m cm^{-1}. ^{1}H NMR (ppm): δ 0.763 (t, 3H, Me), 1.179 (sext., 2H, CH$_2$), 1.647 (q, 2H, CH$_2$), 2.895, 3.582 (s, 3H, Me), 4.85 (d, 17.00 Hz, 1H, HC=), 5.30 (dt, *J* 17.00, 8.00 Hz, 1H, =CH), 7.34 (m, 20H, 4 Ph), 7.65 (m, 10H, 2 Ph).

$[R\overline{u(CO)Cl\{MeOOC}C{=}C(CO_2Me)CH{=}CHCMe_3\}(PPh_3)_2]$

An excess of dimethylacetylenedicarboxylate was added to a solution of 0.3 g (0.328 mmol) of [Ru(CO)Cl(HC=CHCMe$_3$)(PPh$_3$)$_2$] in CH$_2$Cl$_2$ (15 ml). After 1 h stirring the solution was concentrated and Et$_2$O was added to give a precipitate of [Ru(CO)Cl(MeO$_2$CC=CCO$_2$Me)(PPh$_3$)$_2$], which was filtered off. An equivalent volume of hexane was added to the filtrate and the solution was concentrated until a greenish-yellow solid separated. Recrystallization of this solid from CH$_2$Cl$_2$/MeOH gave crystals suitable for an X-ray structure determination. (Yield 40%). (Found: C, 64.02; H, 5.36. C$_{49}$H$_{47}$ClO$_5$P$_2$Ru calcd.: C, 64.36; H, 5.18%). Infrared: ν(C=O) 1910 vs, ν(C=O) 1720 s, ν(C=O–Ru) 1568 s, ν(C=C) 1540 w, ν(COC) 1185 m cm^{-1}. ^{1}H NMR (ppm): δ 0.662 (s, 9H, 3 Me), 2.87, 3.63 (s, 3H, Me), 4.876 (d, *J* 17.00 Hz, 1H, CH=), 5.277 (d, *J* 17.00 Hz, 1H, =CH), 7.347 (m, 20H, 4 Ph), 7.734 (m, 10H, 2 Ph).

$[R\overline{u(CO)Cl\{MeOO}CC{=}C(CO_2Me)CH = CHSiMe_3\}(PPh_3)_2]$

This yellow complex was prepared in the same way as the corresponding derivative of Me$_3$CC≡CH. (Yield 45%). (Found: C, 61.90; H, 5.12. C$_{48}$H$_{47}$ClO$_5$P$_2$RuSi calcd.: C, 61.96; H, 5.09%). Infrared: ν(C≡O) 1910 vs, ν(C=O) 1720 s, ν(C=O–Ru) 1570 s, ν(C=C) 1540 sh, ν(COC) 1205, 1185 w cm^{-1}. ^{1}H NMR (ppm): δ 0.907 (s, 9H, 3 Me), 2.89, 3.64 (s, 3H, Me), 5.217 (d, *J* 19.40 Hz, 1H, HC=), 5.448 (d, *J* 19.40 Hz, 1H, =CH), 7.31 (m, 20H, 4 Ph), 7.635 (m, 10H, 2 Ph).

TABLE 2

FINAL ATOMIC PARAMETERS FOR $[\mathrm{R\overline{u(CO)Cl(MeOO}CC{=}C(COOMe)HC{=}CHCMe_3)(PPh_3)_2}]$. ($U_{eq}=1/3\ \Sigma[U_{ij}.\ a_i^*\cdot a_j^* a_{ij}\cdot\cos a_i a_j]\times 10^3(\times 10^4$ for Ru)

