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# INSERTION REACTIONS OF ACETYLENES WITH HYDRIDOCARBONYLCHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II). X-RAY STRUCTURE OF CARBONYLCHLORO(*cis*-1,2-DIPHENYLETHENYL)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

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## Summary

Reactions between $Ru(CO)ClH(PPh_3)_3$ and phenylacetylene, pent-1-yne and diphenylacetylene in $CH_2Cl_2$ give the red crystalline alkenyl species Ru(CO)Cl-$(RC{=}HR')(PPh_3)_2$ ($R = H$, $R' = C_3H_7$, Ph; $R = R' = Ph$), which can be regarded as resulting from elimination of one phosphine molecule and insertion of the alkyne into the Ru–H bond. The reaction with phenylacetylene in $MeOH/CH_2Cl_2$ (1/1) gives the yellow crystalline complex $Ru(CO)Cl(PhC{=}CH_2)$-$(PPh_3)_3$, seemingly resulting from a simple insertion of the alkyne into the Ru–H bond.

The complexes have been characterized by elemental analysis and $^1H$ NMR and IR spectroscopy. The molecular structure of $Ru(CO)Cl(PhC{=}CHPh)(PPh_3)_2$, determined by X-ray diffraction, can be described as a distorted trigonal bipyramidal species, in which the phosphine molecules occupy the axial positions and the alkenyl ligand has the phenyl groups in a *cis* configuration. Similar molecular structures are probable for the other red complexes. The yellow complex derived from phenylacetylene seems to be a six-coordinate species, in which two phosphine molecules are respectively *cis*- and *trans*-coordinated with respect to the alkenyl ligand.

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## Introduction

Insertion of acetylenes into transition metal–hydrogen, –$\sigma$-carbon, –$\eta^2$-acetylene or –halogen bonds is an important step in catalytic hydrogenation, oligomerization and polymerization and in consequence considerable information about such reac-

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tions has become in recent years [1]. In the case of insertion of acetylenes into transition metal–hydrogen bonds, particular attention has been given to reactions of fluoroacetylenes because of their ability to form stable σ-alkenyl complexes [1].

In the case of reactions of acetylenes with ruthenium hydrido complexes only the reactions of complexes of the type $[RuH(\eta^5\text{-}C_5H_5)(L_2)](L = PPh_3, CO)$ have been described. The reactions of $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ with alk-1-ynes $HC_2R$ (R = COOMe, COMe, $CF_3$, $C_6F_5$) give rise to a variety of unusual products containing unsaturated ligands formed by oligomerization of the alkyne [2]. The complexes $[RuH(\eta^5\text{-}C_5H_5)(L_2)]$ (L = $PPh_3$, CO) react with hexafluorobutyne to give alkenyl complexes resulting from a single or double insertion of the alkyne, and $[RuH(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ reacts with MeOOCC≡CCOOMe in the same way [3,4].

We describe here a study of the reactions of the acetylenes pent-1-yne, phenylacetylene, and diphenylacetylene with $[Ru(CO)ClH(PPh_3)_3]$.

## Results and discussion

### *Five-coordinated alkenyl complexes*

The red crystalline, stable, complexes, obtained by reaction of $Ru(CO)ClH(PPh_3)_3$ with phenylacetylene, pent-1-yne, and diphenylacetylene in $CH_2Cl_2$ are non-electrolytes in acetone. They are moderately soluble in acetone, very soluble in $CH_2Cl_2$ and $CHCl_3$, and insoluble in diethyl ether, methanol and hexane.

The pent-1-yne and phenylacetylene derivatives show no IR bands in the 2100–1700 $cm^{-1}$ region assignable to ν(C≡C), but a band of medium intensity towards 1585–1590 $cm^{-1}$ can be assigned to the olefinic ν(C=C) stretching frequency. The corresponding band is absent from the IR spectrum of the diphenylacetylene derivative. In all these complexes ν(CO) appears as a strong band near 1920 $cm^{-1}$ and ν(Ru–Cl) as a medium intensity band near 295 $cm^{-1}$, corresponding to terminal Ru–Cl bonds.

