Areneruthenium(II) Complexes with Functionalized Phosphines Coordinating as Mono-, Bi- or Tridentate Ligands

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Dedicated to the Memory of *Luigi M. Venanzi*, one of the pioneers of modern coordination chemistry

Areneruthenium(II) compounds [Ru(*p*-cym)Cl_2{κ-*P*-^{i}PrP($CH_2CH_2OMe)_2$}], **3**, and [Ru(arene)Cl_2{κ-*P*-RP($CH_2CO_2Me)_2$}] **4**–**7** (arene = *p*-cym (= 1-methyl-4-isopropylbenzene), mes (= 1,3,5-trimethylbenzene); R = ^{i}Pr, ^{t}Bu) were prepared from the dimers [Ru(arene)Cl_2]$_2$ and the corresponding functionalized phosphine. Treatment of **6** and **7** with *1 equiv.* of $AgPF_6$ affords the monocationic complexes [Ru(mes)Cl{κ^2-*P*,*O*-RP($CH_2C(O)OMe$)(CH_2CO_2Me)}]PF_6, **10** and **11**, while the related reaction of **5**–**7** with *2 equiv.* of $AgPF_6$ produces the dicationic compounds [Ru(*p*-cym){κ^3-*P*,*O*,*O*-^{t}BuP($CH_2C(O)OMe)_2$}]$(PF_6)_2$ (**12**) and [Ru(mes)-{κ^3-*P*,*O*,*O*-RP($CH_2C(O)OMe)_2$}]$(PF_6)_2$, **13** and **14**. Partial hydrolysis of one hexafluorophosphate anion of **12**–**14** leads to the formation of [Ru(arene){κ^2-*P*,*O*-RP($CH_2C(O)OMe$)(CH_2CO_2Me)}(κ-*O*-O_2PF_2)]PF_6, **15**–**17**, of which **17** (arene = mes; R = ^{t}Bu) has been characterized by X-ray crystallography. Compounds **13** and **14** react with 2 equiv. of KO^{t}Bu in ^{t}BuOH/toluene to give the unsymmetrical complexes [Ru(mes){κ^3-*P*,*C*,*O*-RP-($CHCO_2Me$)(CH=C(O)OMe)}], **18** and **19**, containing both a five-membered phosphinoenolate and a three-membered phosphinomethanide ring. The molecular structure of compound **18** has been determined by X-ray structure analysis. The neutral bis(carboxylate)phosphanidoruthenium(II) complexes [Ru(arene){κ^3-*P*,*O*,*O*-RP-($CH_2C(O)O)_2$}], **20**–**23** are obtained either by hydrolysis of **18** and **19**, or by stepwise treatment of **4** and **5** with KO^{t}Bu and basic Al_2O_3. Novel tripodal chelating systems are generated *via* insertion reactions of **19** with PhNCO and PhNCS.

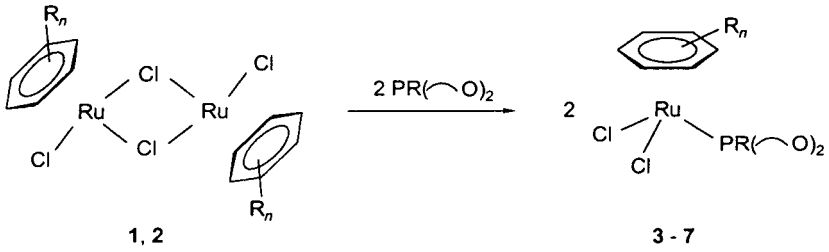
Introduction. – In the search of finding useful ligands for catalytically active transition-metal complexes, the chemistry of substituted phosphines of general composition $R_2P(CH_2)_nY$ has become an area of great interest in recent years (for reviews, see [1]). By far, the most attention was given to compounds where the functional group Y is MeO, C(O)R′ or C(O)OR′, since it was anticipated that the O-donors temporarily are able to protect a vacant coordination site and thus allow the addition of more powerful ligands to the metal center under fairly mild conditions. Moreover, with β-phosphino ketones or esters as coordinating groups, a number of *O*-metallated phosphinoenolate metal complexes have been prepared and found to be appropriate starting materials for C,C coupling reactions with activated alkynes and isocyanates [2], for the generation of metal acetylides from alk-1-ynes [3], and for reversibly binding CO_2 [4].

As a continuation of our work on the reactivity of phosphino esters $R_2PCH_2CO_2R'$ toward d^6 and d^8 metal centers [5], we have recently developed a synthetic route to the *trifunctional* phosphines $RP(CH_2CO_2R')_2$ [6] and started to investigate their coordination capabilities [7]. In this paper, we describe the synthesis of a series of areneruthenium(II) complexes containing the potentially tridentate monophosphanes $RP(CH_2CO_2Me)_2$ (R = ^{i}Pr, ^{t}Bu) and the remarkable conversion of these molecules to

novel unsymmetrical κ^3-*P,C,O*-bonded tripod-type ligands. Moreover, the metal-mediated hydrolysis of these tripodal ligands to coordinated tridentate dianions $[RP(CH_2CO_2)_2]^{2-}$ and the different course of insertion reactions of PhNCO and PhNCS into one of the C–H bonds of the κ^3-*P,C,O*-bonded ligands will also be reported. Some preliminary results of this work have already been published [8].

Results and Discussion. – Similarly to PMe_3 and other tertiary phosphines, the phosphine derivatives ^{t}BuP$(CH_2CH_2OMe)_2$ and RP$(CH_2CO_2Me)_2$ (R = ^{i}Pr,^{t}Bu) react with the dimers **1** and **2** in CH_2Cl_2 at room temperature *via* cleavage of the chloro bridges to give the mononuclear air-stable compounds **3**–**7** in 90–95% yield (*Scheme 1*). The ^{31}P-NMR spectra of **3**–**7** display a *singlet* resonance which is shifted downfield by 30–40 ppm compared with the free phosphine. The assumption that the MeO and CO_2Me groups of the ligands are not involved in the coordination to the metal is supported by the IR spectra in which only one C–O or C=O stretching mode in the same region as for ^{t}BuP$(CH_2CH_2OMe)_2$ or RP$(CH_2CO_2Me)_2$ appears.

