These data were corrected for Lorentz and polarization effects. The structure was solved by Patterson methods. All non-hydrogen atoms were anisotropically refined. The *i*-Pr groups attached to O(2) and O(3) were found to be disordered. The occupancy factors of C(19A) and C(19B) and of C(22A) and C(22B) are set to 0.5. These positions were refined anisotropically, although the positional and thermal parameters were refined individually. Hydrogen atoms attached to C(17), C(18), C(19A), C(19B), C(20), C(21), C(22A), C(22B), C(24), and C(25) are not included in the refinement. Hydrogen atoms that have noted esd's in the positional parameter table were refined isotropically, while only the isotropic thermal parameters of the remaining hydrogens were refined. The final refinement, based on 2860 observed reflections ($I > 3.00\sigma(I)$) and 346 variable parameters, converged with R = 0.059 and R_w = 0.091. The largest parameter shift in the final cycle was 0.82 times its esd. The goodness of fit is 1.59. The weighting scheme was based on counting statistics and included a factor (p = 0.10) to downweight the intense reflections. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.41 and −0.29 e^- Å^{-3}, respectively.

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Registry No. A, 138606-16-3; B, 138629-03-5; C, 138606-14-1; $(Me_2BINO)Ti_2(O\text{-}i\text{-}Pr)_6$, 138606-13-0; $(Me_2BINO)_2Ti$, 138606-15-2.

Supplementary Material Available: Full experimental details of the X-ray structural studies including tables of positional parameters, anisotropic vibrational parameters, bond distances and angles involving non-hydrogen atoms, and bond distances and angles involving hydrogen atoms (57 pages); listings of observed and calculated structure factors (87 pages). Ordering information is given on any current masthead page.

Preparation of Vinylideneruthenium Complexes Promoted by Hemilabile Chelating Phosphine Ligands[1]

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The octahedral ruthenium(II) complexes $[RuCl_2(P\frown O)_2]$ (3, 6) containing the P,O-bound phosphine ligands $i\text{-}Pr_2PCH_2CH_2OMe$ (1) and $i\text{-}Pr_2PCH_2C(O)OMe$ (2) have been prepared from $[RuCl_2(PPh_3)_3]$ and 1 or 2 by ligand exchange. Reaction of 3 with carbon monoxide leads to the formation of $[RuCl_2(CO)_2(\eta^1\text{-}P\text{-}i\text{-}Pr_2PCH_2CH_2OMe)_2]$ (4) in nearly quantitative yield. On treatment of 3 and 6 with HC≡CPh or HC≡CCO$_2$Me, the vinylideneruthenium(II) complexes $[RuCl_2(=C=CHPh)(\eta^1\text{-}P\text{-}i\text{-}Pr_2PCH_2CH_2OMe)(\eta^2\text{-}i\text{-}Pr_2PCH_2CH_2OMe)]$ (5) and $[RuCl_2(=C=CHR)(\eta^1\text{-}P\text{-}i\text{-}Pr_2PCH_2C(O)OMe)(\eta^2\text{-}i\text{-}Pr_2PCH_2C(O)OMe)]$ (7, R = Ph; 8, R = CO$_2$Me) are formed, which are fluxional in solution. From ^{31}P NMR measurements at various temperature, the free enthalpies of activation ΔG_{218}^{*} = 41 kJ/mol for 5, ΔG_{275}^{*} = 53 kJ/mol for 7, and ΔG_{258}^{*} = 49 kJ/mol for 8 for the intramolecular rearrangement have been determined. The X-ray crystal structure analysis of 5 (monoclinic space group $P2_1/c$ with a = 13.129 (1) Å, b = 12.803 (1) Å, c = 18.867 (2) Å, and β = 102.42 (1)°) reveals that in the solid state one phosphine is coordinated via phosphorus and oxygen forming a five-membered chelate whereas the other phosphine is only P-bound with a dangling CH_2CH_2OMe fragment. The Ru=C=C unit is almost linear with Ru–C and C–C distances of 1.749 (5) and 1.339 (7) Å.

Introduction

During the last decade, the chemistry of vinylidene transition-metal complexes has attracted a great deal of attention.[2,3] Among the metal centers used to bind a C=CRR′ unit, ruthenium plays a prominent role. There are, however, only a few examples of vinylideneruthenium complexes which do not contain a cyclopentadienyl or an arene ring as a supporting ligand.[3,4]

In the present paper we describe the synthesis and structure of ruthenium compounds of general composition $[RuCl_2(=C=CHR)L_2]$ in which L is a potential bidentate but hemilabile chelating ligand. It is shown that in contrast to P-i-Pr$_3$, the related ether and ester phosphines $i\text{-}Pr_2PCH_2CH_2OMe$ (1) and $i\text{-}Pr_2PCH_2C(O)OMe$ (2) support the formation of a Ru=C=CHR unit from 1-alkynes HC≡CR as starting materials.