The $^1$H NMR spectrum of the red phenylacetylene derivative shows two doublets (δ 5.53 and 8.43 ppm, *J* 13 Hz, 2H), which are typical of two *trans*-olefinic protons in a HC=CH system. The phenyl group attached to the alkenyl ligand gives rise to a series of separated signals corresponding to its various sets of protons (δ 6.76, d, 2H; 6.96, t, 1H; 7.13, t, 2H), whereas the phosphine phenyl groups give two multiplets (δ 7.2–7.7 ppm) which together correspond to 30H (2 $PPh_3$).

The $^1$H NMR spectrum of the pent-1-yne derivative also shows signals characteristic of two *trans*-olefinic protons in a HC=CHR (R = propyl) system (δ 4.6, m, 1H and δ 6.97, d, *J* 11.76 Hz). The signals corresponding to the protons of the propyl group are also clearly observed: δ 1.36, quartet, $2H(CH_2)$ (**1**); δ 1.06, sextet, $2H(CH_2)$ (**2**); 0.64, t, $3H(CH_3)$ (**3**). The phosphine phenyl groups give a multiplet, δ 7.2–7.7 (30H, $2PPh_3$).

The $^1$H NMR spectrum of the diphenylacetylene derivative shows a singlet, at δ 5.33, corresponding to a single olefinic proton. Two multiplets at δ 6.2–7.0 (10H) are assigned to the phenyl groups attached to the alkenyl ligand (2Ph) and a multiplet at δ 7.1–7.8 (30H) is assigned to the phosphine phenyl groups (2 $PPh_3$).

The spectral data, taken together with the elemental analysis (C,H) results, are consequent with the formulation $[Ru(CO)Cl(RC{=}CHR')(PPh_3)_2]$ (R = H, R′ = Pr, Ph; R = R′ = Ph), which are apparently five-coordinate species. In order to establish the geometry of these five-coordinate species and to decide between the *cis*- and *trans*-configuration for the alkenyl group, a decision which cannot be made on the basis of the $^1$H NMR spectral data for the red diphenylacetylene derivative, we determined the crystal and molecular structure of $[Ru(CO)Cl(PhC{=}CHPh)(PPh_3)_2]$ by single crystal X-ray diffraction.

*The structure of $[Ru(CO)Cl(PhC{=}CHPh)(PPh_3)_2]$*

The crystal consists of individual molecules of $[Ru(CO)Cl(PhC{=}CHPh)(PPh_3)_2]$ held together by Van der Waals forces. Table 1 lists the more relevant bond lengths and angles of the molecule which is represented in Fig. 1.

As assumed on the basis of the spectral data, the Ru atoms appear to be pentacoordinate at the center of an irregular trigonal bipyramid. The two $PPh_3$

TABLE 1

INTERATOMIC BOND LENGTHS (Å) AND ANGLES (°) FOR $Ru(CO)Cl(PhC{=}CHPh)(PPh_3)_2$ (with e.s.d.'s in parentheses)

| | |
|---|---|
| Ru–P(1) | 2.419(3) |
| Ru–P(2) | 2.413(3) |
| Ru–Cl | 2.420(3) |
| Ru–C(1) | 1.79(1) |
| Ru–C(2) | 2.03(1) |
| C(1)–O(1) | 1.15(2) |
| C(2)–C(3) | 1.37(2) |
| C(2)–C(21) | 1.46(2) |
| C(3)–C(31) | 1.47(2) |
| P(1)–C(101) | 1.84(1) |
| P(1)–C(111) | 1.84(1) |
| P(1)–C(121) | 1.82(1) |
| P(2)–C(201) | 1.81(1) |
| P(2)–C(211) | 1.83(1) |
| P(2)–C(221) | 1.81(1) |
| Mean C–C distance in benzene rings: 1.40(2) Å | |
| P(1)–Ru–P(2) | 162.0(1) |
| P(1)–Ru–Cl | 88.4(1) |
| P(1)–Ru–C(1) | 86.7(4) |
| P(1)–Ru–C(2) | 99.4(3) |
| P(2)–Ru–Cl | 84.4(1) |
| P(2)–Ru–C(1) | 88.5(4) |
| P(2)–Ru–C(2) | 97.6(3) |
| Cl–Ru–C(1) | 140.8(4) |
| Cl–Ru–C(2) | 132.7(4) |
| C(1)–Ru–C(2) | 86.4(5) |
| Ru–C(1)–O | 175 (1) |
| Ru–C(2)–C(3) | 130.7(9) |
| Ru–C(2)–C(21) | 102.3(8) |
| C(21)–C(2)–C(3) | 127 (1) |
| C(2)–C(3)–C(31) | 125 (1) |
| Mean C–P–C: 103.2(6)° | |
| Mean Ru–P–C: 115.1(4)° | |
| Mean C–C–C in benzene rings: 120(1)° | |