Scheme 1

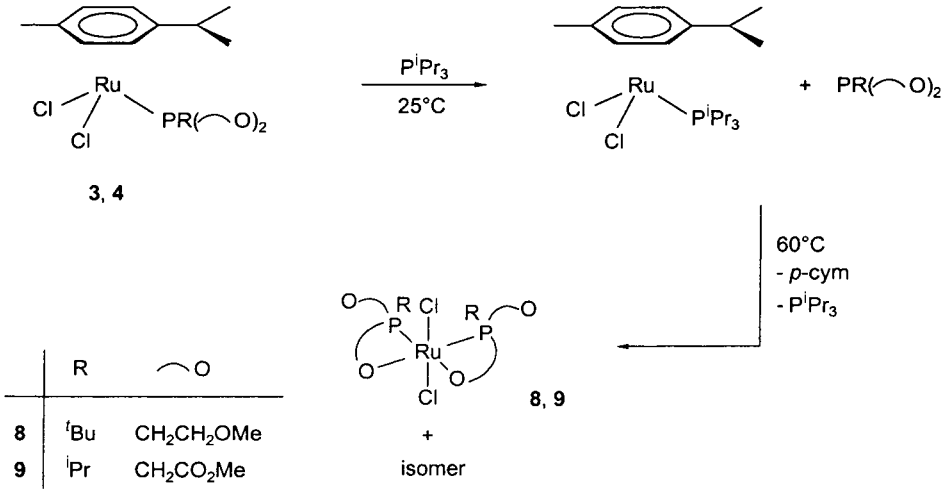


1, 2 **3 - 7**

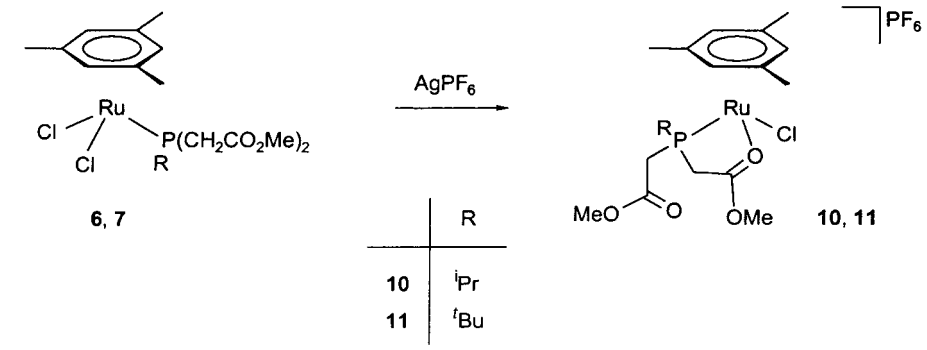
	arene	PR(⌒O)$_2$
3	*p*-cym	^{t}BuP$(CH_2CH_2OMe)_2$
4	*p*-cym	^{i}PrP$(CH_2CO_2Me)_2$
5	*p*-cym	^{t}BuP$(CH_2CO_2Me)_2$
6	mes	^{i}PrP$(CH_2CO_2Me)_2$
7	mes	^{t}BuP$(CH_2CO_2Me)_2$

Attempts to displace the more weakly bound *p*-cymene (= 1-methyl-4-(1-methylethyl)benzene) ligand by P^{i}Pr$_3$ and generate an arene-free Ru^{II} complex of general composition $[RuCl_2(P^iPr_3)\{\kappa^3$-*P,O,O*-RP$(\cap O)_2\}]$ failed. Treatment of **3** or **4** with 1 equiv. of P^{i}Pr$_3$ in benzene leads to ligand exchange and affords both [Ru(*p*-cym)Cl_2(P^{i}Pr$_3$)] [9] and the uncoordinated functionalized phosphine (*Scheme 2*). Heating the solution to 60° for 6–8 h yields a mixture of products in which, apart from some unidentified compounds, the complexes **8** and **9** [7b] are the dominating species.

Scheme 2



Scheme 3

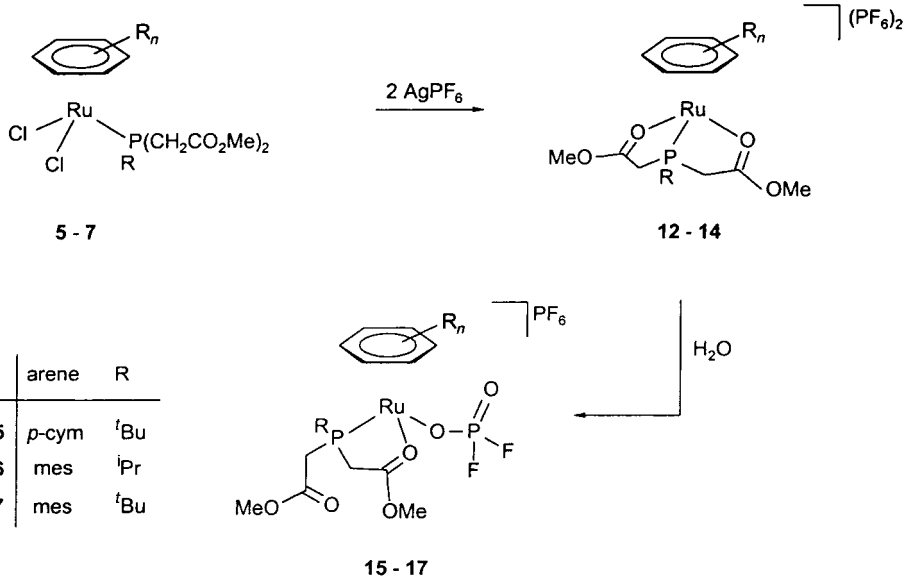


The reaction of the mesitylene (=1,3,5-trimethylbenzene; mes) compounds **6** and **7** with an equimolar amount of $AgPF_6$ in CH_2Cl_2 results in the abstraction of one chloride and the formation of the cationic chelate complexes **10** and **11** in nearly quantitative yields (*Scheme 3*). The composition of **10** and **11**, which are orange-yellow, moderately air-sensitive solids dissolving in polar solvents such as acetone, $MeNO_2$, and CH_2Cl_2, has been confirmed by elemental analysis and conductivity measurements. As expected, the ^{1}H- and ^{13}C-NMR spectra of **10** and **11** display two sets of signals for the configurationally different CH_2CO_2Me moieties indicating that there is no intramolecular exchange of the coordinated and the dangling CH_2COOMe groups at room temperature. In contrast to **6** and **7**, the IR spectra of **10** and **11** show two strong $\tilde{\nu}$(C=O) bands at 1713 and 1610 cm^{-1} (**10**), and 1721 and 1613 cm^{-1} (**11**), supporting the assumption that one of the CO_2Me units is coordinated (*via* the C=O O-atom)

while the other is free (for a discussion of the IR data of coordinated and non-coordinated C=O groups, see [10]).

The coordination of *both* C=O bonds of $RP(CH_2CO_2Me)_2$ to the Ru-center can be achieved upon treatment of **5**–**7** with 2 equiv. of $AgPF_6$ in CH_2Cl_2. After removal of the solvent and extraction of the residue with acetone, the complexes **12**–**14**, in which the intact phosphine behaves as a tridentate bis-chelating ligand, were isolated as orange, practically air-stable solids in 78–82% yield. The structural proposal for **12**–**14**, shown in *Scheme 4*, is well-supported by the spectroscopic data and the conductivity in $MeNO_2$. Since there is only one C=O stretching mode at *ca.* 1610–1620 cm^{-1}, which is lowered by *ca.* 110 cm^{-1} compared with the monodentate phosphine in **5**–**7**, the IR spectra in particular leave no doubt that both CH_2CO_2Me units are involved in the coordination to the metal.

Scheme 4



	arene	R
12, **15**	*p*-cym	^{t}Bu
13, **16**	mes	^{i}Pr
14, **17**	mes	^{t}Bu

In polar solvents such as CH_2Cl_2, in the presence of small amounts of H_2O, partial hydrolysis of the hexafluorophosphate anion of **12**–**14** occurs, leading to the monocationic difluorophosphinatoruthenium(II) complexes **15**–**17** in excellent yields. Such a transition-metal-mediated conversion of PF_6^- to $PO_2F_2^-$ is not without precedence [11], and, with areneruthenium(II) compounds has been observed in the formation of $[(C_6Me_6Ru)_2(\mu\text{-}O_2PF_2)_3]PF_6$ from $[Ru(acetone)_3(C_6Me_6)](PF_6)_2$ and H_2O [12]. Typical spectroscopic features of **15**–**17** are the P=O and the two C=O stretching modes in the IR spectra, the two sets of signals for the H- and C-atoms of the inequivalent CH_2CO_2Me fragments in the ^{1}H- and ^{13}C-NMR spectra, and the *doublet*-of-*doublets*-of-*doublets* (due to P,P and twofold P,F couplings) for the P-atom of the $PO_2F_2^-$ ligand in the ^{31}P-NMR spectra. The ^{19}F-NMR spectra of **15**–**17** display apart

