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Vinylidene transition metal complexes XXXIV [1]. The preparation and structure of neutral vinylidene and allenylidene ruthenium(II) compounds of the half-sandwich type containing $^{i}Pr_2PCH_2CO_2Me$ as supporting ligand.

T. Braun, P. Steinert, H. Werner *

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

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Abstract

The reaction of the tetrameric compound $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (**1**; $Cp^* = C_5Me_5$) with $^{i}Pr_2PCH_2CO_2Me$ gives the monomeric species $[Cp^*RuCl\{\kappa^2(P, O)\text{-}^{i}Pr_2PCH_2CO_2Me\}]$ (**2**) which is an excellent starting material for the synthesis of neutral half-sandwich type ruthenium complexes containing substituted vinylidenes and allenylidenes as ligands. Compound **2** reacts with $HC{\equiv}CCO_2Me$ to give $[Cp^*RuCl(=C=CHCO_2Me)(^{i}Pr_2PCH_2CO_2Me)]$ (**4**), and the corresponding reaction of **2** with $HC{\equiv}CCPh_2OH$ affords $[Cp^*RuCl(=C=CHCPh_2OH)(^{i}Pr_2PCH_2CO_2Me)]$ (**5**) which on treatment with acidic alumina yields $[Cp^*RuCl(=C=C=CPh_2)(^{i}Pr_2PCH_2CO_2Me)]$ (**6**). In contrast, the reaction of **2** with $Me_3SiC{\equiv}CCO_2Et$ gives, instead of an alkyne or vinylidene ruthenium derivative, the cyclobutadiene complex $[Cp^*RuCl\{\eta^4\text{-}C_4(SiMe_3)_2(CO_2Et)_2\}]$ (**7**) which is accessible also from **1** and $Me_3SiC{\equiv}CCO_2Et$ in almost quantitative yield. The crystal and molecular structures of **2** and **4** have been determined.

Keywords: Ruthenium; Vinylidene; Phosphinoester; Allenylidene; Crystal structure

1. Introduction

Although recently neutral vinylidene ruthenium complexes have attracted a great deal of attention [2], half-sandwich type compounds of the general composition $[Cp'Ru(=C=CRR')(L)X]$ ($Cp' = C_5H_5$, C_5Me_5 or other cyclopentadienyl derivatives) are, to the best of our knowledge, unknown. This is particularly surprising in so far as the related cationic species $[Cp'Ru(=C=CRR')(L)_2]^+$ belong to the most prominent class of transition metal vinylidenes containing $[Cp'M(=C=CRR')]$ as a molecular unit [3]. They have been prepared by protonation or alkylation of the corresponding ruthenium alkynyls but owing to the non-availability of anionic compounds $[Cp'Ru(C{\equiv}CR)(L)X]^-$ this method can not be applied to the synthesis of $[Cp'Ru(=C=CRR')(L)X]$.

We recently described the preparation of ruthenium(II) complexes $[RuCl_2(L)_2]$ which contain a *P*, *O*-bonded phosphine such as $^{i}Pr_2PCH_2CH_2OMe$ or $^{i}Pr_2PCH_2C(=O)OMe$ as a potentially bidentate but hemilabile chelating ligand [4]. The oxygen donors in these functionalized phosphines may be regarded as intramolecular solvent ligands which form only weak metal–oxygen bonds and thus, by M–O bond cleavage, allow the addition of better donor ligands to the metal center under fairly mild conditions [5]. By using $HC{\equiv}CPh$ and $HC{\equiv}CCO_2Me$ as substrates, it was shown that from $[RuCl_2(L)_2]$ ($L = {}^{i}Pr_2PCH_2CH_2OMe$, $^{i}Pr_2PCH_2C(=O)OMe$) octahedral vinylidene ruthenium(II) compounds $[RuCl_2(=C=CHR)(\eta^1\text{-}L)(\eta^2\text{-}L)]$ that are highly fluxional in solution can be obtained [4]. We now report the synthesis and structure of the monophosphine complex $[Cp^*RuCl(L)]$ ($L = {}^{i}Pr_2PCH_2C(=O)OMe$) and show that it is an excellent starting material for making neutral half-sandwich type ruthenium complexes containing substituted vinylidenes or allenylidenes as ligands.

[1] For Part XXXIII, see Ref. [1]. Dedicated to Professor Fausto Calderazzo, an old friend, in recognition of his important contributions to organometallic and coordination chemistry.

* Corresponding author.

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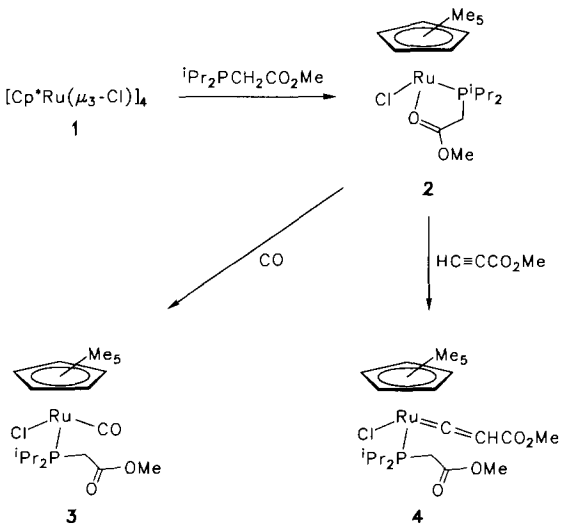
2. Results of preparative studies