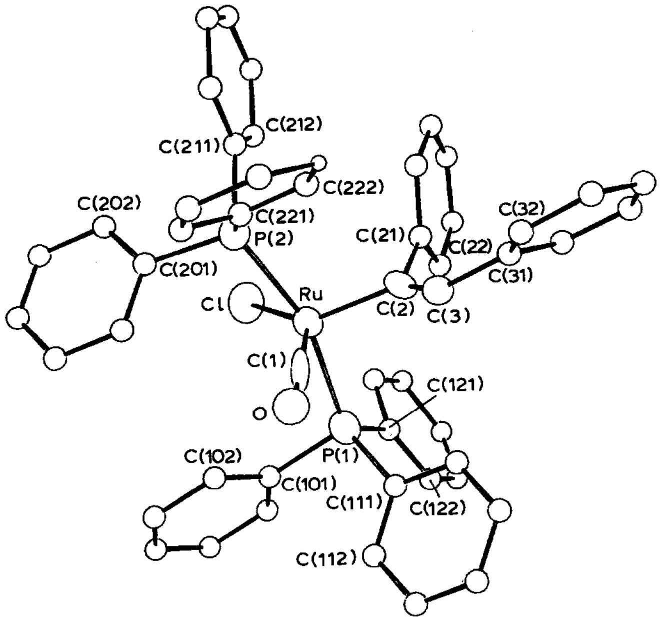


Fig. 1. ORTEP [16] drawing of the molecular structure showing the pentacoordination at Ru. The atom numbering is the same as that used in Table 2; numbering of the carbons of the phenyl rings is omitted for clarity as are the H atoms.

molecules are in the axial positions and the CO, Cl, and bisphenylethenyl ligands in the equatorial plane. The distortion of the coordination polyhedron involves the non-linearity of the two Ru–P bonds and the different bond distances and angles in the equatorial plane defined by the Cl, C(1) and C(2) atoms. The Ru atom deviates 0.04(5) Å from this plane towards the P(1) atom. The two Ru–P bonds are bent towards the line through Cl and C(1), the angle between the planes defined by C(1), Ru and P(1) and P(1), Ru and P(2) being 75(1)°. The bisphenylethenyl ligand has the two phenyl groups in a *cis*-disposition, the angle between them being 65(1)°, confirming that there has been a *cis*-insertion of bisphenylacetylene into the Ru–H bond. The C(2)–C(3) bond length, 1.37(2) Å, confirms its double bond character, even though its $\nu$(C=C) stretching mode was not observed in the IR spectrum.

The Ru–C(1) bond length, 1.79 (1) Å, is similar to those in other five-coordinate ruthenium carbonyl complexes, such as [Ru(CO)(NO)I($PPh_3$)$_2$] (1.80(4) Å [5]) and both isomers of [Ru(CO)$C_2S_2$($CF_3$)$_2$($PPh_3$)$_3$] (1.83(1) and 1.85(1) Å [6,7]), but shorter than those in [Ru(CO)$_3$($PPh_3$)$_2$] (1.90(1) Å [8]) and in the six-coordinated complex *trans*-[Ru(CO)$_2$Cl{MeOOCC=C(COOMe)Cl}($PMe_2Ph$)$_2$] (1.92(2) and 1.87(2) Å [9]). The comparison with the nitrosyl-containing complex **5** should be made with care because the CO and NO groups are disordered, and the value of 1.80(4) Å corresponds to the mean of the Ru–C and Ru–N bond distances. Nevertheless, the metal–carbon (carbonyl) distance seems to increase with the CO content, the longest value 1.87(2) Å being observed for [Ru(CO)$_3$($PPh_3$)$_2$] [8], in which the $\pi$-back-bonding must be spread over the three CO ligands.