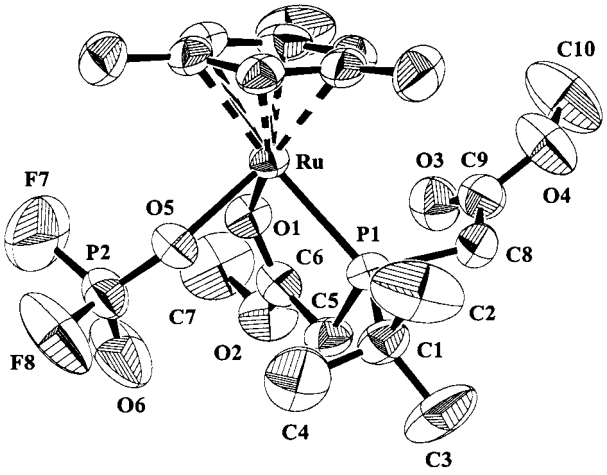


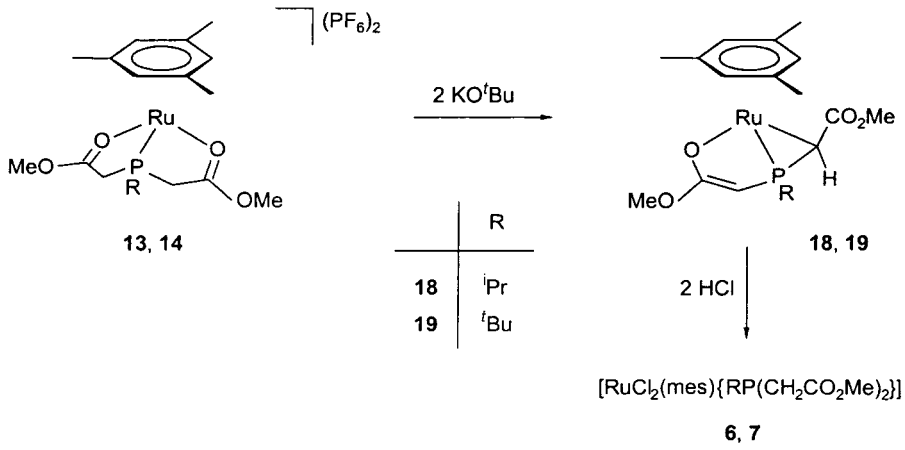
Fig. 1. *ORTEP Diagram of compound* **17** (H-atoms omitted for clarity). Selected bond distances [Å] and angles [deg]: Ru–O(1) 2.112(3), Ru–O(5) 2.114(3), Ru–P(1) 2.3645(12), O(1)–C(6) 1.227(5), O(2)–C(6), 1.311(5), C(5)–C(6) 1.479(7), P(1)–C(1) 1.870(5), P(1)–C(5) 1.829(5), P(1)–C(8) 1.826(5), P(2)–O(5) 1.471(3), P(2)–O(6) 1.415(5); O(1)–Ru–O(5) 84.29(12), O(1)–Ru–P(1) 79.63(9), O(5)–Ru–P(1) 88.58(10), Ru–O(1)–C(6) 122.5(3), Ru–O(5)–P(2) 136.1(2), Ru–P(1)–C(1) 124.7(17), Ru–P(1)–C(5) 100.13(16), Ru–P(1)–C(8) 116.15(17), C(1)–P(1)–C(5) 106.2(2), C(1)–P(1)–C(8) 103.6(2), C(5)–P(1)–C(8) 103.7(2), P(1)–C(5)–C(6) 108.5(3), O(1)–C(6)–C(5) 123.7(4).

from the signal for the PF_6^- anion a resonance for the F-atoms of the $PO_2F_2^-$ unit which appears as the *AB* part of an *ABX* spin system.

The molecular structure of the cation of compound **17** is shown in *Fig. 1*. In agreement with the spectroscopic data, the phosphinodiester is bonded to Ru in a κ^2-*P*,*O*-mode, forming a five-membered chelate ring and leaving one CO_2Me group uncoordinated. The 'bite angle' O(1)–Ru–P(1) of 79.63(9)° is quite similar to that of the neutral complex $[RuCl_2\{\kappa^2\text{-}P,O\text{-}^t BuP(CH_2C(O)OMe)(CH_2CO_2Me)\}_2]$ (81.8(2)° and (82.0(2)°) [13] and also to that of the related Os cation $[OsCl(mes)(\kappa^2\text{-}P,N\text{-}^i Pr_2PCH_2CH_2NMe_2)]^+$ (81.74(10)°) [14]. Moreover, the Ru–O(1) and Ru–P(1) distances are comparable with those of cationic Ru compounds containing $R_2PCH_2CO_2R'$ as bidentate ligands [15]. The geometry of the coordinated $PO_2F_2^-$ anion is distorted tetrahedral, the bond angle O(6)–P(2)–O(5) (121.8(3)°) being the largest and F(7)–P(2)–F(8) (97.0(4)°) the smallest. The bond lengths P(2)–O(5), P(2)–O(6), P(2)–F(7) and P(2)–F(8) are in the expected range [16] and thus deserve no further comment.

The mes complexes **13** and **14** react with 2 equiv. of KO*t*Bu in a 1:1 mixture of *t*-BuOH and toluene to give instead of the anticipated bis(enolate)ruthenium(II) compounds $[Ru(mes)\{\kappa^3\text{-}P,O,O\text{-}RP(CH{=}C(O)OMe)_2\}]$ the moisture-sensitive bicyclic products **18** and **19** in 60–65% yield (*Scheme 5*). The spectroscopic data of **18** and **19** indicate quite clearly that the two $PCHCO_2Me$ units are not equally bonded to the metal center. While one chelating moiety forms a five-membered phosphinoenolate

Scheme 5



ring resulting from *O*-metallation of one $PCHCO_2Me$ group, the other one constitutes a three-membered Ru-phosphinomethanide unit, which is the *C*-metallation product. Characteristic features illustrating the different bonding mode of the $PCHCO_2Me$ fragments in **18** and **19** are the two signals for the PCH protons at, respectively, δ 3.45 or 3.55 ($PCH_{enolate}$), and δ 1.69 or 1.67 ppm ($PCH_{methanide}$) in the ^{1}H-NMR, and the two resonances for the corresponding carbon nuclei at δ 44.6 or 44.0 ($PCH_{enolate}$) and δ 4.9 or -8.7 ($PCH_{methanide}$) in the ^{13}C-NMR spectra. We note first that attempts to prepare a structurally related *p*-cymene derivative [Ru(*p*-cym){κ^3-*P*,*C*,*O*-^{t}BuP(CH=C(*O*)OMe)-(*C*HCO_2Me)}] by treatment of **12** with KO^{t}Bu in the molar ratio of 1:2 failed, and, second, that complexes with a Ru(κ^2-*P*,*C*-Me_2PCH_2) moiety but without an arene ligand are well-known [17] and have recently been used for the synthesis of monomeric hydroxo, phenolato, and amido Ru derivatives [18]. It should also be mentioned that, upon treatment of **18** or **19** with 2 equiv. of gaseous HCl in toluene, the dichloro compounds **6** and **7** are regenerated.

The molecular structure of **18** was confirmed by a single-crystal X-ray structure analysis (see *Fig. 2*). The five-membered phosphinoenolate-metal unit is nearly planar with the MeO substituent lying in the ring plane. The electron delocalization within the $RuPC_2O$ cycle is indicated by the short distances P–C(2) and C(1)–C(2) and also by the C(1)–O(1) bond length, which is between a C–O and a C=O bond. The interatomic bond distances and angles of the three-membered phosphinomethanide-metal fragment are comparable to those found in [$Mn(CO)_4$(κ^2-*P*,*C*-Ph_2PCH_2)] [19], [$Mo(CO)_2(C_5H_5)$(κ^2-*P*,*C*-Ph_2PCH_2)] [20], and [MCl(mes)(κ^2-*P*,*C*-$^i Pr_2PCHCO_2Me$)] (M = Ru, Os) [21]. The dihedral angle between the planes of the five-membered $RuPC_2O$ and the three-membered RuPC ring in **18** is 81.77°.