Atom	x	y	z	U_{eq} (Å^2)
Ru	0.19798(8)	0.35744(3)	0.35605(10)	35(3)
Cl	0.1678(3)	0.3074(1)	0.5071(4)	63(1)
P(1)	0.3888(3)	0.393(1)	0.3748(3)	39(1)
P(2)	0.0044(3)	0.3728(1)	0.3481(3)	39(1)
O(1)	0.2529(9)	0.4235(3)	0.5140(9)	64(4)
O(2)	0.1595(7)	0.3202(2)	0.1805(9)	49(3)
O(3)	0.1836(10)	0.3448(3)	−0.0133(10)	74(4)
O(4)	0.1314(9)	0.4267(3)	−0.0760(10)	66(4)
O(5)	0.3136(9)	0.4175(3)	−0.0611(9)	76(5)
C(1)	0.2325(10)	0.3976(4)	0.4542(12)	40(4)
C(2)	0.1813(10)	0.3479(4)	0.1130(12)	48(5)
C(3)	0.2092(10)	0.3811(4)	0.1831(12)	42(4)
C(4)	0.2317(10)	0.4145(4)	0.1305(12)	42(4)
C(5)	0.2679(12)	0.4473(4)	0.2043(12)	49(5)
C(6)	0.2821(14)	0.4800(4)	0.1523(16)	70(6)
C(7)	0.3160(18)	0.5151(5)	0.2262(18)	89(8)
C(8)	0.2159(14)	0.4199(4)	−0.0124(14)	54(5)
C(9)	0.3074(19)	0.4255(7)	−0.2017(15)	116(10)
C(10)	0.1550(21)	0.3079(4)	−0.0682(18)	108(10)
C(71)	0.3980(28)	0.5068(7)	0.3416(28)	185(16)
C(72)	0.2197(25)	0.5310(8)	0.2971(36)	200(19)
C(73)	0.3449(48)	0.5431(8)	0.1471(30)	339(32)
C(101)	0.4144(10)	0.2975(3)	0.2854(14)	46(5)
C(102)	0.5084(14)	0.2932(4)	0.2216(19)	78(7)
C(103)	0.5257(16)	0.2592(5)	0.1620(21)	93(8)
C(104)	0.4506(15)	0.2306(5)	0.1654(19)	81(8)
C(105)	0.3591(14)	0.2345(4)	0.2314(19)	80(7)
C(106)	0.3403(12)	0.2688(4)	0.2899(15)	58(6)
C(111)	0.4478(11)	0.3263(4)	0.5372(15)	57(6)
C(112)	0.5233(12)	0.2976(4)	0.5561(18)	76(7)
C(113)	0.5651(18)	0.2869(7)	0.6840(28)	108(11)
C(114)	0.5324(21)	0.3060(9)	0.7845(2)	130(14)
C(115)	0.4586(22)	0.3366(8)	0.7675(22)	146(13)
C(116)	0.4163(18)	0.3455(7)	0.6420(16)	111(10)
C(121)	0.4844(9)	0.3739(4)	0.3232(13)	44(5)
C(122)	0.5512(11)	0.3959(4)	0.4103(15)	59(6)
C(123)	0.6190(13)	0.4234(5)	0.3666(20)	75(7)
C(124)	0.6190(14)	0.4298(4)	0.2364(21)	74(7)
C(125)	0.5505(13)	0.4077(5)	0.1466(17)	75(7)
C(126)	0.4830(11)	0.3806(4)	0.1903(14)	55(5)
C(201)	−0.0870(10)	0.3444(4)	0.2399(14)	47(5)
C(202)	−0.1702(12)	0.3589(5)	0.1501(14)	62(6)
C(203)	−0.2369(14)	0.3354(6)	0.0660(17)	80(8)
C(204)	−0.2182(15)	0.2966(6)	0.0761(20)	89(9)
C(205)	−0.1403(14)	0.2818(5)	0.1666(21)	84(8)
C(206)	−0.0704(13)	0.3050(5)	0.2486(20)	82(8)
C(211)	−0.0551(10)	0.3673(3)	0.4991(12)	41(4)
C(212)	−0.1683(11)	0.3587(4)	0.4997(14)	54(5)
C(213)	−0.2137(12)	0.3579(4)	0.6170(16)	56(6)
C(214)	−0.1505(13)	0.3651(4)	0.7285(16)	58(6)
-2di				