Results

Preparation of the Ruthenium Complexes 3–5. Following earlier work from our laboratory in which it was illustrated that the coordinatively unsaturated compound $[RhCl(P\text{-}i\text{-}Pr_3)_2]_n$[5,6] serves as an excellent starting material for the synthesis of vinylidenerhodium(I) complexes,[7] we attempted to prepare an analogous bis(triisopropyl-

(1) Part XIX of the series Vinylidene Transition-Metal Complexes. For part XVIII, see: Werner, H.; Weinand, R.; Knaup, W.; Peters, K.; von Schnering, H. G. *Organometallics* **1991**, *10*, 3967.

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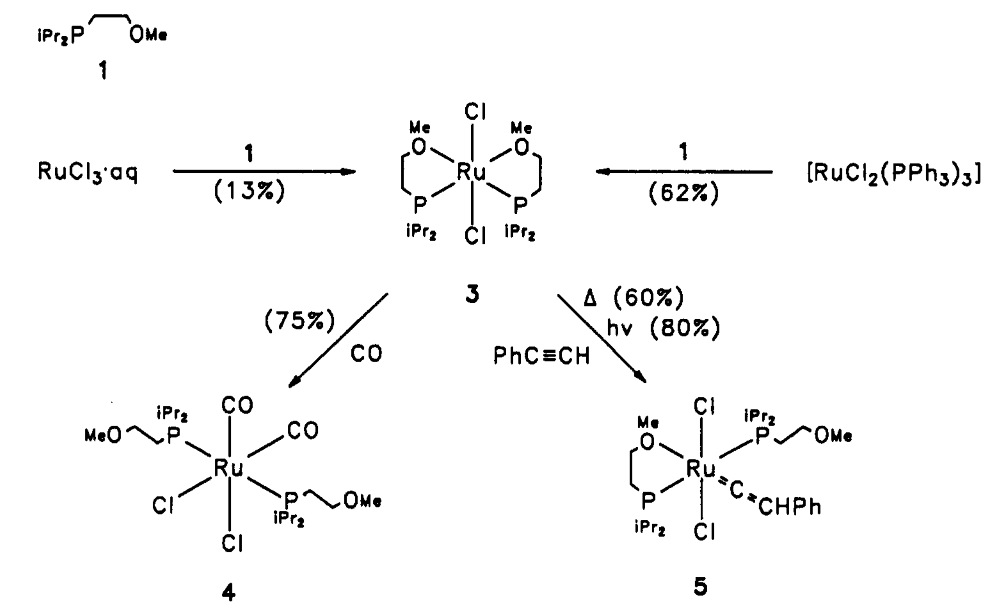
Scheme I



phosphine)ruthenium derivative $[RuCl_2(P\text{-}i\text{-}Pr_3)_2]_n$ either from $RuCl_3$·aq or $[RuCl_2(PPh_3)_3]$ and P-*i*-Pr_3. These experiments led, however, only to the isolation of the carbonylhydridometal compound $[RuHCl(CO)(P\text{-}i\text{-}Pr_3)_2]$,[8] which was shown not to be an appropriate precursor for the preparation of vinylideneruthenium complexes.[9]

We therefore turned our attention from P-*i*-Pr_3 to the related potentially bidentate phosphine ligand *i*-$Pr_2PCH_2CH_2OMe$ (1), which in contrast to P-*i*-Pr_3 forms also in the solid state a monomeric species $[RhClL_2]$.[10] Whereas on treatment of $RuCl_3$·aq with 1 either in methanol or 2-methoxyethanol the compound $[RuCl_2(\eta^2\text{-}i\text{-}Pr_2PCH_2CH_2OMe)_2]$ (3) is obtained in only minor quantities, the reaction of $[RuCl_2(PPh_3)_3]$ with 1 gives the target molecule 3 in 62% yield (Scheme I). It is a bright-red moderately air-stable solid which is easily soluble in benzene and polar organic solvents such as CH_2Cl_2, $CHCl_3$, and acetone.

The ^{31}P NMR spectrum of 3 shows only one signal for the two phosphorus atoms, and thus, provided that the chlorines are trans to each other, two configurations, *cis*-P,P and *trans*-P,P seem to be possible. Owing to the recently described X-ray structural analysis of $[RuCl_2(\eta^2\text{-}Ph_2PCH_2CH_2OMe)_2]$ which proved that in the basal plane of the octahedron both the phosphorus and the oxygen atoms are in the cis position,[11] we favor a similar structure for complex 3. The assumption that the methoxy groups of the two phosphine ligands are coordinated (and not free) is strongly supported by the ^1H NMR spectrum in which the signal of the OCH_3 protons is shifted by ca. 0.5 ppm to lower fields as compared with 1.