If instead of **13** or **14** the dichlororuthenium(II) derivatives **4** and **5** are reacted with 2 equiv. of KO^{t}Bu in *t*-BuOH/toluene 1:1 and, after removal of the solvent, the crude products are chromatographed on basic Al_2O_3 with MeOH, the neutral phosphino-bis(carboxylate) complexes **20** and **21** are obtained as orange-yellow, nearly air-stable

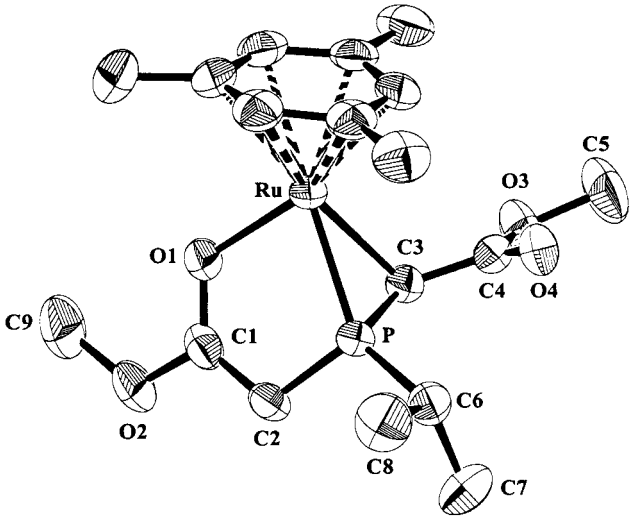
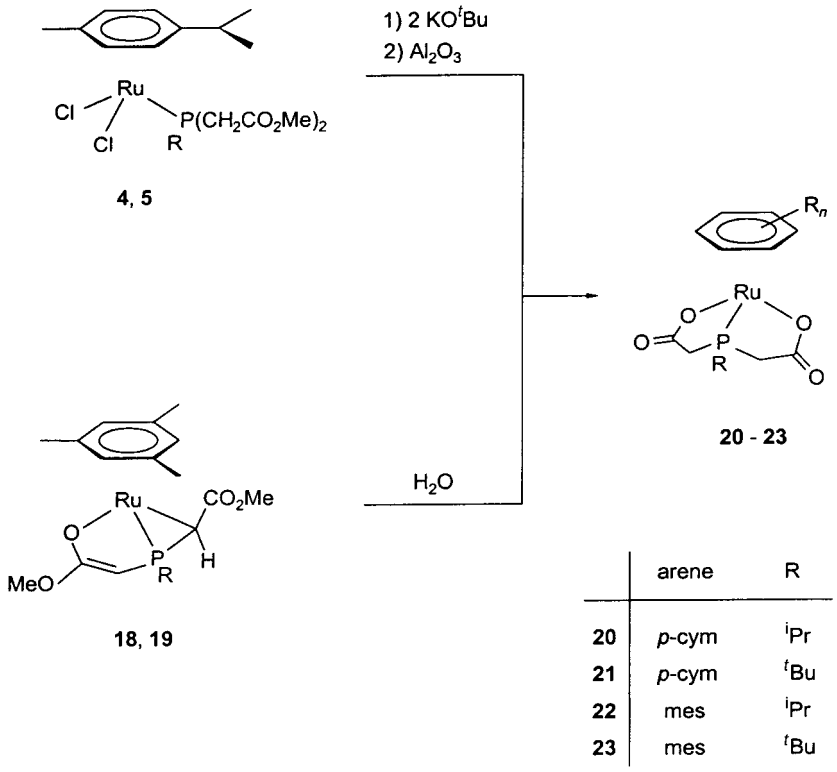


Fig. 2. *ORTEP Diagram of compound* **18** (H-atoms omitted for clarity). Selected bond distances [Å] and angles [deg]: Ru–O(1) 2.053(3), Ru–C(3) 2.217(4), Ru–P 2.301(2), O(1)–C(1) 1.295(5), C(1)–O(2) 1.323(4), C(1)–C(2) 1.394(5), P–C(2) 1.671(4), P–C(3) 1.727(4), P–C(6) 1.884(4), C(3)–C(4) 1.374(5); O(1)–Ru–C(3) 88.03(14), O(1)–Ru–P 80.65(11), C(3)–Ru–P 44.91(11), Ru–O(1)–C(1) 116.7(2), Ru–P–C(2) 104.2(2), Ru–P–C(3) 64.98(13), Ru–P–C(6) 138.25(14), Ru–C(3)–C(4) 111.3(3), Ru–C(3)–P 70.11(13), O(1)–C(1)–C(2) 127.7(3), O(2)–C(1)–C(2) 118.0(3), O(1)–C(1)–O(2) 114.2(3), C(1)–C(2)–P 110.5(3), C(2)–P–C(3) 106.1(2), C(2)–P–C(6) 112.5(2), C(3)–P–C(6) 119.8(2), P–C(3)–C(4) 118.0(3).

solids in moderate yields (*Scheme 6*). The strucutrally analogous mes compounds **22** and **23** are more conveniently prepared by treatment of a solution of **18** or **19** in acetone with an excess of H_2O. In this case the yield is 81–83%. In agreement with the proposed structure, the NMR spectra of **20**–**23** are quite simple and confirm the symmetrical bonding mode of the tridentate $[RP(CH_2CO_2)_2]^{2-}$ unit. The IR spectra of **20**–**23** display one strong $\tilde{\nu}$(C=O) band at 1637 or 1647 cm^{-1}, corresponding to previously published data [22]. In the ^{1}H-NMR spectra, the diastereoisotopic CH_2 protons of the CH_2CO_2 fragments give rise to two *doublets*-of-*doublets* at δ *ca.* 2.65 ppm presenting the *AB* part of an *ABX* spectrum. With regard to the formation of **20** and **21** from **4** and **5**, it should be mentioned that recently a similar CH_3–O-bond cleavage of bifunctional phosphines $R_2PCH_2CO_2Me$ has been observed in the coordination sphere of Ru^{II} [23] and also of Ir^{I} [5d]. As far as the mechanism of the reactions of **18** and **19** to yield **22** and **23** is concerned, we assume that the ring strain of the bicyclic rutheniumphosphinoenolate/-methanide system facilitates the hydrolysis of the CO_2Me units. In this context we note, that the phosphinoenolate compound [RuCl(mes){κ^2-*P*,*O*-^{i}Pr$_2$PCH=C(*O*)OMe}] equally reacts almost instantaneously with traces of H_2O to give the related phosphinoacetate derivative [RuCl(mes){κ^2-*P*,*O*-^{i}Pr$_2$PCH$_2$C(*O*)O}] [21a].