TABLE 2 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(215)	−0.0386(14)	0.3737(4)	0.7314(16)	66(6)
C(216)	0.0086(11)	0.3760(4)	0.6139(14)	54(5)
C(221)	−0.0314(10)	0.4199(4)	0.3002(14)	49(5)
C(222)	−0.0234(12)	0.4310(4)	0.1735(16)	64(6)
C(223)	−0.0454(15)	0.4691(6)	0.1414(24)	103(10)
C(224)	−0.0774(16)	0.4954(6)	0.2346(25)	100(10)
C(225)	−0.0874(16)	0.4835(5)	0.3585(24)	94(9)
C(226)	−0.0633(13)	0.4461(4)	0.3941(17)	69(6)

$[R\overline{u(CO)Cl\{MeO}OCC{=}C(CO_2Me)CH{=}CHPh\}(PPh_3)_2]$

This complex was prepared in the way described for the other mixed bis-insertion derivatives. The impure yellow solid obtained by precipitation with hexane was purified by crystallization from CH_2Cl_2/MeOH. (Yield 30%) (Found: C, 65.61; H, 4.85; $C_{51}H_{43}ClO_5P_2Ru$ calcd.: C, 65.56; H, 4.64%). Infrared: ν(C≡O) 1925 vs, ν(C=O) 1735 s, ν(C=O-Ru) 1575 s, ν(C=C) 1555 s, ν(COC) 1200 m cm^{-1}. ^{1}H NMR (ppm) δ: 2.966, 3.635 (s, 3H, Me), 5.618 (d, J 16.00 Hz, 1H, HC=), 6.076 (d, J 16.00 Hz, 1H, =CH), 6.993–7.167 (2 m, 5H, 1 Ph), 7.309 (m, 20H, 4 Ph), 7.735 (m, 10H, 2 Ph).

Crystal structure

Crystals of $[R\overline{u(CO)Cl\{MeO}OCC{=}C(CO_2Me)CH = CHCMe_3\}(PPh_3)_2]$ were grown from a solution in CH_2Cl_2/MeOH (1/1).

Crystal data. $C_{49}H_{47}ClO_5P_2Ru$, M = 914.32, monoclinic, $P2_1/n$, a 12.121(2), b 36.123(10), c 10.541(2) Å, β 96.71(2)°, $D_x = 1.32$ g cm^{-3}, $Z = 4$, μ(Mo-K_α) 0.489 mm^{-1}.

A single crystal of dimensions 0.15 × 0.15 × 0.20 mm was used to collect data on a CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.7107 Å). A total of 6758 reflections with $2° < \theta < 23.5°$ were measured in the $\omega/2\theta$ scan mode. Of these, 4988, observed reflections meeting the criterion $I > 3\sigma(I)$ were used. No absorption correction was applied. No crystal decay was observed from two reference reflections measured every 50 min.

Structure solution and refinement

The heavy atom method followed by the usual Fourier synthesis allowed the location of all atoms except hydrogens. The structure was refined by full matrix least-squares methods. The thermal motion was considered as anisotropic.

A total of 523 parameters were varied. The refinement converged at $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.056$ for observed reflexions only. Hydrogens were not taken into account in the calculations.

Most of the calculations were performed by means of the X RAY 70 system [3]. Atomic scattering factors for neutral atoms and anomalous dispersion correction factors for Ru, P and Cl were taken from International Tables [4]. The final atomic coordinates are collected in Table 2. Lists of structure factors and thermal parameters are available from the authors.

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References

1 M.R. Torres, A. Vegas, A. Santos and J. Ros, J. Organomet. Chem., 309 (1986) 169.

2 M.R. Torres, A. Santos, J. Ros and X. Solans, Organometallics, in press.

3 J.M. Stewart, F.A. Kundell and J.C. Baldwin, "X-Ray 70" System, Computer Science Center, University of Maryland, 1970.

4 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. 4, pp. 72–98.

5 C.K. Johnson (1965). ORTEP Report ORNL-3794. Oak Ridge National Laboratory. Tenessee.