The hemilabile nature of the two phosphine ligands in 3 is illustrated by the reaction with carbon monoxide. Independent of whether THF or toluene is used as the solvent and the reaction is carried out at +25, 0, or −15 °C, only one product can be isolated, which, according to elemental analysis and spectroscopic data, is the dicarbonyl complex $[RuCl_2(CO)_2(\eta^1\text{-}P\text{-}i\text{-}Pr_2PCH_2CH_2OMe)_2]$ (4). In contrast, the work of Lindner et al. has shown that the related starting material $[RuCl_2(\eta^2\text{-}Ph_2PCH_2CH_2OMe)_2]$ reacts stepwise with CO to give first a monocarbonyl- and then a dicarbonylruthenium derivative.[11,12] Compound 4 forms white air-stable crystals for which the structure depicted in Scheme I is proposed. The trans position of the two phosphines is confirmed by the ^1H NMR spectrum, which shows two signals for the diastereotopic $PCHCH_3$ protons with a pattern typical for a linear R_3P–M–PR_3 unit.[13]

Whereas 3 is rather inert toward ethene and CH_2=$CHCO_2Me$, it smoothly reacts with phenylacetylene either in benzene at 70 °C or, even more favorably, under irradiation in toluene at room temperature to give the vinylideneruthenium(II) complex 5. By the photochemical route, the yield (of isolated product) is 80%. Although there is no direct evidence for the initial formation of an alkynemetal compound $[RuCl_2(PhC{\equiv}CH)L_2]$, we nevertheless assume that such an intermediate is formed, which quickly rearranges to give the vinylidene isomer (Scheme I). Complex 5 is an orange, moderately air-stable solid which has been characterized by elemental analysis as well as X-ray crystallography. The most characteristic features in the ^{13}C NMR spectrum are the low-field signals at δ 350.1 and 109.9, which by comparison are assigned to the α-C and β-C vinylidene carbon atoms.[3]

More noteworthy, however, is the temperature-dependent ^{31}P NMR spectrum of 5, which indicates that the compound is fluxional in solution. Whereas at room temperature in toluene-d_8 only one signal at δ 22.4 is observed, at −80 °C the spectrum displays a typical AB pattern and shows two doublets at δ 33.0 and 11.5. The large coupling constant $J(PP)$ = 357 Hz is consistent with two trans-phosphorus atoms. By increase of the temperature, the two doublets first broaden and then coalesce at ca. −55 °C from which a ΔG^* value of 41 kJ/mol can be calculated.[14] The observed phenomenon is reversible and may be explained by a rapid exchange in the chelating behavior of

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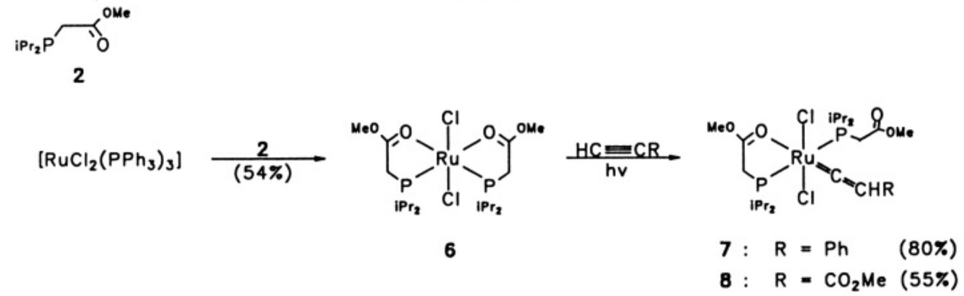
Scheme II



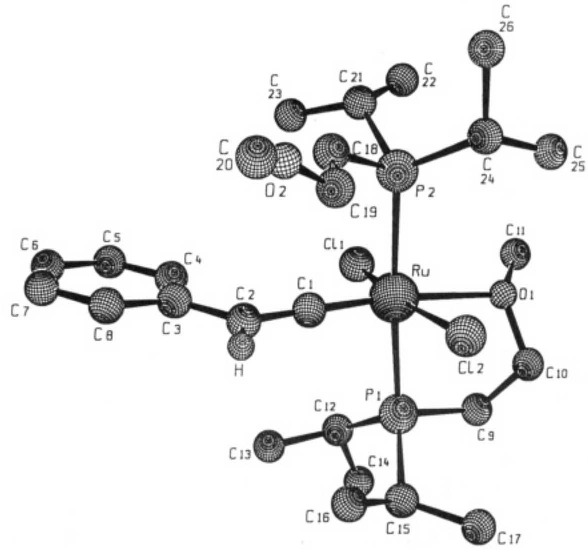


Figure 1. SCHAKAL drawing of complex **5**.