The Ru–C(2) bond length, 2.03(1) Å, agrees well with those in the formally six-coordinate ruthenium alkenyl complexes $[Ru(\eta^5\text{-}C_5H_5)\{C_2(CF_3)\cdot C_4F_6H\}]$ (2.05(1) Å [10]), $[Ru\{CH{=}C(COOBu)Me\}H(PPh_3)_3]$ (2.06(1) Å [11]) and $[Ru\{\eta^5\text{-}C_5H_4C(CF_3)_2OH\}\{MeOOCC{=}C(COOMe)H\}(PPh_3)]$ (2.04(4) Å [12]), but it is significantly shorter than that observed in the six-coordinate *trans*-$[Ru(CO)_2Cl\{MeOOCC{=}C(COOMe)Cl\}(PMe_2Ph)_2]$ 2.16(2) Å [9]. Analysis of the possible significance of these differences would not be justified in view of the fairly high *R* value in our structure determination and of the scarcity of relevant data.

*Six-coordinate alkenyl complexes*

When the reaction between phenylacetylene and $Ru(CO)ClH(PPh_3)_3$ is carried out in $MeOH/CH_2Cl_2$ (1/1) at room temperature, a yellow crystalline product is formed, the higher carbon content of which compared with that of the red complex corresponds to the presence of one more molecule of phosphine. The air-stable yellow complex is a non-electrolyte in acetone and its solubility is similar to that of the red complex.

There are no bands in the $\nu(C{\equiv}C)$ frequency region in the IR and Raman spectra, and the presence of a medium intensity IR band at 1585 $cm^{-1}$, assignable to $\nu(C{=}C)$, seems to indicate the presence of an alkenyl group. The $\nu(CO)$ frequency appears as a strong IR band at 1908 $cm^{-1}$, and a medium intensity band at 302 $cm^{-1}$ is assigned to a $\nu(Ru\text{-}Cl)$ stretching frequency and corresponds to a terminal Cl–Ru bond.

In the $^1H$ NMR spectrum there are a singlet ($\delta$ 5.40) corresponding to olefinic protons and two multiplets in the phenyl groups region, with a ratio of phenyl to olefinic protons of 25/1. The singlet could correspond to one proton or to two geminal protons; only the second possibility is consistent with the analytical data, and for this formulation there would be 50 phenyl protons ($3Ph_3$ + PhC=), and the phenyl multiplets ($\delta$ 7.5–7.7, 20H; $\delta$ 6.8–7.4 ppm, 30H) could be assigned, respectively, to PhC= + *trans*-$PPh_3$ and to 2 *cis*-$PPh_3$ protons, the *cis*- or *trans*-positions of phosphine molecules being defined with respect to the alkenyl ligand. From spectral and analytical data we can assign to this yellow complex the molecular formula $[Ru(CO)Cl(PhC{=}CH_2)(PPh_3)_3]$, and it can be described as a hexacoordinate species in which the alkenyl ligand contains a geminal $CH_2$ group and one phosphine molecule is *trans*- and two phosphine molecules are *cis*-coordinated with respect to the alkenyl group. This complex can be also regarded as resulting from an insertion of phenylacetylene into the Ru–H bond which is different from that which gives rise to the red complex.

From the spectral and structural data we conclude that the red, pentacoordinate species can be considered as resulting from a single *cis*-insertion of alkyne into the Ru–H bond. The yellow, hexacoordinated phenylacetylene derivative also results from a single insertion of phenylacetylene into the Ru–H bond but we cannot say whether this is a *cis*- or *trans*-process.

No other products, resulting from a bis- or tris-insertion of alkyne into Ru–H and C–H bonds or from alkyne polymerization, were isolated. Thus $RuH(CO)Cl(PPh_3)_3$ differs markedly from $RuH(\eta^5\text{-}C_5H_5)(PPh_3)_2$ in the reactions with alkynes [2].

It should be noted that, in the attempts to recrystallize the yellow complex red crystals of the pentacoordinate species were obtained frequently. The red complex can be also transformed into the yellow complex by addition of $PPh_3$ in

MeOH/$CH_2Cl_2$ (1/1). This interconversion could involve an $\eta$-alkyne hydrido species as intermediate:

$$[Ru(CO)Cl(PhC{=}CH_2)(PPh_3)_3] \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} [Ru(CO)ClH(\eta\text{-}PhC{\equiv}CH)(PPh_3)_2] \rightleftharpoons$$

$$[Ru(CO)Cl(HC{=}CHPh)(PPh_3)_2]$$

Attempts to isolate any such intermediate species were unsuccessful. The solution resulting from the reaction in $CH_2Cl_2$ contains a green species which was isolated by column chromatography on Florisil, but not in sufficient amount for characterization.