While compound **19**, in contrast to some phosphinoenolate-metal complexes studied by *Braunstein et al.* [4], is inert toward CO_2, it reacts quite smoothly with

Scheme 6

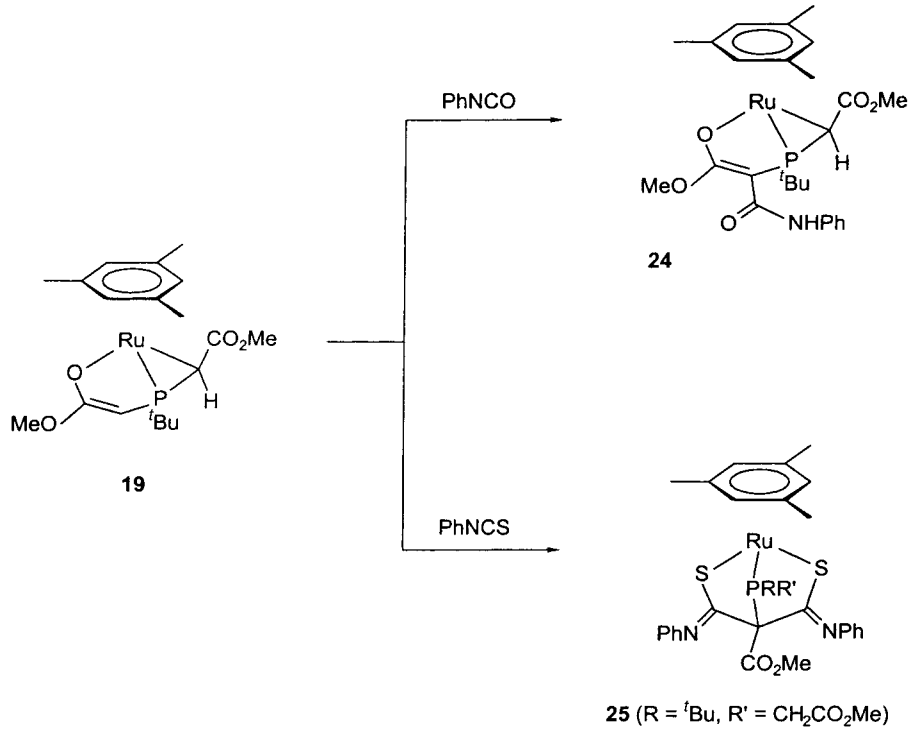


	arene	R
20	*p*-cym	^{i}Pr
21	*p*-cym	^{t}Bu
22	mes	^{i}Pr
23	mes	^{t}Bu

PhNCO in toluene at room temperature to afford the 1:1 adduct **24** as a yellow microcrystalline solid in 70% isolated yield (*Scheme 7*). The ring-substituted derivative formally results from the addition of the C–H bond of the PCH= unit of the enolate across the C=N bond of the substrate. Although such an insertion reaction is not without precedence [2][13][14], the formation of **24** is noteworthy insofar as, even in the presence of excess PhNCO, no insertion into the C–H bond of the phosphinomethanide ligand and also no enlargement of the RuPC three-membered ring takes place. Characteristic spectroscopic features of **24** are the N–H stretching mode at 3380 cm^{-1} in the IR, the signal for the NH proton at δ 9.10 in the ^{1}H-NMR, and the three resonances for the C=O C-atoms at δ 176.2 (*doublet*), 173.9 (*singlet*), and 165.5 ppm (*doublet*) in the ^{13}C-NMR spectrum.

Not only PhNCO but also the corresponding PhNCS reacts with **19** in toluene at 25°. In this case, however, instead of the anticipated 1:1, the 1:2 adduct **25** is formed. Based on the elemental analysis (C, H, N, S) and the spectroscopic data of **25**, the structure shown in *Scheme 7* is tentatively assigned. The presence of noncoordinated CO_2Me groups is indicated in the IR spectrum by the strong $\tilde{\nu}$(C=O) absorption at 1726 cm^{-1} which appears at almost the same position as found for **5**. The ^{13}C-NMR spectrum of **25** displays four signals at around δ 170.9 to 167.2 ppm, which are assigned

Scheme 7



to the C-atoms of the CO_2Me and C=NPh fragments. The alternative structure for **25**, in which the tridentate ligand contains two exocyclic C=S bonds while the metal center is coordinated to P- and to two N-atoms, can be excluded, since the IR spectrum shows no absorption between 1050 and 1200 cm^{-1} (typical for a C=S stretching mode) but an intensive $\tilde{\nu}$(C=N) band for the C=NPh units at 1577 cm^{-1}. Regarding the mechanism of formation of **25**, a reasonable assumption is that the insertion of the two isothiocyanates occurs stepwise, and an 1:1 adduct is generated as an intermediate. However, we can only speculate about the structure of this hypothetical species because all our attempts to isolate such a compound from the reaction of **19** with an equimolar amount of PhNCS failed.

In conclusion, the work presented in this paper has shown that trifunctionalized phosphines of the general composition $RP(CH_2CO_2Me)_2$ containing bulky substituents R are able to behave as mono-, bi-, or tridentate ligands. In the coordination sphere of Ru^{II}, they can also be converted to unsymmetrical dianionic κ^3-*P*,*C*,*O*-bonded tripod-type units, which can further be modified by insertion of both PhNCO and PhNCS into one of the C–H bonds of the bicyclic skeleton. Although some tentative experiments remained unsuccessful, the new complexes **24** and **25** offer the opportunity to generate by acid cleavage of the metal–ligand bonds the formation of oligofunctional chiral phosphines.

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Experimental Part

General. All experiments were carried out under Ar by Schlenk techniques. Solvents were dried by known procedures and distilled under Ar before use. The starting materials **1**, **2** [24], and the phosphines ^{t}BuP($CH_2CH_2OMe)_2$ and RP($CH_2CO_2Me)_2$ (R = ^{i}Pr, ^{t}Bu) [6] were prepared as described in the literature. Melting and decomposition points were determined by DTA. IR Spectra: in cm^{-1}; *Perkin-Elmer 1420* spectrophotometer. NMR Spectra: at r.t., *Bruker AC-200* and *Bruker AMX-400* instruments; chemical shifts δ are expressed in ppm downfield from $SiMe_4$ (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). MS: *Finnigan MAT* instrument. The conductivity Λ was measured in $MeNO_2$ with a *Schott Konduktometer CG 851*.

*[RuCl$_2$(*p*-*cym*){κ-P-^{t}*BuP*(*CH$_2$CH$_2$OMe)$_2$*}]* (**3**). A suspension of **1** (1.0 g, 1.63 mmol) in 40 ml of CH_2Cl_2 was treated with ^{t}BuP($CH_2OMe)_2$ (842 mg, 4.08 mmol) and stirred for 3 h at r.t. The mixture was filtered, and the filtrate was concentrated to *ca.* 5 ml *in vacuo*. After addition of 20 ml of hexane, a red-brown solid precipitated, which was separated from the mother liquor, washed three times with 10-ml portions of hexane, and dried: 1.51 g (90%) of **3**. M.p. 118° (dec.). IR (CH_2Cl_2): 1096 (C–O). ^{1}H-NMR (200 MHz, $CDCl_3$): 5.55 (*m*, C_6H_4); 3.72–3.51 (*m*, 2 PCH_2CH_2O); 3.26 (*s*, 2 MeO); 2.80 (*sept.*, ^3J(H,H) = 6.9, Me_2CH); 2.39–2.22 (*m*, 2 PCH_2CH_2O); 2.07 (*s*, *Me*C_6H_4); 1.29 (*d*, ^3J(P,H) = 13.1, 3 PCMe); 1.25 (*d*, ^3J(H,H) = 6.9, *Me*$_2$CH). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 108.1, 94.5 (2*s*, *ipso*-C of C_6H_4); 88.6 (*d*, ^2J(P,C) = 3.9, C_6H_4); 83.6 (*d*, ^2J(P,C) = 5.2, C_6H_4); 68.4 (*s*, PCH_2CH_2O); 58.1 (*s*, MeO); 35.4 (*d*, ^1J(P,C) = 21.4, P*C*Me); 30.4 (*s*, Me_2CH); 28.1 (*d*, ^2J(P,C) = 3.2, PC*Me*); 25.0 (*d*, ^1J(P,C) = 21.4, PCH_2); 22.2 (*s*, *Me*$_2$CH); 17.7 (*s*, *Me*–C_6H_4). ^{31}P-NMR (81.0 MHz, $CDCl_3$): 28.2 (*s*). Anal. calc. for $C_{20}H_{37}Cl_2O_2PRu$ (512.5): C 46.88, H 7.28; found: C 47.02, H 7.16.