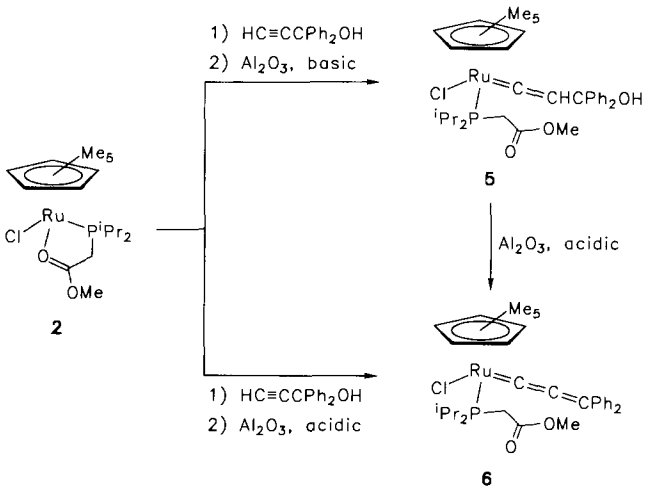
The labile tetrameric cluster $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ [6], which has been used previously for the preparation of 16-electron species $[Cp^*Ru(PR_3)Cl]$ containing bulky phosphines [7,8], reacts smoothly with the phosphinoester $^iPr_2PCH_2CO_2Me$ to give the 1:1 adduct **2** (see Scheme 1) in almost quantitative yield. The functionalized phosphine is coordinated in a chelating mode with the carbomethoxy group linked to the metal via the C=O and not the OCH_3 oxygen. This view is supported by the IR spectrum, in which the C=O stretching frequency is lowered by approximately 80 cm^{-1} compared with the free phosphine, and has been confirmed by X-ray crystallography. We note that earlier work by Braunstein et al. [9] and more recent studies by Demerseman et al. [10] have similarly proved that in ruthenium(II) and palladium(II) complexes with the diphenylphosphinoesters $Ph_2PCH_2CO_2R$ (R = Me, Et) the C=O oxygen is bound to the metal center.

The hemilabile nature of the phosphinoester ligand in **2** becomes immediately apparent when the compound is treated with carbon monoxide. At room temperature in benzene, an almost spontaneous reaction occurs which affords the monocarbonyl complex **3** as a yellow moderately air-stable solid. In contrast to its position in the case of **2**, the ν(C=O) frequency in the IR spectrum of **3** appears at 1720 cm^{-1} and thus at the same position as in free $^iPr_2PCH_2CO_2Me$ [11]. It should be mentioned that very recently Lindner et al. described the synthesis of neutral half-sandwich type ruthenium derivatives $[Cp^*Ru(P\text{-}O)_2Cl]$ in which diphenylphosphinoethers are coordinated to the metal in a η^1 mode [12].

Compound **2** is rather inert to an excess of the phosphinoester, but it reacts with methyl propiolate in benzene at room temperature to give the substituted ruthenium vinylidene **4** in moderate yield. This result is noteworthy in so far as the triisopropylphosphine complex $[Cp^*Ru(P^iPr_3)Cl]$, on treatment with acetylene, affords a ruthenacyclopentadiene derivative instead of $[Cp^*Ru(=C=CH_2)(P^iPr_3)Cl]$ [7b]. Although there is no direct evidence for the initial formation of an alkyne ruthenium intermediate in the reaction of **2** with $HC{\equiv}CCO_2Me$, we assume that such a species is formed, and quickly rearranges to give the vinylidene isomer. Complex **4** is an orange crystalline solid which has been characterized by elemental analysis and by X-ray crystallography. The most characteristic features in the NMR spectra are the low-field ^{13}C NMR signals at δ 329.93 and 104.89, which are assigned to the α-C and β-C vinylidene carbon atoms, and the ^1H NMR signal at δ 4.74 for the vinylidene proton at β-C.



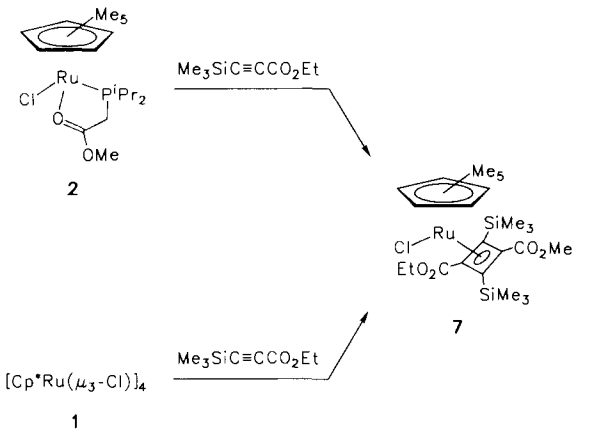
Scheme 1.



Scheme 2.

The hemilabile chelate complex **2** reacts not only with $HC{\equiv}CCO_2Me$ but also with $HC{\equiv}CCPh_2OH$ to form the γ-functionalized ruthenium vinylidene **5** (Scheme 2). In contrast to the outcome of the analogous reactions of $[RhCl(P^iPr_3)_2]_n$ [13] and $[CpRu(PMe_3)_2Cl]$ [14] with the same alkynol $HC{\equiv}CCPh_2OH$, the yield of compound **5** is rather low (31%), perhaps owing to side reactions initiated by the phosphinoester ligand. After chromatographic work-up on deactivated basic alumina, the substituted vinylidene complex **5** is isolated as orange crystals which can be handled briefly in air but decompose at 85°C.