Studies of the reactions of $Ru(CO)ClH(PPh_3)_3$ with other alkynes and alkenes and of those of the insertion products are in progress.

## Experimental

The $^1H$ 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 with 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.

$Ru(CO)ClH(PPh_3)_3$ was prepared as previously described [13].

*[Ru(CO)Cl{trans-HC=CH($C_3H_7$)}($PPh_3$)$_2$]*

An excess of pent-1-yne was added to a solution of $Ru(CO)ClH(PPh_3)_3$ (0.3 g, 0.315 mmol) in $CH_2Cl_2$ (10 ml) until the solution became red. After 0.5 h stirring the solution was concentrated and chromatographed on a Florisil column. Elution with $CH_2Cl_2$ gave a red solution, from which a red orange solid was precipitated by addition of light petroleum (Yield 65%). (Found: C, 66.6; H, 5.4. $C_{42}H_{39}ClOP_2Ru$ calcd.: C, 66.5; H, 5.18%). Infrared $\nu$(CO) 1920vs, $\nu$(C=C) 1582m, $\nu$(Ru–Cl) 295 $cm^{-1}$. $^1H$ NMR (ppm): $\delta$ 4.6 (m, 1H (H=C)), 6.97 (d, $J$ 11.76 Hz, 1H (=CH)), 1.86 (quartet, 2H ($CH_2$)(**1**)), $\delta$ 1.05 (sextet, 2H ($CH_2$)(**2**)), 0.64 (t, 3H ($CH_3$)(**3**)), $\delta$ 7.2–7.7, 30H, 2$PPh_3$) (in $CDCl_3$).

*[Ru(CO)Cl{trans-HC=CH(Ph)}($PPh_3$)$_2$]*

An excess of phenylacetylene was added to a solution of $HRu(CO)Cl(PPh_3)_3$ (0.3 g, 0.315 mmol) in $CH_2Cl_2$ (10 ml) until the solution became red. After 0.5 h stirring the solution was concentratred and a red solid precipitated by addition of diethyl ether (yield 70%). The product was recrystallized from $CH_2Cl_2$/diethyl ether solution (Found: C, 68.6; H, 4.9. $C_{45}H_{37}ClOP_2Ru$ calcd.: C, 68.2; H, 4.7%). Infrared: $\nu$(CO) 1915vs, $\nu$(C=C) 1590m, $\nu$(Ru–Cl) 295m $cm^{-1}$. $^1H$ NMR (ppm) $\delta$ 5.58 (d, $J$ 13 Hz, 1H (HC=)), 8.43 (d, $J$ 13 Hz, 1H (=CH)), 6.76 (d, 2H) 6.96 (t, 1H), 7.13 (t, 2H) (C=CPh) 7.2–7.7 (2 multiplets, 30H (phosphine phenyl groups)) (in $CDCl_3$).

*[Ru(CO)Cl(PhC=$CH_2$)($PPh_3$)$_3$]*

Use of same reactants in 1/1 $CH_2Cl_2$/MeOH (10 ml) gave a yellow solution from which after 0.5 h stirring at room temperature yellow needles separated (yield

TABLE 2. ATOMIC PARAMETERS FOR $Ru(CO)Cl(PhC{=}CHPh)(PPh_3)_2$ (Thermal parameters are defined as $U_{eq} = 1/3\Sigma\ [U_{ij} a_i^{\star} a_j^{\star} a_i a_j \cos(a_i a_j)] \times 10^4$