*[RuCl$_2$(*p*-*cym*){κ-P-^{i}*PrP*(*CH$_2$CO$_2$Me)$_2$*}]* (**4**). As described for **3**, from **1** (1.0 g, 1.63 mmol) and ^{i}PrP($CH_2CO_2Me)_2$ (900 mg, 4.09 mmol): 1.58 g (92%) of **4**. Red-brown solid. M.p. 137°. IR (CH_2Cl_2): 1723 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 5.58 (*m*, C_6H_4); 3.68 (*s*, 2 MeO); 3.38 (*AB* of *ABX*; $\delta(H_A)$ 3.40, $\delta(H_B)$ 3.35, $^2J(P,H_A) = 7.9$, $^2J(P,H_B) = 12.5$, ^2J(H,H) = 15.8, 2 PCH_2); 3.01 (*m*, Me_2CHP); 2.80 (*sept.*, ^3J(H,H) = 7.0, Me_2CH), 2.06 (*s*, *Me*–C_6H_4); 1.30 (*dd*, ^3J(P,H) = 15.6, ^3J(H,H) = 7.2, *Me*$_2$CHP); 1.20 (*d*, ^3J(H,H) = 7.0, *Me*$_2$CH). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.3 (*d*, ^2J(P,C) = 5.7, CO_2); 109.0, 94.4 (2*s*, *ipso*-C of C_6H_4); 89.8 (*d*, ^2J(P,C) = 4.0, C_6H_4); 83.9 (*d*, ^2J(P,C) = 6.1, C_6H_4); 52.1 (*s*, MeO); 30.5 (*s*, Me_2CH); 29.1 (*d*, ^1J(P,C) = 21.5 Me_2CHP); 27.1 (*d*, ^1J(P,C) = 23.0, PCH_2); 21.9 (*s*, *Me*$_2$CH); 17.8 (*s*, Me–C_6H_4); 17.7 (*s*, *Me*$_2$CHP). ^{31}P-NMR (81.0 MHz, $CDCl_3$): 27.6 (*s*). Anal. calc. for $C_{19}H_{31}Cl_2O_4PRu$ (526.4): C 43.35, H 5.94; found: C 43.18, H 6.19.

*[RuCl$_2$(*p*-*cym*){κ-P-^{t}*BuP*(*CH$_2$CO$_2$Me)$_2$*}]* (**5**). As described for **3**, from **1** (1.0 g, 1.63 mmol) and ^{t}BuP($CH_2CO_2Me)_2$ (956 mg, 4.08 mmol): 1.61 g (91%) of **5**. Red-brown solid. M.p. 134° (dec.). IR (CH_2Cl_2): 1722 (C=O). ^{1}H-NMR (200 MHz, $CDCl_3$): 5.81–5.61 (*m*, C_6H_4); 3.67 (*s*, 2 MeO); 3.44 (*AB* of *ABX*; $\delta(H_A)$ 3.52, $\delta(H_B)$ 3.30, $^2J(P,H_A) = 12.2$, $^2J(P,H_B) = 7.7$, ^2J(H,H) = 15.2, 2 PCH_2); 2.89 (*sept.*, ^3J(H,H) = 7.0, Me_2CH); 2.08 (*s*, *Me*–C_6H_4); 1.36 (*d*, ^3J(P,H) = 14.5, ^{t}Bu); 1.23 (*d*, ^3J(H,H) = 7.0, *Me*$_2$CH). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 170.4 (*d*, ^2J(P,C) = 5.6, CO_2); 109.1, 94.0 (2*s*, *ipso*-C of C_6H_4); 89.7 (*d*, ^2J(P,C) = 3.7, C_6H_4); 84.0 (*d*, ^2J(P,C) = 6.5, C_6H_4); 52.0 (*s*, MeO); 36.4 (*d*, ^1J(P,C) = 16.6, Me_3C); 30.4 (*s*, Me_2CH); 28.7 (*s*, Me_3C); 28.4 (*d*, ^1J(P,C) = 21.3, PCH_2); 22.0 (*s*, *Me*$_2$CH); 17.3 (*s*, *Me*–C_6H_4). ^{31}P-NMR (81.0 MHz, $CDCl_3$): 35.5 (*s*). Anal. calc. for $C_{20}H_{33}Cl_2O_4PRu$ (540.3): C 44.46, H 6.16; found: C 44.37, H 6.21.

*[RuCl$_2$(*mes*){κ-P-^{i}*PrP*(*CH$_2$CO$_2$Me)$_2$*}]* (**6**). As described for **3**, from **2** (1.0 g, 1.71 mmol) and ^{i}PrP($CH_2CO_2Me)_2$ (942 mg, 4.28 mmol): 1.67 g (95%) of **6**. Red-brown solid. M.p. 172°. IR (CH_2Cl_2): 1715 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 5.08 (*s*, C_6H_3), 3.64 (*s*, 2 MeO); 3.37 (*AB* of *ABX*; $\delta(H_A)$ 3.48, $\delta(H_B)$ 3.26, $^2J(P,H_A) = 9.3$, $^2J(P,H_B) = 11.1$, ^2J(H,H) = 14.8, 2 PCH_2); 2.69 (*m*, Me_2CHPh); 2.17 (*s*, *Me*–C_6H_3); 1.27 (*dd*, ^3J(P,H) = 15.5, ^3J(H,H) = 7.1, *Me*$_2$CHP). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.1 (*d*, ^2J(P,C) = 5.7, CO_2); 103.0 (*d*, ^2J(P,C) = 2.8, Me*C* of mes); 84.5 (*d*, ^2J(P,C) = 3.9, CH of mes); 52.1 (*s*, MeO); 29.1 (*d*, ^1J(P,C) = 21.1, Me_2CHP); 27.3 (*d*, ^1J(P,C) = 20.1, PCH_2); 18.8 (*s*, *Me*$_2$CHP); 18.1 (*s*, *Me*–C_6H_3). ^{31}P-NMR (81.0 MHz, $CDCl_3$): 31.5 (*s*). Anal. calc. for $C_{18}H_{29}Cl_2O_4PRu$ (512.4): C 42.20, H 5.71; found: C 41.91, H 5.59.

*[RuCl$_2$(*mes*){κ-P-^{t}*BuP*(*CH$_2$CO$_2$Me)$_2$*}]* (**7**). As described for **3**, from **2** (1.0 g, 1.71 mmol) and ^{t}BuP($CH_2CO_2Me)_2$ (1.0 g, 4.28 mmol): 1.66 g (92%) of **7**. Red-brown solid. M.p. 140°. IR (CH_2Cl_2): 1730 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 5.11 (*s*, C_6H_3); 3.64 (*s*, 2 MeO); 3.45 (*AB* of *ABX*; $\delta(H_A)$ 3.51, $\delta(H_B)$ 3.38,

$^2J(P,H_A) = 10.6$, $^2J(P,H_B) = 8.3$, $^2J(H,H) = 14.2$, 2 PCH_2); 2.26 (*s*, 3 *Me*–C_6H_3); 1.34 (*d*, $^3J(P,H) = 14.3$, *t*-Bu); ^{13}C-NMR (50.3 MHz, $CDCl_3$): 169.9 (*d*, $^2J(P,C) = 5.5$, CO_2); 103.9 (*d*, $^2J(P,C) = 2.8$, Me*C* of mes); 83.9 (*d*, $^2J(P,C) = 4.6$, CH of mes); 52.0 (*s*, MeO); 35.7 (*d*, $^1J(P,C) = 20.3$, Me_3C); 28.7 (*d*, $^2J(P,C) = 3.7$, Me_3C), 26.8 (*d*, $^1J(P,C) = 15.7$, PCH_2); 19.0 (*s*, *Me*–C_6H_3). ^{31}P-NMR (81.0 MHz, $CDCl_3$): 39.0 (*s*). Anal. calc. for $C_{19}H_{31}Cl_2O_4PRu$ (526.4): C 43.35, H 5.94; found: C 42.96, H 5.76.