Table I. Selected Bond Distances and Angles with Esd's for 5

Bond Distances (Å)			
Ru–Cl1	2.382 (2)	P2–C18	1.85 (1)
Ru–Cl2	2.366 (3)	P2–C21	1.83 (1)
Ru–P1	2.377 (2)	P2–C24	1.80 (1)
Ru–P2	2.446 (2)	O1–C10	1.45 (1)
Ru–O1	2.385 (6)	O1–C11	1.42 (1)
Ru–C1	1.749 (7)	O2–C19	1.31 (2)
P1–C9	1.85 (1)	O2–C20	0.96 (2)
P1–C12	1.848 (9)	C1–C2	1.34 (1)
P1–C15	1.844 (9)	C2–C3	1.47 (1)
Bond Angles (deg)			
Cl1–Ru–Cl2	166.70 (8)	O1–Ru–C1	173.5 (3)
Cl1–Ru–P1	87.54 (8)	Ru–P1–C9	102.1 (3)
Cl1–Ru–P2	94.81 (8)	Ru–P1–C12	116.2 (3)
Cl1–Ru–O1	83.5 (2)	Ru–P1–C15	122.9 (3)
Cl1–Ru–C1	97.5 (3)	Ru–P2–C18	111.9 (3)
Cl2–Ru–P1	90.03 (8)	Ru–P2–C21	119.1 (4)
Cl2–Ru–P2	87.07 (8)	Ru–P2–C24	116.4 (4)
Cl2–Ru–O1	83.2 (2)	Ru–O1–C10	109.7 (5)
Cl2–Ru–C1	95.7 (3)	Ru–O1–C11	125.0 (5)
P1–Ru–P2	176.43 (8)	C19–O2–C20	157 (2)
P1–Ru–O1	80.3 (2)	Ru–C1–C2	176.6 (7)
P1–Ru–C1	93.4 (2)	C1–C2–C3	127.7 (8)
P2–Ru–O1	97.3 (1)	C2–C3–C4	123.5 (7)
P2–Ru–C1	89.0 (2)	C2–C3–C8	119.2 (8)

the two phosphine ligands. We note that Lindner et al. observed a similar exchange process for the monocarbonyl compound $[RuCl_2(CO)(\eta^1\text{-}P\text{-}Ph_2PCH_2CH_2OMe)(\eta^2\text{-}Ph_2PCH_2CH_2OMe)]$ and the tris(phosphine)ruthenium complex $[RuCl_2(\eta^1\text{-}P\text{-}Me_2PCH_2CH_2OMe)_2(\eta^2\text{-}Me_2PCH_2CH_2OMe)]$; in both cases, however, coalescence occurs at considerably higher temperatures.[12,15]

Molecular Structure of 5. A single-crystal X-ray diffraction investigation of complex **5** confirms the structural proposal shown in Scheme I. The SCHAKAL drawing (Figure 1) reveals that the geometry about the ruthenium(II) center is nearly octahedral. The two chlorines and the two phosphorus atoms are trans to each other, and the oxygen atom of one methoxy group is trans to the vinylidene ligand. The smallest corner-to-center-to-corner angle of the octahedron is found for P1–Ru–O1 (80.3 (1)°) (Table I), which is probably due to the ring strain in the five-membered $RuPC_2O$ chelating system. The positions of the atoms O2 and C20 in the dangling $CH_2CH_2OCH_3$ fragment at P2 converge only with very high thermal parameters, and thus, some of the calculated bond lengths are unusually short. The reason is probably the high mobility of the uncoordinated β-methoxyethyl group, which leads to slightly different orientations of these atoms in the unit cells. Careful analysis of the electron density map around these atoms revealed no independent disordered position. A similar effect has also been observed in the related rhodium complex $[RhCl(\eta^1\text{-}P\text{-}i\text{-}Pr_2PCH_2CH_2OMe)(\eta^2\text{-}i\text{-}Pr_2PCH_2CH_2OMe)]$.[10]

The vinylidene orientation is easily understood in terms of the d^6 metal configuration and the π-acid character of the phosphines.[2,3] The Ru–C1–C2 unit is almost linear (176.6 (7)°) with the phenyl ring at C2 lying essentially in the $RuCl_2(C{=}C)$ plane (dihedral angle Ru, C1,C2,Cl1,Cl2/C3,C4,C5,C6,C7,C8: 7.6 (1)°). The Ru–C1 distance (1.749 (7) Å) is by far the shortest reported ruthenium–vinylidene carbon bond length[3,16] and even slightly shorter than the metal–carbon bond length in the square-planar rhodium compound *trans*-$[RhCl({=}C{=}CHMe)(P\text{-}i\text{-}Pr_3)_2]$ (1.775 (6) Å).[7d] We note that in contrast the Ru–O1 distance (2.385 (6) Å) is significantly longer than in $[RuCl_2(CO)(\eta^1\text{-}P\text{-}Ph_2PCH_2CH_2OMe)(\eta^2\text{-}Ph_2PCH_2CH_2OMe)]$ (2.278 (8) Å),[11] which could be attributed to the strong trans effect of the vinylidene ligand. The Ru–Cl and Ru–P bond lengths lie in the expected range[11,14] and deserve no further comment.