The conversion of **5** into the corresponding allenylidene ruthenium compound **6** occurs in acidic alumina (activity grade I). The synthesis of **6** can also be performed from the chelate complex **2** as the starting material if this is treated first with the alkynol $HC{\equiv}C\text{-}CPh_2OH$ and then with Al_2O_3. The spectroscopic data of **6** are in some respects quite similar to, but in part distinctly different from, those observed for rhodium allenylidenes that were recently prepared in our labo-



Scheme 3.

ratory [13]. Typical features of **6** are the strong C=C=C stretch in the IR spectrum at 1865 cm^{-1} and the low-field ^{13}C NMR signals for the α-C and β-C allenylidene carbon atoms at δ 269.81 (doublet) and 232.79 (singlet). It is noteworthy that in the ^{13}C NMR spectra of *trans*-[RhCl(=C=C=CRPh)(P^iPr_3)$_2$] (R = H, Ph, Tol) [13] the signal from the α-C of the Rh=C=C=C chain appears at higher field than that from the β-C, which is the opposite to what is found for the Ru=C=C=C unit in **6**.

While both $HC{\equiv}CCO_2R$ and $Me_3SiC{\equiv}CCO_2R$ behave similarly towards [RhCl(P^iPr_3)$_2$]$_n$ and form rhodium vinylidenes by either a 1.2-H or a 1.2-$SiMe_3$ shift [15,16], the reaction of **2** with $Me_3SiC{\equiv}CCO_2Et$ takes a completely different course (see Scheme 3). Instead of a vinylidene ruthenium derivative, the tetrasubstituted cyclobutadiene complex **7** is obtained and, after chromatographic work-up, is isolated as a light brown microcrystalline solid. If the tetrameric cluster **1** is used as starting material, compound **7** is formed in 90% yield. We note that Campion et al. have already investigated the reaction of **1** with $HC{\equiv}CSiMe_3$ and obtained, in addition to a ruthenacyclopentadiene derivative, the ruthenium cyclobutadiene [Cp*RuCl{η^4-$C_4H_2(SiMe_3)_2$}] as the major product [7b]. Related [CpRu(X)(η^4-C_4Ph_4)] complexes are also known [17].

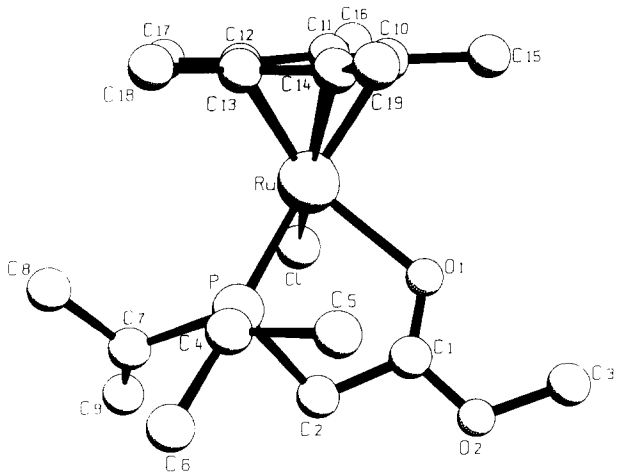


Fig. 1. Molecular structure (SCHAKAL drawing) of complex **2**.

Table 1
Selected intramolecular bond distances (Å) and bond angles (°) of complex **2**, with e.s.d.s

Ru-Cl	2.451(1)	Ru-C(12)	2.117(4)
Ru-P	2.321(1)	Ru-C(13)	2.142(4)
Ru-O(1)	2.249(3)	Ru-C(14)	2.155(4)
Ru-C(10)	2.183(4)	O(1)-C(1)	1.217(5)
Ru-C(11)	2.188(4)	O(2)-C(1)	1.322(5)
Cl-Ru-P	88.22(4)	Ru-P-C(7)	122.6(3)
Cl-Ru-O(1)	82.44(8)	O(1)-C(1)-O(2)	123.1(4)
P-Ru-O(1)	78.61(8)	O(1)-C(1)-C(2)	123.1(4)
Ru-O(1)-C(1)	119.1(3)	O(2)-C(1)-C(2)	113.8(4)
Ru-P-C(2)	100.3(2)	C(1)-O(2)-C(3)	116.2(4)
Ru-P-C(4)	117.9(2)	P-C(2)-C(1)	108.2(3)

3. Structural studies

A single-crystal X-ray diffraction investigation of complex **2** confirms the structure shown in Scheme 1. The SCHAKAL drawing (Fig. 1) reveals that the phosphinoester is coordinated in a κ^2 mode forming a five-membered chelate ring with the ruthenium via the phosphorus and the C=O oxygen atom. The Ru–O(1) bond (2.249(3) Å) is distinctly longer than in [Cp(PPh$_3$)RuC(=CHCO$_2$Me)OC(Me)O] (**8**) (2.132(1) Å) [18] but almost identical to that in cationic areneruthenium compounds with tridentate ligands arising from the addition of alkynes to phosphinoketones $Ph_2PCHRC(=O)R'$ [19]. As expected, the C(1)–

Table 2
Selected intramolecular bond distances (Å) and bond angles (°) of complex **4**, with e.s.d.s