[RuCl(mes){κ-P,O-^{i}*PrP(CH$_2$C(O)OMe)(CH$_2$CO$_2$Me)}]PF$_6$* (**10**). A soln. of **6** (120 mg, 0.23 mmol) in 20 ml of CH_2Cl_2 was treated with $AgPF_6$ (59 mg, 0.23 mmol) and stirred for 1 h at r.t. A change of color from red-brown to orange occurred. The mixture was filtered, and the filtrate was evaporated to dryness *in vacuo*. The remaining orange solid was washed twice with 5-ml portions of Et_2O and dried: 133 mg (91%) of **10**. M.p. 165° (dec.). Λ 72 $cm^2\Omega^{-1}mol^{-1}$. IR (KBr): 1713 ($(C{=}O)_{uncoord}$), 1610 ($(C{=}O)_{coord}$). ^{1}H-NMR (400 MHz, (D_6)acetone): 5.45 (*s*, C_6H_3); 4.05, 3.82 (2*s*, 2 MeO); 3.73 (*m*, PCH_2); 3.41 (*AB* of *ABX*; $\delta(H_A)$ 3.53, $\delta(H_B)$ 3.28, $^2J(P,H_A) = 11.4$, $^2J(P,H_B) = 9.1$, $^2J(H,H) = 17.4$, PCH_2); 2.84 (*m*, Me_2CH); 2.28 (*s*, 3 *Me*–C_6H_3); 1.38 (*dd*, $^3J(P,H) = 20.7$, $^3J(H,H) = 7.4$, 3 H, Me_2CH); 1.33 (*dd*, $^3J(P,H) = 14.4$, $^3J(H,H) = 7.1$, 3 H, Me_2CH). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 187.1 (*d*, $^2J(P,C) = 10.2$, CO_{2coord}), 170.5 (*s*, $CO_{2uncoord}$); 109.6 (*s*, Me*C* of mes); 79.8 (*d*, $^2J(P,C) = 4.7$, CH of mes); 57.1, 53.5 (2*s*, 2 MeO); 35.9 (*d*, $^1J(P,C) = 33.4$, PCH_2); 28.5 (*d*, $^1J(P,C) = 17.3$, PCH_2); 26.0 (*d*, $^1J(P,C) = 33.3$, Me_2CH); 19.6 (*s*, *Me*–C_6H_3); 18.5 (*d*, $^2J(P,C) = 4.8$, 1 C, Me_2CH); 17.3 (*d*, $^2J(P,C) = 7.4$, 1 C, Me_2CH). ^{31}P-NMR (81.0 MHz, CD_2Cl_2): 48.3 (*s*), –145.8 (*sept.*, $^1J(P,F) = 707.9$, PF_6^-). Anal. calc. for $C_{18}H_{29}ClF_6O_4P_2Ru$ (621.9): C 34.76, H 4.70; found: C 35.01, H 4.66.

[RuCl(mes){κ^2-P,O-^{t}*BuP(CH$_2$C(O)OMe)(CH$_2$CO$_2$Me)}]PF$_6$* (**11**). As described for **10**, from **7** (135 mg, 0.26 mmol) and $AgPF_6$ (65 mg, 0.26 mmol): 150 mg (92%) of **11**. Orange solid. M.p. 170° (dec.). Λ 75 $cm^2\Omega^{-1}mol^{-1}$. IR (CH_2Cl_2): 1721 ($(C{=}O)_{uncoord}$), 1613 ($(C{=}O)_{coord}$). ^{1}H-NMR (400 MHz, (D_6)acetone): 5.45 (*s*, C_6H_3); 4.04, 3.77 (2*s*, 2 MeO); 3.69, 3.39 (2*m*, 2 PCH_2); 2.29 (*s*, 3 *Me*–C_6H_3); 1.42 (*d*, $^3J(P,H) = 16.1$, *t*-Bu). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 186.8 (*d*, $^2J(P,C) = 8.8$, CO_{2coord}); 169.8 (*s*, $CO_{2uncoord}$); 110.0 (*s*, Me*C* of mes); 79.4 (*d*, $^2J(P,C) = 4.3$, CH of mes); 57.1, 53.3 (2*s*, 2 MeO); 35.6 (*d*, $^1J(P,C) = 23.9$, Me_3C); 33.9 (*d*, $^1J(P,C) = 28.7$, PCH_2); 31.4 (*d*, $^1J(P,C) = 14.3$, PCH_2); 28.3 (*d*, $^2J(P,C) = 2.9$, Me_3C); 19.7 (*s*, *Me*–C_6H_3). ^{31}P-NMR (81.0 MHz, CD_2Cl_2): 47.3 (*s*), –145.8 (*sept.*, $^1J(P,F) = 707.9$, PF_6^-). Anal. calc. for $C_{19}H_{31}ClF_6O_4P_2Ru$ (635.9): C 35.89, H 4.91, Ru 15.89; found: C 35.73, H 5.20, Ru 15.92.

*[Ru(*p*-cym){κ*^{3}-P,O,O-^{t}*BuP(CH$_2$C(O)OMe)$_2$]](PF$_6$)$_2$* (**12**). A soln. of **5** (313 mg, 0.58 mmol) in 20 ml of CH_2Cl_2 was treated with $AgPF_6$ (293 mg, 1.16 mmol) and stirred for 30 min at r.t. After a short time, an orange-yellow solid precipitated. The solvent was evaporated *in vacuo*, the residue was extracted with 20 ml of acetone, and the extract was brought to dryness *in vacuo*. An orange solid was isolated, which was washed twice with small quantities of THF and dried: 361 mg (82%) of **12**. M.p. 182° (dec.). Λ 111 $cm^2\Omega^{-1}mol^{-1}$. IR (CH_2Cl_2): 1622 (C=O). ^{1}H-NMR (400 MHz, (D_6)acetone): 6.79–6.61 (*m*, C_6H_4), 4.09 (*s*, 2 MeO); 4.12–3.76 (*m*, 2 PCH_2); 2.80 (*sept.*, $^3J(H,H) = 6.9$, Me_2CH); 2.19 (*s*, *Me*–C_6H_4); 1.72 (*d*, $^3J(P,H) = 18.4$, *t*-Bu); 1.31 (*d*, $^3J = 6.9$, Me_2CH). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 187.9 (*d*, $^2J(P,C) = 13.5$, CO_2); 106.3, 100.9 (2*s*, *ipso*-C of C_6H_4); 87.9 (*d*, $^2J(P,C) = 3.6$, C_6H_4); 87.6 (*d*, $^2J(P,C) = 2.8$, C_6H_4); 58.4 (*s*, MeO); 33.4 (*d*, $^1J(P,C) = 29.9$, PCH_2); 32.7 (*d*, $^1J(P,C) = 31.2$, Me_3C); 32.0 (*s*, Me_2CH); 26.6 (*d*, $^2J(P,C) = 3.4$, Me_3C); 22.4 (*s*, Me_2CH); 18.5 (*s*, *Me*–C_6H_4).^{31}P-NMR (81.0 MHz, (D_6)acetone): 65.8 (*s*), –139.1 (*sept.*, $^1J(P,F) = 707.0$, PF_6^-). Anal. calc. for $C_{20}H_{33}F_{12}O_4P_3Ru$ (759.5): C 31.63, H 4.38; found: C 31.70, H 4.11.