Preparation of the Ester Phosphine Complexes 6–8. After we had successfully used the ether phosphine **1** for the synthesis of the new vinylideneruthenium complex **5**, we explored whether the recently prepared phosphinoester derivative **2**[17] can serve for the same purpose. The preparation of the starting material $[RuCl_2(\eta^2\text{-}i\text{-}Pr_2PCH_2C(O)OMe)_2]$ (**6**) was straightforward. Treatment of $[RuCl_2(PPh_3)_3]$ with 4 equiv of **2** in dichloromethane gave compound **6** in 50% isolated yield. As the ^{31}P NMR spectrum shows only one signal, we assume that the structure of the bis-chelate complex is similar to that of

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the ether phosphine analogue 3 (see Scheme II). Coordination of the carbomethoxy group via the C=O and not the OCH_3 oxygen is strongly supported by the IR spectrum in which the C=O stretching frequency is lowered by 80 cm^{-1} compared with the free phosphine. The structural proposal is also in agreement with earlier work by Braunstein et al.,[18,19] which proved that in ruthenium(II) and palladium(II) complexes with the ester phosphines $Ph_2PCH_2C(O)OEt$ and $[Ph_2PCHC(O)OEt]^-$ as chelating ligands it is again the C=O and not the OC_2H_5 oxygen that is bound to the metal center.

Compound 6 reacts with PhC≡CH or $HC≡CCO_2Me$ in toluene under UV irradiation to yield the vinylideneruthenium(II) complexes 7 and 8 (Scheme II). These are yellow to orange crystalline solids which are only slightly air-sensitive and, like 5, easily soluble in CH_2Cl_2, acetone, and aromatic hydrocarbons. The hemilabile character of the chelate ligand is evidenced by its stereodynamic behavior, resulting from the smooth rupture of the Ru–O bond. In the ^{31}P NMR spectra of 7 and 8, coalescence of the two signals for the two different phosphorus atoms occurs at +2 and −15 °C, respectively, from which $\Delta G^{\ddagger}$ values of 53 and 49 kJ/mol are calculated.[14] The free enthalpy of activation for the intramolecular rearrangement in 7 and 8 is obviously larger than in the case of 5, which is consistent with the increased donor strength of the C=O compared with the OCH_3 group. The ^{13}C NMR spectra of 7 and 8 reveal absorptions at δ 354.6 and 109.4 and δ 340.3 and 102.4, which are typical for the vinylidene carbon atoms.

Conclusions

In this work we have described a simple preparative route to octahedral vinylideneruthenium(II) complexes not containing a cyclopentadienyl or an arene ring as a supporting ligand. The decisive point is to use the dichloro bis(phosphine) compounds 3 and 6 as starting materials, which according to the hemilabile behavior of the P,O-bound phosphine ligands 1 and 2 readily create a free coordination site to which the 1-alkyne can be added. As the formation of the vinylidene complexes is rather facile, no conclusions regarding the mechanism of the alkyne to vinylidene rearrangement can be drawn. To obtain good to excellent yields, photochemical activation seems to be essential, which is in complete agreement with other work from our laboratory describing the synthesis of the vinylidenerhodium compounds *trans*-[RhCl(=C=C(R)-$SiMe_3$)(P-*i*-Pr_3)$_2$] from [RhCl(P-*i*-Pr_3)$_2$]$_n$ and silylalkynes.[6b]

Experimental Section

All experiments were carried out under an atmosphere of argon by using Schlenk tube techniques. For the photochemical reactions, a water-cooled reactor with a Philips HPK 125-W Hg lamp was used. The starting materials 1,[10] 2,[17] and [$RuCl_2(PPh_3)_3$][20] were prepared by published methods. Melting points were determined by DTA.

Preparation of [$RuCl_2(\eta^2$-*i*-$Pr_2PCH_2CH_2OMe)_2$] (3). Method a. A solution of $RuCl_3·3H_2O$ (100 mg, 0.38 mmol) in 10 mL of 2-methoxyethanol was treated dropwise with 1 (212 μL, 1.14 mmol) and heated for 48 h under reflux. After cooling to room temperature, the solution was concentrated to ca. 1 mL and then chromatographed on Al_2O_3 (neutral, activity grade III, length of column 5 cm). With benzene/acetone (1:1) a red fraction was eluted from which, after removal of the solvent in vacuo, a bright-red microcrystalline powder was isolated, yield 26 mg (13%).

Method b. A solution of [$RuCl_2(PPh_3)_3$] (1.0 g, 1.04 mmol) in 10 mL of benzene was treated with 1 (0.44 mL, 2.29 mmol) and stirred for 30 min at room temperature. After ca. 2 min a color change from dark-brown to dark-red occurred. The solvent was removed in vacuo, and the oily residue was treated with 8 mL of diethyl ether. A bright-red solid was formed, which was filtered off, repeatedly washed with ether, and dried in vacuo: yield 336 mg (62%); mp 48 °C dec. Anal. Calcd for $C_{18}H_{42}Cl_2O_2P_2Ru$: C, 41.22; H, 8.07. Found: C, 40.98; H, 7.93. ^1H NMR (C_6D_6): δ 3.63 (m, 4 H, CH_2OMe), 3.60 (s, 6 H, OCH_3), 2.76 (m, 4 H, PC*H*CH_3), 2.05 (m, 4 H, PCH_2), 1.22 and 1.17 (both dvt, *N* = 12.9, *J*(HH) = 7.3 Hz, 24 H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6): δ 72.3 (s, CH_2OMe), 62.1 (s, OCH_3), 27.0 (vt, *N* = 21.6 Hz, PCH_2), 25.9 (vt, *N* = 20.6 Hz, P*C*HCH_3), 20.0 and 19.9 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6): δ 69.8 (s).