Ru-Cl	2.388(1)	C(1)-C(2)	1.322(5)
Ru-P	2.351(1)	C(2)-C(3)	1.447(5)
Ru-C(1)	1.785(3)	C(3)-O(1)	1.204(4)
Ru-C(5)	2.239(3)	C(3)-O(2)	1.355(4)
Ru-C(6)	2.224(3)	P-C(15)	1.848(3)
Ru-C(7)	2.215(3)	P-C(18)	1.848(3)
Ru-C(8)	2.372(3)	P-C(21)	1.870(4)
Ru-C(9)	2.364(3)	O(3)-C(16)	1.186(4)
C(2)-H(2)	0.78(3)	O(4)-C(16)	1.338(5)
Cl-Ru-P	83.10(3)	C(3)-O(2)-C(4)	115.7(3)
Cl-Ru-C(1)	104.7(1)	P-C(15)-C(16)	117.8(3)
P-Ru-C(1)	87.0(1)	C(15)-C(16)-O(3)	126.4(4)
Ru-C(1)-C(2)	172.3(3)	C(15)-C(16)-O(4)	110.0(3)
C(1)-C(2)-C(3)	123.6(4)	O(3)-C(16)-O(4)	123.6(4)
C(2)-C(3)-O(1)	126.7(3)	C(16)-O(4)-C(17)	116.2(4)
C(2)-C(3)-O(2)	111.4(3)	C(1)-C(2)-H(2)	119.0(2)
O(1)-C(3)-O(2)	121.8(3)	C(3)-C(2)-H(2)	117.0(2)

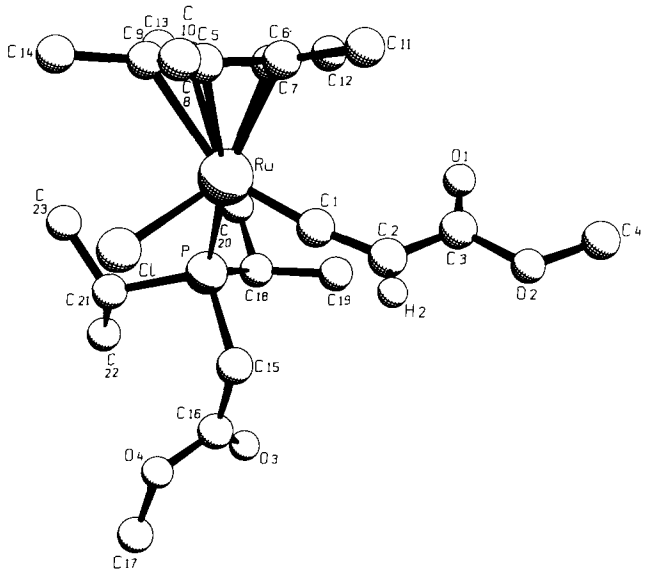


Fig. 2. Molecular structure (SCHAKAL drawing) of complex **4**.

O(1) distance (Table 1) is slightly longer than in the uncoordinated carbomethoxy unit of **4**, and the angles around C(1) deviate somewhat from 120° owing to the steric requirements in the five-membered chelate ring.

The molecular structure of compound **4** is shown in Fig. 2 and the most important bond distances and angles are listed in Table 2. The environment of the ruthenium atom corresponds to that of a three-legged piano stool with a nearly planar (mean deviation 0.03 Å) C_5 ring ligand. The distances between the metal and the carbon atoms differ significantly, as found for complex **8** [18], and reflect in a characteristic way the strong trans influence of the vinylidene unit. The Ru–C(1) bond is rather short and certainly one of the shortest ruthenium vinylidene carbon bonds reported to date [3a,4,20]. The Ru–C(1)–C(2) moiety is almost linear (172.3(3)°), the small deviation probably originating from a slight steric hindrance between C(2) and the two isopropyl groups. In agreement with the "metallaallene" type structure, the Ru=C=C unit, the atoms C(3), O(1), O(2) and C(4) of the carbomethoxy group and the hydrogen atom H(2) lie in the same plane. The C(1)–C(2), Ru–P and Ru–Cl bond lengths are in the expected range and merit no further comment.

4. Experimental section

All reactions were carried out under argon and in carefully dried solvents. The starting materials [Cp*-Ru(μ_3-Cl)]$_4$ (**1**) [6] and ^{i}Pr$_2$PCH$_2$CO$_2$Me [11] were prepared by known methods. IR, Perkin Elmer 457; NMR, Jeol FX 90 Q, Bruker AC 200, Bruker WM 400. Melting points were determined by DTA.

*4.1. Preparation of [Cp*RuCl{κ²(P,O)-^{i}Pr$_2$PCH$_2$CO$_2$Me}] (2)*

A solution of 216 mg (0.20 mmol) of **1** in 2 ml of benzene was treated dropwise with 157 μl (0.80 mmol) of ^{i}Pr$_2$PCH$_2$CO$_2$Me and stirred for 1 min at room temperature. The solvent was removed in vacuo, and the residue was treated with 2 ml of pentane to give an orange microcrystalline solid. Yield: 351 mg (95%); m.p. 55°C (dec.). Anal. found: C, 48.98; H, 7.48. $C_{19}H_{34}ClO_2PRu$ calcd.: C, 49.40; H, 7.42%. IR (C_6H_6): ν(C=O) 1640 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 3.12 (s, 3H, OCH_3); 2.75 (s, br, 2H, PCH_2); 2.25 (m, br, 2H, PC*H*CH$_3$); 1.69 and 1.03 (both s, br, 27H, PCHCH_3, C_5Me_5). ^{31}P NMR (36.2 MHz, d^8-toluene, 178 K): 65.54 (s).