| Atom | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$ (Å$^3$) |
|---|---|---|---|---|
| Ru | 0.14383(3) | 0.44628(9) | −0.10452(4) | 356(3) |
| Cl | 0.1898(1) | 0.6298(3) | −0.1245(1) | 550(1) |
| P(1) | 0.1276(1) | 0.5497(3) | −0.0265(1) | 408(1) |
| P(2) | 0.1827(1) | 0.3405(3) | −0.1706(1) | 394(1) |
| C(1) | 0.1457(4) | 0.2977(13) | −0.0708(4) | 421(5) |
| C(2) | 0.0818(4) | 0.3944(12) | −0.1258(4) | 420(4) |
| C(3) | 0.0584(4) | 0.2835(13) | −0.1171(4) | 424(4) |
| O | 0.1500(3) | 0.2050(9) | −0.0478(3) | 639(4) |
| C(21) | 0.0689(4) | 0.4999(11) | −0.1587(4) | 343(3) |
| C(22) | 0.0686(4) | 0.4816(13) | −0.2111(5) | 568(4) |
| C(23) | 0.0587(5) | 0.5866(15) | −0.2421(5) | 651(4) |
| C(24) | 0.0503(5) | 0.7075(15) | −0.2217(6) | 668(4) |
| C(25) | 0.0498(5) | 0.7276(15) | −0.1716(6) | 680(4) |
| C(26) | 0.0596(4) | 0.6210(13) | −0.1399(5) | 545(4) |
| C(31) | 0.0141(4) | 0.2539(13) | −0.1372(5) | 528(4) |
| C(32) | 0.0066(5) | 0.1235(16) | −0.1480(6) | 782(5) |
| C(33) | −0.0355(6) | 0.0864(20) | −0.1683(7) | 1035(6) |
| C(34) | −0.0676(6) | 0.1804(19) | −0.1750(7) | 967(6) |
| C(35) | −0.0612(5) | 0.3080(16) | −0.1618(6) | 760(5) |
| C(36) | −0.0188(5) | 0.3488(14) | −0.1431(5) | 623(4) |
| C(101) | 0.0960(4) | 0.4510(12) | 0.0160(4) | 421(3) |
| C(102) | 0.0549(4) | 0.4062(14) | 0.0031(5) | 579(4) |
| C(103) | 0.0304(5) | 0.3257(17) | 0.0358(6) | 805(5) |
| C(104) | 0.0472(6) | 0.2952(17) | 0.0816(6) | 828(5) |
| C(105) | 0.0876(6) | 0.3445(18) | 0.0971(6) | 865(5) |
| C(106) | 0.1126(5) | 0.4233(16) | 0.0637(6) | 712(4) |
| C(111) | 0.1022(4) | 0.7104(12) | −0.0218(4) | 457(3) |
| C(112) | 0.0768(5) | 0.7419(15) | 0.0194(6) | 698(4) |
| C(113) | 0.0598(6) | 0.8721(18) | 0.0243(6) | 857(5) |
| C(114) | 0.0698(6) | 0.9586(18) | −0.0122(6) | 888(5) |
| C(115) | 0.0954(5) | 0.9282(16) | −0.0539(6) | 737(4) |
| C(116) | 0.1120(4) | 0.8007(13) | −0.0581(5) | 540(4) |
| C(121) | 0.1805(4) | 0.5744(12) | 0.0054(4) | 454(3) |
| C(122) | 0.1875(4) | 0.6875(14) | 0.0322(5) | 565(4) |
| C(123) | 0.2297(5) | 0.7028(14) | 0.0563(5) | 625(4) |
| C(124) | 0.2597(5) | 0.6080(16) | 0.0520(6) | 698(4) |
| C(125) | 0.2544(5) | 0.4965(16) | 0.0254(6) | 778(5) |
| C(126) | 0.2122(5) | 0.4792(15) | 0.0002(6) | 698(4) |
| C(201) | 0.2410(4) | 0.3530(12) | −0.1554(5) | 482(3) |
| C(202) | 0.2545(5) | 0.3050(15) | −0.1085(5) | 680(4) |
| C(203) | 0.2995(6) | 0.3289(18) | −0.0930(6) | 887(5) |
| C(204) | 0.3270(6) | 0.4028(17) | −0.1252(6) | 852(5) |
| C(205) | 0.3142(5) | 0.4458(17) | −0.1700(6) | 777(5) |
| C(206) | 0.2698(5) | 0.4206(14) | −0.1863(5) | 617(4) |
| C(211) | 0.1808(4) | 0.3986(12) | −0.2345(4) | 461(3) |
| C(212) | 0.1904(5) | 0.3115(15) | −0.2730(6) | 689(4) |
| C(213) | 0.1899(6) | 0.3572(18) | −0.3222(7) | 897(5) |
| C(214) | 0.1838(6) | 0.4857(17) | −0.3311(6) | 848(5) |
| C(215) | 0.1735(5) | 0.5716(17) | −0.2946(6) | 792(5) |
| C(216) | 0.1730(5) | 0.5293(15) | −0.2440(5) | 654(4) |
| C(221) | 0.1717(4) | 0.1698(12) | −0.1781(4) | 427(3) |
| C(222) | 0.2024(4) | 0.0735(13) | −0.1702(4) | 492(3) |
| C(223) | 0.1909(5) | −0.0601(15) | −0.1774(5) | 644(4) |
| C(224) | 0.1488(5) | −0.0897(14) | −0.1932(5) | 604(4) |
| C(225) | 0.1184(4) | 0.0072(13) | −0.0202(5) | 541(4) |
| C(226) | 0.1288(4) | 0.1372(14) | −0.1944(5) | 569(4) |