Preparation of [$RuCl_2(CO)_2(\eta^1$-*P*-*i*-$Pr_2PCH_2CH_2OMe)_2$] (4). A stream of CO was passed for 5 min through a solution of 3 (86 mg, 0.16 mmol) in 5 mL of toluene at room temperature. The color of the solution changed from red to light-yellow. The solvent was removed, and the residue was recrystallized from hexane to give a white microcrystalline solid: yield 70 mg (75%); mp 90 °C dec. Anal. Calcd for $C_{20}H_{42}Cl_2O_4P_2Ru$: C, 41.38; H, 7.29. Found: C, 41.64; H, 7.54. IR (THF): ν(CO) 1985, 1935 cm^{-1}. ^1H NMR (C_6D_6): δ 3.64 (m, 4 H, CH_2OMe), 3.08 (s, 6 H, OCH_3), 2.50 (m, 8 H, PCH_2 and PC*H*CH_3), 1.61 and 1.38 (both dvt, *N* = 15.0, *J*(HH) = 7.1 Hz, 24 H, PCHC*H*$_3$). ^{31}P NMR (C_6D_6): δ 31.0 (s).

Preparation of [$RuCl_2$(=C=CHPh)(η^1-*P*-*i*-$Pr_2PCH_2CH_2OMe$)(η^2-*i*-$Pr_2PCH_2CH_2OMe$)] (5). Method a. A solution of 3 (215 mg, 0.41 mmol) in 5 mL of benzene was treated with PhC≡CH (99 μL, 0.90 mmol) and heated under reflux for 16 h. After cooling to room temperature, the solution was concentrated to ca. 0.5 mL in vacuo and then chromatographed on SiO_2 (activity grade I, length of column 6 cm). With hexane/acetone (4:1) an orange fraction was eluted from which the solvent was removed in vacuo. The oily residue was treated with 5 mL of pentane to give an orange microcrystalline solid, yield 152 mg (60%).

Method b. A solution of 3 (105.0 mg, 0.20 mmol) and PhC≡CH (48.3 μL, 0.44 mmol) in 13 mL of toluene was irradiated for 30 min with a 125-W Hg lamp. The solution was filtered, the solvent was removed, and the residue was washed with 15 mL of pentane: yield 100 mg (80%); mp 109 °C dec. Anal. Calcd for $C_{26}H_{48}Cl_2O_2P_2Ru$: C, 49.84; H, 7.72; Cl, 11.31. Found: C, 50.09; H, 7.53; Cl, 11.32. IR (KBr): ν(C=C) 1590 cm^{-1}. ^1H NMR (C_6D_6): δ 7.1 (m, 5 H, C_6H_5), 4.67 (t, *J*(PH) = 3.7 Hz, 1 H, C*H*Ph), 3.72 (m, 4 H, CH_2OMe), 3.27 (s, 6 H, OCH_3), 2.73 (m, 4 H, PC*H*CH_3), 2.02 (m, 4 H, PCH_2), 1.38 and 1.22 (both dvt, *N* = 13.9, *J*(HH) = 6.9 Hz, 24 H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6): δ 350.1 (t, *J*(PC) = 15.9 Hz, Ru=C), 133.8, 128.6, 126.0, 124.2 (all s, C_6H_5), 109.9 (t, *J*(PC) = 4.2 Hz, CHPh), 70.3 (s, CH_2OMe), 60.0 (s, OCH_3), 23.6 (vt, *N* = 19.9 Hz, PCH_2), 21.8 (vt, *N* = 18.8 Hz, P*C*HCH_3), 19.6 and 19.1 (both s, PCH*C*H$_3$). ^{31}P NMR ($C_6D_5CD_3$, −80 °C): δ 33.0 and 11.5 (both d, AB system, *J*(PP) = 357 Hz).

Preparation of [$RuCl_2(\eta^2$-*i*-$Pr_2PCH_2C(O)OMe)_2$] (6). A solution of [$RuCl_2(PPh_3)_3$] (1.0 g, 1.04 mmol) in 10 mL of dichloromethane was treated with 2 (0.83 mL, 4.22 mmol) and stirred for 30 min at room temperature. After ca. 2 min a color change from dark-brown to red occurred. The solution was worked up as described for 3 to give a bright-red microcrystalline solid: yield 307 mg (54%); mp 105 °C dec. Anal. Calcd for $C_{18}H_{38}Cl_2O_4P_2Ru$: C, 39.14; H, 6.93. Found: C, 39.44; H, 7.10. IR (KBr): ν(C=O) 1650 cm^{-1}. ^1H NMR (C_6D_6): δ 3.60 (s, 6 H, OCH_3), 3.33 (vt, *N* = 9.6 Hz, 4 H, PCH_2), 2.48 (m, 4 H, PC*H*CH_3), 1.31 and 1.25 (both dvt, *N* = 13.4, *J*(HH) = 6.7 Hz, 24 H, PCHC*H*$_3$). ^{13}C NMR (C_6D_6): δ 181.9 (s, *C*O_2Me), 54.7 (s, OCH_3), 36.0 (vt, *N* = 21.7 Hz, PCH_2), 27.6 (vt, *N* = 23.1 Hz, P*C*HCH_3), 19.3 and 19.0 (both s, PCH*C*H$_3$). ^{31}P NMR (C_6D_6): δ 71.8 (s).