*4.2. Preparation of [Cp*RuCl(CO)(^{i}Pr$_2$PCH$_2$CO$_2$Me)] (3)*

A stream of CO was passed for 1 min through a solution of 139 mg (0.30 mmol) of **2** in 2 ml of benzene at room temperature. The solvent was removed in vacuo, and the oily residue was treated twice with 5 ml of pentane to give a yellow microcrystalline solid. Yield: 95 mg (64%); m.p. 103°C (dec.). Anal. found: C, 48.53; H, 6.98. $C_{20}H_{34}ClO_3PRu$ calcd.: C, 49.03; H, 6.99%. IR (KBr): ν(C≡O) 1910, ν(C=O) 1720 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ 3.37 (dd, part of an ABX pattern, J(PH) = 9.0, J(HH) = 14.1 Hz, 1H, PCH_2); 3.31 (d, J(PH) = 2.3 Hz, 3H, OCH_3); 2.96 (dd, part of an ABX pattern, J(PH) = 7.7, J(HH) = 14.1 Hz, 1H, PCH_2); 2.52 (sept, J(HH) = 7.0 Hz, 1H, PC*H*CH$_3$); 2.23 (sept, J(HH) = 7.0 Hz, 1H, PC*H*CH$_3$); 1.56 (d, J(PH) = 1.4 Hz, 15H, C_5Me_5); 1.26 (dd, J(PH) = 15.6, J(HH) = 7.2 Hz, 3H, PCHCH_3); 1.17 (dd, J(PH) = 15.3, J(HH) = 7.0 Hz, 3H, PCHCH_3); 1.11 (dd, J(PH) = 13.2, J(HH) = 7.0 Hz, 3H, PCHCH_3); 0.90 (dd, J(PH) = 15.4, J(HH) = 7.1 Hz, 3H, PCHCH_3). ^{13}C NMR (100.6 MHz, C_6D_6): δ 207.92 (d, J(PC) = 20.5 Hz, CO); 170.29 (d, J(PC) = 8.6 Hz, CO_2Me); 95.93 (d, J(PC) = 1.8 Hz, C_5Me_5); 51.36 (s, OCH_3); 29.68 (d, J(PC) = 13.0 Hz, PCH_2); 26.46 (d, J(PC) = 16.1 Hz, P*C*HCH$_3$); 26.24 (d, J(PC) = 22.1 Hz, P*C*HCH$_3$); 18.95 (s, PCH*C*H$_3$); 18.56 (d, J(PC) = 2.8 Hz, PCH*C*H$_3$); 18.22 (d, J(PC) = 3.1 Hz, PCH*C*H$_3$); 17.99 (d, J(PC) = 2.0 Hz, PCH*C*H$_3$); 10.34 (s, C_5Me_5). ^{31}P NMR (81.0 MHz, C_6D_6): δ 55.08 (s).

*4.3. Preparation of [Cp*RuCl(=C=CHCO$_2$Me)(^{i}Pr$_2$P-CH$_2$CO$_2$Me)] (4)*

A solution of 285 mg (0.62 mmol) of **2** in 5 ml of benzene was treated with 53 μl (0.62 mmol) of HC≡CCO$_2$Me, and stirred for 1 min at room temperature. The solution was concentrated to ca. 1 ml and

then chromatographed on Al_2O_3 (neutral, activity grade V, length of column 3 cm). Benzene eluted a yellow fraction from which the solvent was removed in vacuo. Then 1 ml of acetone was added and the solution was cooled to −78°C. After some hours orange crystals separated and were filtered off, washed with 2 ml of pentane (0°C) and dried in vacuo. Yield 137 mg (40%); m.p. 99°C (dec.). Anal. found: C, 50.64; H, 6.98. $C_{23}H_{38}ClO_4PRu$ calcd.: C, 50.59; H, 7.01%. IR (KBr): ν(C=O) 1715, ν(C=C) 1580 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 4.74 (s, 1H, C*H*CO_2Me); 3.50 (dd, part of an ABX pattern, J(PH) = 9.0, J(HH) = 14.3 Hz, 1H, PCH_2); 3.44 and 3.31 (both s, 6H, OCH_3); 3.19 (dd, part of an ABX pattern, J(PH) = 9.0, J(HH) = 14.3 Hz, 1H, PCH_2); 2.60 (dsept, J(PH) = 3.2, J(HH) = 7.0 Hz, 1H, P*CH*CH_3); 2.47 (sept, J(HH) = 7.1 Hz, 1H, P*CH*CH_3); 1.60 (s, 15H, C_5Me_5); 1.16 (m, 6H, PCHC*H*$_3$); 1.10 (dd, J(PH) = 15.5, J(HH) = 7.1 Hz, 3H, PCHC*H*$_3$); 0.95 (dd, J(PH) = 15.5, J(HH) = 7.0 Hz, 3H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 329.93 (d, J(PC) = 21.5 Hz, Ru=C); 170.11 (d, J(PC) = 7.0 Hz, CH_2CO_2Me); 167.38 (s, $CHCO_2Me$); 104.89 (s, $CHCO_2Me$); 103.60 (d, J(PC) = 2.4 Hz, C_5Me_5); 51.51 and 50.38 (both s, OCH_3); 29.78 (d, J(PC) = 17.9 Hz, PCH_2); 26.71 (d, J(PC) = 21.6 Hz, P*C*HCH$_3$); 26.13 (d, J(PC) = 24.7 Hz, P*C*HCH$_3$); 19.36, 19.04, 18.47 (all s, PCH*C*H$_3$); 10.30 (s, C_5Me_5). ^{31}P NMR (81.0 MHz, C_6D_6): δ 51.50 (s).