70%). (Found: C, 71.4; H, 4.8. $C_{63}H_{51}ClOP_3Ru$ calcd.: C, 71.8; H, 4.9%). Infrared $\nu$(CO) 1908vs; $\nu$(C=C) 1585m; $\nu$(Ru–Cl) 300m $cm^{-1}$. $^1H$ NMR (ppm): $\delta$ 5.4 (2, 2H (=$CH_2$)), 7.5–7.7 (m, 20H (PhC= + $PPh_3$)), 6.8–7.4 (m, 30H (2 $PPh_3$)) (in $CDCl_3$).

*[Ru(CO)Cl(PhC=CHPh)(PPh$_3$)$_2$]*

An excess of solid PhC≡CPh was added to a solution of $Ru(CO)ClH(PPh_3)_3$ (0.3 g, 0.315 mmol) in $CH_2Cl_2$ (10 ml) until the solution became red and the mixture was refluxed with stirring. After 0.5 h the solution was concentrated and chromatographed on a Florisil column. Elution with $CH_2Cl_2$ gave a red-orange solution from which a red-orange solid was isolated by addition of hexane or light petroleum. The green residue which remained in the column was eluted with $CH_2Cl_2$, but it could be not isolated in sufficient amount for characterization. Recrystallization of the red solid from $CH_2Cl_2$/diethyl ether gave crystals suitable for an X-ray structure determination (yield 75%). (Found: C, 70.0; H, 4.9. $C_{51}H_{41}ClOP_2Ru$ calcd.: C, 70.5; H, 4.8%). Infrared: $\nu$(CO) 1923vs; $\nu$(Ru–Cl) 290m $cm^{-1}$. $^1H$ NMR (ppm) $\delta$ 5.33 (s, 1H (=CH)), 6.2–7.0 (2 multiplets, 10H (olefin phenyl groups)), 7.17–7.8 (m, 30H (phosphine phenyl groups)) (in $CDCl_3$).

*X-ray diffraction data*

The crystals are monoclinic, $C2/c$, with cell dimensions $a$ 30.282(3), $b$ 10.341(3), $c$ 26.969(2) Å, $\beta$ 90.97(2)°. (By least-squares refinement on diffractometer angles for 25 centered reflexions, $\lambda$ 0.7107 Å), $Z = 8$, $D_x$ 1.37 g $cm^{-3}$, $\mu$(Mo-$K_\alpha$) 0.539 $mm^{-1}$, crystal dimensions: 0.15 × 0.15 × 0.25 mm. Intensities for 4836 unique reflexions. ($2° \leqslant \theta \leqslant 21°$) measured on a CAD-4 diffractometer, $\omega/2\ \theta$ scan mode, with graphite-monochromated Mo-$K_\alpha$ radiation, scan width $\omega = 0.80 + 0.35$ tg $\theta$)°. 1935 reflections, with $I \leqslant 2\sigma(I)$ were considered as unobserved. No absorption correction was applied. No crystal decay was observed from two reference reflexions measured every 50 min.

*Structure solution and refinement*

The heavy atom method followed by the usual Fourier synthesis, led to location of all atoms except hydrogens. The structure was refined by full matrix-least squares methods. The thermal motion was taken as anisotropic for Ru, Cl, P and C≡O and C=C groups and isotropic for all phenyl groups. A total of 265 parameters were varied. The refinement converged at $R = 0.069$ for observed reflexions only.

Most of the calculations were performed by means of the X RAY 70 system [14]. Atomic scattering factors for neutral atoms and anomalous dispersion correction factors for Ru, P and Cl were taken from International Tables for X-ray Crystallography [15]. 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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