Preparation of [$RuCl_2$(=C=CHPh)(η^1-*P*-*i*-Pr_2PCH_2C(O)OMe)(η^2-*i*-Pr_2PCH_2C(O)OMe)] (7). A solution of 6 (200 mg, 0.36 mmol) and PhC≡CH (86.9 μL, 0.79 mmol) in 13 mL of toluene was irradiated for 30 min with a 125-W Hg lamp. The solution was filtered, and the filtrate was worked-up as described for 5 to give an orange microcrystalline solid: yield 189 mg (80%);

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Table II. Crystallographic Data for 5

formula	$C_{26}H_{48}Cl_2O_2P_2Ru$
fw	626.60
cryst size, mm	0.4 × 0.4 × 0.5
cryst system	monoclinic
space group	$P2_1/c$ (No. 14)
cell dimens determn	23 reflcns, 11° < θ < 14°
a, Å	13.129 (1)
b, Å	12.803 (1)
c, Å	18.867 (2)
β, deg	102.42 (1)
V, Å^3	3097.1
Z	4
d_{calcd}, g cm^{-3}	1.34
diffractometer	Enraf-Nonius CAD4
radiation (graphite monochromated)	Mo Kα (0.709 30 Å)
temp, °C	20 ± 1
μ, cm^{-1}	7.9
scan method	ω/2θ
2θ(max), deg	44
tot. no. of reflcns scanned	3680
no. of unique reflcns	3291
no. of obsd reflcns ($F_o > 3\sigma(F_o)$)	2187
no. of params refined	298
R	0.040
R_w	0.042
reflex/param ratio	7.34
resid electron density, e Å^{-3}	+0.45/−0.39

mp 144 °C dec. Anal. Calcd for $C_{26}H_{48}Cl_2O_4P_2Ru$: C, 47.71; H, 7.39. Found: C, 47.84; H, 7.09. IR (KBr): $\nu(C{=}O)_{free}$ 1710, $\nu(C{=}O)_{coord}$ 1650, $\nu(C{=}C)$ 1585 cm^{-1}. ^{1}H NMR ($C_6D_5CD_3$, 70 °C): δ 7.1 (m, 5 H, C_6H_5), 4.76 (t, J(PH) = 3.6 Hz, 1 H, CHPh), 3.32 (vt, N = 6.9 Hz, 4 H, PCH_2), 3.23 (s, 6 H, OCH_3), 2.87 (m, 4 H, $PCHCH_3$), 1.41 and 1.20 (both dvt, N = 14.4, J(HH) = 7.3 Hz, 2 H, $PCHCH_3$). ^{13}C NMR ($C_6D_5CD_3$, 70 °C): δ 354.6 (t, J(PC) = 14.6 Hz, Ru=C), 176.5 (br, CO_2Me), 133.2, 128.7, 125.9, 124.5 (all s, C_6H_5), 109.4 (t, J(PC) = 4.9 Hz, CHPh), 52.9 (s, OCH_3), 27.9 (vt, N = 19.2 Hz, PCH_2), 23.4 (vt, N = 21.8 Hz, $PCHCH_3$), 18.7 and 18.5 (both s, $PCHCH_3$). ^{31}P NMR ($C_6D_5CD_3$, −80 °C): δ 39.0 and 26.9 (both d, AB system, J(PP) = 369 Hz).

Preparation of [$RuCl_2(=C=CHCO_2Me)(\eta^1$-P-i-$Pr_2PCH_2C(O)OMe)(\eta^2$-i-$Pr_2PCH_2C(O)OMe)$] (8). A solution of 6 (149.6 mg, 0.27 mmol) and $HC\equiv CCO_2Me$ (72.1 μL, 0.81 mmol) in 13 mL of toluene was irradiated for 1 h with a 125-W Hg lamp. The solution was filtered, the solvent was removed in vacuo, and the oily residue was treated with 5 mL of ether to give yellow crystals: yield 95 mg (55%); mp 120 °C dec. Anal. Calcd for $C_{22}H_{42}Cl_2O_6P_2Ru$: C, 41.52; H, 6.65. Found: C, 40.68; H, 7.10. IR (KBr): $\nu(C{=}O)_{free}$ 1720, $\nu(C{=}O)_{coord}$ 1645, $\nu(C{=}C)$ 1575 cm^{-1}. ^{1}H NMR ($C_6D_5CD_3$, 70 °C): δ 4.52 (t, J(PH) = 2.9 Hz, 1 H, $CHCO_2Me$), 3.55 (s, 3 H, $CHCO_2CH_3$), 3.27 (vt, N = 6.8 Hz, 4 H, PCH_2), 3.24 (s, 6 H, $PCH_2CO_2CH_3$), 2.84 (m, 4 H, $PCHCH_3$), 1.32 and 1.29 (both dvt, N = 14.6, J(HH) = 7.4 Hz, 24 H, $PCHCH_3$). ^{13}C NMR ($C_6D_5CD_3$, 70 °C): δ 340.3 (t, J(PC) = 14.6 Hz, Ru=C), 176.1 (br, PCH_2CO_2Me), 165.7 (s, $CHCO_2Me$), 102.4 (s, $CHCO_2Me$), 53.0 (s, $PCH_2CO_2CH_3$), 50.4 (s, $CHCO_2CH_3$), 27.9 (vt, N = 18.8 Hz, PCH_2), 23.6 (vt, N = 22.2 Hz, $PCHCH_3$), 18.5 and 18.3 (both s, $PCHCH_3$). ^{31}P NMR ($C_6D_5CD_3$, −70 °C): δ 41.2 and 28.4 (both d, AB system, J(PP) = 345 Hz).