4.4. Preparation of [Cp*RuCl(=C=CHCPh$_2$OH)-(^{i}Pr$_2$PCH$_2$CO$_2$Me)] (5)

A solution of 207 mg (0.45 mmol) of **2** in 2 ml of benzene was treated with 187 mg (0.90 mmol) of HC≡CCPh$_2$OH, and stirred for 24 h at room temperature. The solution was concentrated to ca. 1 ml in vacuo and then chromatographed on Al_2O_3 (basic, activity grade V, length of column 3 cm). Benzene eluted an orange fraction from which the solvent was removed in vacuo. The oily residue was extracted with 5 ml of ether, the extract was evaporated to dryness in vacuo and the residue was treated with 5 ml of pentane to give an orange microcrystalline solid. Yield 94 mg (31%); m.p. 85°C (dec.). Anal. found: C, 60.88; H, 6.46. $C_{34}H_{46}ClO_3PRu$ calcd.: C, 60.93; H, 6.91%. IR (C_6H_6): ν(OH) 3520, ν(C=O) 1715, ν(C=C) 1620 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.74 and 7.15 (both m, 10H, C_6H_5); 4.68 (s, 1H, C*H*CPh$_2$OH); 4.51 (s, br, 1H, OH); 3.58 (dd, part of an ABX pattern, J(PH) = 8.8, J(HH) = 14.3 Hz, 1H, PCH_2); 3.47(dd, part of an ABX pattern, J(PH) = 9.3, J(HH) = 14.8 Hz, 1H, PCH_2); 3.24 (s, 3H, OCH_3); 2.39 (dsept, J(PH) = 1.8, J(HH) = 7.0 Hz, 1H, P*CH*CH_3); 2.02 (dsept, J(PH) = 2.7, J(HH) = 7.1 Hz, 1H, P*CH*CH_3); 1.48 (d, J(PH) = 1.2 Hz, 15H, C_5Me_5); 1.19 (dd, J(PH) = 15.3, J(HH) = 7.2 Hz, 3H, PCHC*H*$_3$); 1.06 (dd, J(PH) = 12.7, J(HH) = 7.1 Hz, 3H, PCHC*H*$_3$); 0.98 (dd, J(PH) = 16.1, J(HH) = 6.7 Hz, 3H, PCHC*H*$_3$); 0.61 (dd, J(PH) = 14.3, J(HH) = 7.1 Hz, 3H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 333.06 (d, J(PC) = 20.1 Hz, Ru=C); 171.20 (d, J(PC) = 10.2 Hz, CO_2Me); 151.38 and 150.26 (both s, *ipso*-carbons of C_6H_5); 128.40, 128.33, 127.63, 127.00, 126.67, 126.57 (all s, *ortho*-, *meta*- and *para*-carbons of C_6H_5); 121.72 (s, $CHCPh_2OH$); 102.32 (d, J(PC) = 2.4 Hz, C_5Me_5); 75.31 (s, CPh_2OH); 51.20 (s, OCH_3); 27.88 (d, J(PC) = 16.0 Hz, PCH_2); 26.36 (d, J(PC) = 18.9 Hz, P*C*HCH$_3$); 25.41 (d, J(PC) = 27.5 Hz, P*C*HCH$_3$); 19.25 and 18.64 (both s, PCH*C*H$_3$); 18.45 (d, J(PC) = 4.7 Hz, PCH*C*H$_3$); 17.26 (d, J(PC) = 3.1 Hz, PCH*C*H$_3$); 10.57 (s, C_5Me_5). ^{31}P NMR (162.0 MHz, C_6D_6): δ 56.99 (s).

4.5. Preparation of [Cp*RuCl(=C=C=CPh$_2$)(^{i}Pr$_2$P-CH$_2$CO$_2$Me)] (6)

A solution of 244 mg (0.53 mmol) of **2** in 5 ml of benzene was treated with 220 mg (1.1 mmol) of HC≡CCPh$_2$OH, and stirred for 20 h at room temperature. The solution was concentrated to ca. 1 ml in vacuo and then chromatographed on Al_2O_3 (acid, activity grade I, length of column 5 cm). A CH_2Cl_2/benzene (3 : 1) mixture eluted a red fraction from which the solvent was removed in vacuo. The residue was washed with 2 ml of pentane to give a red microcrystalline solid. Yield 62 mg (18%); m.p. 66°C (dec.). Anal. found: C, 62.33; H, 6.67. $C_{34}H_{44}ClO_2PRu$ calcd.: C, 62.61; H, 6.79%. IR (KBr): ν(C=C=C) 1865, ν(C=O) 1715 cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 7.88, 7.27, 7.03 (all m, 10H, C_6H_5); 4.16 (dd, part of an ABX pattern, J(PH) = 9.4, J(HH) = 14.5 Hz, 1H, PCH_2); 3.78 (dd, part of an ABX pattern, J(PH) = 9.5, J(HH) = 14.6 Hz, 1H, PCH_2); 3.28 (s, 3H, OCH_3); 2.39 (dsept, J(PH) = 3.3, J(HH) = 6.8 Hz, 1H, P*CH*CH_3); 2.24 (sept, J(HH) = 7.1 Hz, 1H, P*CH*CH_3); 1.61 (d, J(PH) = 0.8 Hz, 15H, C_5Me_5); 1.29 (dd, J(PH) = 18.4, J(HH) = 7.1 Hz, 3H, PCHC*H*$_3$); 1.18 (dd, J(PH) = 13.2, J(HH) = 7.1 Hz, 3H, PCHC*H*$_3$); 0.97 (dd, J(PH) = 15.6, J(HH) = 7.1 Hz, 3H, PCHC*H*$_3$); 0.72 (dd, J(PH) = 15.6, J(HH) = 7.1 Hz, 3H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 269.81 (d, J(PC) = 22.6 Hz, Ru=C); 232.79 (s, C=CPh$_2$); 171.42 (s, CO_2Me); 167.72 (s, CPh_2); 138.12 (s, *ipso*-carbons of C_6H_5); 129.10, 128.10, 128.05 (all s, *ortho*-, *meta*- and *para*-carbons of C_6H_5); 102.49 (d, J(PC) = 2.3 Hz, C_5Me_5); 51.16 (s, OCH_3); 29.86 (d, J(PC) = 15.1 Hz, PCH_2); 27.12 (d, J(PC) = 19.2 Hz, P*C*HCH$_3$); 25.98 (d, J(PC) = 25.3 Hz, P*C*HCH$_3$); 19.03 (d, J(PC) = 2.3 Hz, PCH*C*H$_3$); 18.87 and 18.77 (both s, PCH*C*H$_3$); 18.05 (d, J(PC) = 2.5 Hz, PCH*C*H$_3$); 10.91 (s, C_5Me_5). ^{31}P NMR (162.0 MHz, C_6D_6): δ 55.80 (s).

4.6. Preparation of [Cp*RuCl{η^4-$C_4(SiMe_3)_2(CO_2Et)_2$}] (7)

(a) A solution of 225 mg (0.49 mmol) of **2** in 5 ml of benzene was treated with 277 μl (1.46 mmol) of $Me_3SiC{\equiv}CCO_2Et$, and stirred for 2 min at room temperature. The solvent was removed in vacuo, the oily residue was treated with 3 ml of pentane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 2 cm). Pentane eluted a brown fraction which was concentrated to ca. 2 ml and cooled to −78°C. After some hours a light brown microcrystalline solid had formed, it was filtered off and dried. Yield 55 mg (18%).

(b) A solution of 60 mg (0.06 mmol) of **1** in 2 ml of benzene was treated with 85 μl (0.45 mmol) of $Me_3SiC{\equiv}CCO_2Et$, and stirred for 1 min at room temperature. The solvent was removed in vacuo, and the oily residue was treated with 2 ml of pentane at 0°C to give a light brown microcrystalline solid. Yield 123 mg (90%); m.p. 174°C (dec.). Anal. found: C, 50.76; H, 7.22. $C_{26}H_{43}ClO_4RuSi_2$ calcd.: C, 51.00; H, 7.08%. ^{1}H NMR (400 MHz, C_6D_6): δ 3.49 (q, J(HH) 7.2 Hz, 4H, CH_2CH_3); 1.50 (s, 15H, C_5Me_5); 1.00 (t, J(HH) = 7.2 Hz, 6H, CH_2CH_3); 0.40 (s, 18H, $SiMe_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 165.07 (s, CO_2Et); 101.87 (s, C_5Me_5); 85.59 and 81.74 (both s, CCO_2Et, $CSiMe_3$); 60.50 (s, CH_2CH_3); 14.08 (s, CH_2CH_3); 9.33 (s, C_5Me_5); 2.48 (s, $SiMe_3$). ^{29}Si NMR (40 MHz, C_6D_6): δ −4.28 (s).

4.7. Determination and refinement of the structures of 2 and 4

The space groups and cell constants were determined on an Enraf-Nonius CAD4 diffractometer which was subsequently used for the data collection. Cell constants were obtained by a least-squares fit of 23 high-angle reflections using CAD centering routines and are listed along with other crystallographic data and data collection parameters in Table 3. The crystal stability and orientation was checked by measuring standard reflections every hour. All calculations were performed on a Micro-VAX computer using the program package SDP [21] from Enraf-Nonius. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction (Ψ-scan method) was applied, the minimum transmission for **2** was 94.29%, for **4** 92.77%. Both structures were solved by Direct Methods (SHELXS-86). Atomic coordinates (Tables 4 and 5) and anisotropic thermal parameters of

Table 3
Data of the X-ray structure analysis of **2** and **4**

Compound	**2**	**4**
Formula	$C_{19}H_{34}ClO_2PRu$	$C_{23}H_{38}ClO_4PRu$
M	462.0	546.1
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ [14]	$P2_1/n$ [14]
a [Å]	11.09(1)	7.961(5)
b [Å]	15.759(8)	29.75(1)
c [Å]	12.59(1)	11.414(8)
β [°]	93.78(5)	107.12(3)
Z	4	4
V [Å^3]	2195(3)	2583(3)
d_{calc} [g cm^{-3}]	1.397	1.404
F(000)	960.0	1136.0
μ (Mo Kα) [cm^{-1}]	9.0	7.8
Radiation (graphite monochromated)	Mo K_α (0.70930 Å)	Mo K_α (0.70930 Å)
T [K]	223	293
Scan method	ω/θ	ω/θ
2θ (max) [°]	46	50
h, k, l range	12, 17, ±13	9, 35, ±13
Measured reflections	3363	4374
Unique reflections	2995	3688
Observed reflections [$F_o > 3\sigma(F_o)$]	2679	3436
Refined parameters	328	312
R	0.037	0.029
R_w	0.046	0.031
Reflection/param ratio	8.17	11.01
Residual electron density [e Å^{-3}]	+0.87/−0.86	+0.57/−0.29

Table 4
Positional parameters for complex **2**, with e.s.d.s [a]