X-ray Structural Analysis of 3. Single crystals were grown from ether. Crystal data collection parameters are summarized in Table II. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction (ψ-scan method) was applied; the minimal transmission was 95.3%. The structure was solved by direct methods (SHELXS-86). Atomic coordinates (see Table III) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares (unit weights). The positions of all hydrogen atoms were calculated according to ideal geometry and were refined using the riding method. All calculations were performed on a Micro-VAX computer using the program package SDP[21] from Enraf-Nonius. For other details, see Table II.

Table III. Positional Parameters and Esd's for 5

atom	x	y	z	B_{eq},[a] Å^2
Ru	0.24978 (5)	0.03876 (5)	0.76152 (3)	3.38 (1)
Cl1	0.3450 (2)	−0.0780 (2)	0.7018 (1)	4.50 (5)
Cl2	0.1558 (2)	0.1798 (2)	0.7974 (1)	5.89 (6)
P1	0.4086 (2)	0.1305 (2)	0.8038 (1)	4.22 (5)
P2	0.0812 (2)	−0.0453 (2)	0.7157 (1)	4.78 (6)
O1	0.2501 (5)	0.1469 (4)	0.6586 (3)	5.8 (2)
O2	−0.0558 (9)	−0.079 (1)	0.8868 (5)	26.5 (4)
C1	0.2612 (6)	−0.0319 (6)	0.8422 (4)	3.8 (2)
C2	0.2661 (7)	−0.0819 (7)	0.9052 (4)	5.1 (2)
C3	0.3041 (6)	−0.1879 (6)	0.9245 (4)	4.1 (2)
C4	0.3552 (7)	−0.2480 (7)	0.8820 (5)	5.4 (2)
C5	0.3900 (8)	−0.3479 (8)	0.9028 (5)	6.8 (3)
C6	0.3742 (7)	−0.3880 (8)	0.9663 (5)	6.3 (3)
C7	0.3238 (8)	−0.3319 (7)	1.0094 (5)	6.0 (2)
C8	0.2882 (7)	−0.2324 (7)	0.9887 (4)	5.2 (2)
C9	0.4200 (7)	0.2079 (8)	0.7233 (5)	6.7 (3)
C10	0.3146 (8)	0.2381 (8)	0.6806 (6)	7.9 (3)
C11	0.2565 (9)	0.1099 (9)	0.5886 (5)	8.0 (3)
C12	0.5290 (6)	0.0513 (7)	0.8202 (5)	5.6 (2)
C13	0.5453 (7)	−0.0088 (7)	0.8921 (5)	6.9 (3)
C14	0.6258 (7)	0.1126 (8)	0.8161 (5)	6.7 (3)
C15	0.4282 (8)	0.2225 (7)	0.8807 (5)	5.8 (2)
C16	0.3836 (8)	0.1819 (8)	0.9434 (5)	7.4 (3)
C17	0.3919 (8)	0.3340 (7)	0.8604 (6)	7.9 (3)
C18	0.0233 (9)	−0.096 (1)	0.7902 (6)	11.4 (4)
C19	−0.0041 (9)	−0.035 (1)	0.8424 (6)	10.8 (4)
C20	−0.092 (1)	−0.082 (2)	0.9260 (8)	17.5 (7)
C21	0.0770 (9)	−0.1693 (9)	0.6672 (6)	9.2 (3)
C22	0.078 (2)	−0.164 (1)	0.5941 (7)	19.8 (7)
C23	0.1399 (9)	−0.2516 (8)	0.7057 (9)	13.7 (6)
C24	−0.0231 (9)	0.038 (1)	0.6706 (8)	13.5 (5)
C25	−0.0088 (9)	0.1128 (9)	0.6170 (6)	9.9 (4)
C26	−0.1316 (9)	−0.015 (1)	0.648 (1)	18.1 (6)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = {}^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

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Supplementary Material Available: An ORTEP drawing of complex 5, showing the atom-numbering scheme, and tables of bond distances, bond angles, least-squares planes, positional parameters, and general displacement parameter expressions (12 pages); a table of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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