Atom	x	y	z	B (Å^2)
Ru	0.01502(4)	0.29121(3)	0.79934(4)	2.212(9)
Cl	0.1086(2)	0.2681(1)	0.9787(1)	4.19(4)
P	−0.1553(2)	0.2213(1)	0.8523(1)	2.83(3)
O(1)	−0.0801(4)	0.3961(3)	0.8816(3)	3.07(9)
O(2)	−0.2184(4)	0.4357(3)	0.9929(4)	4.3(1)
C(1)	−0.1578(6)	0.3781(4)	0.9417(5)	3.2(1)
C(2)	−0.1931(6)	0.2884(5)	0.9654(5)	3.6(1)
C(3)	+0.1837(8)	0.5233(5)	0.9776(7)	5.3(2)
C(4)	−0.2942(6)	0.2253(5)	0.7625(5)	3.7(1)
C(5)	−0.3294(6)	0.3177(5)	0.7411(6)	4.1(2)
C(6)	−0.4031(7)	0.1748(6)	0.7937(8)	6.5(2)
C(7)	−0.149(1)	0.1125(5)	0.9099(7)	6.9(3)
C(8)	−0.131(1)	0.0469(5)	0.8240(7)	7.0(3)
C(9B)	−0.160(3)	0.082(2)	1.016(3)	6.2(8)
C(9A)	−0.080(1)	0.103(1)	1.010(1)	4.6(3)
C(9C)	−0.216(2)	0.084(2)	0.987(2)	2.6(4)
C(10)	0.1030(6)	0.3736(4)	0.6883(5)	3.3(1)
C(11)	0.1891(5)	0.3160(5)	0.7329(5)	3.3(1)
C(12)	0.1460(6)	0.2309(4)	0.7101(5)	3.2(1)
C(13)	0.0351(6)	0.2384(4)	0.6447(5)	2.9(1)
C(14)	0.0063(5)	0.3264(4)	0.6336(5)	2.9(1)
C(15)	0.1087(9)	0.4682(5)	0.6975(7)	5.8(2)
C(16)	0.3065(6)	0.3379(7)	0.7936(6)	5.6(2)
C(17)	0.2121(7)	0.1503(5)	0.7392(6)	4.9(2)
C(18)	−0.0311(7)	0.1668(5)	0.5879(6)	4.6(2)
C(19)	−0.0933(6)	0.3645(5)	0.5624(6)	4.6(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\,[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

Table 5
Positional parameters for complex **4**, with e.s.d.s [a]

Atom	x	y	z	B (Å^2)
Ru	0.31124(4)	0.16353(1)	0.19809(2)	2.796(5)
Cl	0.0714(1)	0.19930(3)	0.05151(9)	4.28(2)
P	0.2903(1)	0.11267(3)	0.03663(8)	3.20(2)
O(1)	0.4138(3)	0.0605(1)	0.4541(3)	5.11(7)
O(2)	0.1577(3)	0.03883(9)	0.4800(2)	4.64(6)
O(3)	0.0652(5)	0.0206(1)	−0.1227(3)	6.92(9)
O(4)	−0.1152(4)	0.0781(1)	−0.1924(3)	6.17(8)
C(1)	0.2114(5)	0.1212(1)	0.2663(3)	3.24(8)
C(2)	0.1477(5)	0.0925(1)	0.3311(3)	3.81(9)
C(3)	0.2560(5)	0.0633(1)	0.4243(3)	3.76(8)
C(4)	0.2540(6)	0.0094(2)	0.5767(4)	5.4(1)
C(5)	0.3598(5)	0.2268(1)	0.3092(3)	3.71(8)
C(6)	0.4371(5)	0.1907(1)	0.3850(3)	3.47(8)
C(7)	0.5698(5)	0.1716(1)	0.3375(3)	3.65(8)
C(8)	0.5859(5)	0.2008(1)	0.2401(3)	3.95(9)
C(9)	0.4562(5)	0.2337(1)	0.2211(4)	4.05(9)
C(10)	0.2158(5)	0.2572(1)	0.3244(4)	5.4(1)
C(11)	0.3986(6)	0.1766(2)	0.5011(3)	5.0(1)
C(12)	0.6989(5)	0.1361(2)	0.3990(4)	5.1(1)
C(13)	0.7326(5)	0.1984(2)	0.1818(4)	5.9(1)
C(14)	0.4254(6)	0.2720(1)	0.1328(4)	5.9(1)
C(15)	0.0737(5)	0.0850(1)	0.0053(3)	4.06(9)
C(16)	0.0125(6)	0.0568(1)	−0.1079(4)	4.7(1)
C(17)	−0.1849(8)	0.0551(2)	−0.3090(5)	8.7(2)
C(18)	0.4424(5)	0.0646(1)	0.0527(4)	4.23(9)
C(19)	0.4331(7)	0.0341(2)	0.1570(4)	6.2(1)
C(20)	0.6305(6)	0.0800(2)	0.0652(5)	7.3(1)
C(21)	0.2728(6)	0.1385(2)	−0.1161(3)	5.1(1)
C(22)	0.2977(7)	0.1064(2)	−0.2150(4)	7.0(1)
C(23)	0.3871(7)	0.1791(2)	−0.1074(4)	7.0(1)
H(2)	0.046(4)	0.091(1)	0.318(3)	0.5(7)

[a] See footnote to Table 4.

the non-hydrogen atoms were refined by full-matrix least-squares (unit weights). One of the isopropyl-methyl groups (C9) of compound **2** showed a 2:1:1 disorder; all three positions were refined independently with isotropic temperature factors. The positions of all hydrogen atoms except those of the disordered isopropyl group were located in a final difference Fourier synthesis and refined isotropically. The position of the hydrogen atom H2 of complex **4** was taken from a difference Fourier synthesis and refined isotropically. The other hydrogen atoms were placed at calculated positions and refined by the riding method. The four highest peaks of the last difference Fourier synthesis of **4** were located near the ruthenium atom. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-58361, the names of the authors, and the journal citation.

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