[Ru(mes){κ^3-P,O,O-^{i}*PrP(CH$_2$C(O)OMe)$_2$]](PF$_6$)$_2$* (**13**). As described for **12**, from **6** (243 mg, 0.47 mmol) and $AgPF_6$ (240 mg, 0.95 mmol): 271 mg (78%) of **13**. Orange solid. M.p. 157° (dec.). Λ 108 $cm^2\Omega^{-1}mol^{-1}$. IR (CH_2Cl_2): 1609 (C=O). ^{1}H-NMR (400 MHz, CD_3NO_2): 5.76 (*s*, C_6H_3); 4.09 (*s*, 2 MeO); 3.61 (*AB* of *ABX*; $\delta(H_A)$ 3.69, $\delta(H_B)$ 3.52, $^2J(P,H_A) = 8.6$, $^2J(P,H_B) = 12.7$, $^2J(H,H) = 19.0$, 2 PCH_2); 3.21 (*dsept.*, $^2J(P,H) = 3.2$, $^3J(H,H) = 7.0$, Me_2CH); 2.35 (*s*, 3 *Me*–C_6H_3); 1.55 (*dd*, $^3J(P,H) = 19.2$, $^3J(H,H) = 7.0$, Me_2CH). ^{31}P-NMR (81.0 MHz, CD_3NO_2): 50.1 (*s*), –142.9 (*sept.*, $^1J(P,F) = 707.2$, PF_6^-). Anal. calc. for $C_{18}H_{29}F_{12}O_4P_3Ru$ (731.4): C 29.56, H 4.00; found: C 29.69, H 4.25.

[Ru(mes){κ^3-P,O,O-^{t}*BuP(CH$_2$C(O)OMe)$_2$]](PF$_6$)$_2$* (**14**). As described for **12**, from **7** (250 mg, 0.47 mmol) and $AgPF_6$ (240 mg, 0.95 mmol). 283 mg (80%) of **14**. Orange solid. M.p. 167° (dec.). Λ 116 $cm^2\Omega^{-1}mol^{-1}$. IR (CH_2Cl_2): 1621 (C=O). ^{1}H-NMR (200 MHz, CD_2Cl_2): 5.66 (*s*, C_6H_3); 4.06 (*s*, 2 MeO); 3.88 (*AB* of *ABX*; $\delta(H_A)$ 3.66, $\delta(H_B)$ 3.11, $^2J(P,H_A) = 7.7$, $^2J(P,H_B) = 12.0$, $^2J(H,H) = 18.3$, 2 PCH_2); 2.35 (*s*, 3 *Me*–C_6H_3); 1.54 (*d*, $^3J(P,H) = 18.0$, *t*-Bu). ^{13}C-NMR (100.6 MHz, CD_3NO_2): 187.7 (*d*, $^2J(P,C) = 13.2$, CO_2); 111.6 (*d*, $^2J(P,C) = 0.9$, Me*C* of mes); 80.1 (*d*, $^2J(P,C) = 3.3$, CH of mes); 59.0 (*s*, MeO); 34.1 (*d*, $^1J(P,C) = 27.8$, PCH_2); 32.7 (*d*, $^1J(P,C) = 28.4$, Me_3C); 26.9 (*d*, $^2J(P,C) = 4.0$, Me_3C); 20.4 (*s*, *Me*–C_6H_3). ^{31}P-NMR (81.0 MHz, CD_3NO_2): 54.6 (*s*); –141.2 (*sept.*, $^1J(P,F) = 707.0$, PF_6^-). Anal. calc. for $C_{19}H_{31}F_{12}O_4P_3Ru$ (745.4): C 30.61, H 4.19; found: C 30.49, H 4.06.

*[Ru(*p-*cym){κ²*-P,O-*ᵗBuP(CH₂C(O)OMe)(CH₂CO₂Me)}(κ*-O-*O₂PF₂)]PF₆* (**15**). A soln. of **12** (107 mg, 0.20 mmol) in 20 ml of CH_2Cl_2 was treated with $AgPF_6$ (100 mg, 0.40 mmol) at r.t. In a few s, an orange-yellow solid precipitated. After the mixture had been stirred for 12 h in the absence of light, the solvent was evaporated *in vacuo*. The residue was extracted with 20 ml of acetone, the extract was brought to dryness *in vacuo*, and the remaining oily residue recrystallized from CH_2Cl_2/OEt_2 1:5. Orange-red crystals were obtained, which were washed with Et_2O and dried: 126 mg (89%) of **15**. M.p. 187° (dec.). Λ 81 $cm^2\Omega^{-1}mol^{-1}$. IR (CH_2Cl_2): 1720 ($(C{=}O)_{uncoord}$), 1611 ($(C{=}O)_{coord}$), 1292 (P=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 6.48, 5.98, 5.72 (3*m*, C_6H_4); 4.02 (*s*, MeO); 3.75–3.53 (*m*, PCH_2); 3.70 (*s*, MeO); 2.94 (*AB* of *ABX*; $\delta(H_A)$ 3.14, $\delta(H_B)$ 2.73, $^2J(P,H_A) = 13.0$, $^2J(P,H_B) = 7.3$, $^2J(H,H) = 17.2$, 2 PCH_2); 2.50 (*sept.*, $^3J(H,H) = 6.8$, Me_2CH); 2.00 (*s*, *Me*–C_6H_4), 1.31 (*d*, $^3J(P,H) = 16.5$, *t*-Bu); 1.30 (*d*, $^3J(H,H) = 7.3$, 3 H, Me_2CH); 1.24 (*d*, $^3J(H,H) = 6.8$, 3 H, Me_2CH). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 186.9 (*d*, $^2J(P,C) = 10.7$, CO_{2coord}); 168.6 (*d*, $^2J(P,C) = 1.7$, $CO_{2uncoord}$); 103.1, 96.0 (2*s*, *ipso*-C of C_6H_4); 87.7 (*d*, $^2J(P,C) = 5.7$, C_6H_4); 87.3, 85.5 (2*s*, C_6H_4); 84.3 (*d*, $^2J(P,C) = 4.1$, C_6H_4); 57.2, 53.1 (2*s*, 2 MeO); 34.3 (*d*, $^1J(P,C) = 23.8$, Me_3C); 31.4 (*s*, Me_2CH); 30.1 (*m*, PCH_2); 26.8 (*d*, $^2J(P,C) = 3.6$, Me_3C); 22.5, 21.7 (2*s*, Me_2CH); 18.0 (*s*, *Me*–C_6H_4). ^{31}P-NMR (81.0 MHz, (D_6)acetone): 65.1 (*s*), −13.0 (*m*, O_2PF_2), −139.1 (*sept.*, $^1J(P,F) = 707.7$, PF_6^-). Anal. calc. for $C_{20}H_{33}F_8O_6P_3Ru$ (715.5): C 33.58, H 4.65; found: C 33.70, H 4.82.

[Ru(mes){κ²-P,O-*ⁱPrP(CH₂C(O)OMe)(CH₂CO₂Me)}(κ*-O-*O₂PF₂)]PF₆* (**16**). As described for **15**, from **13** (97 mg, 0.19 mmol) and $AgPF_6$ (96 mg, 0.38 mmol): 117 mg (90%) of **16**. Orange-brown solid. M.p. 168° (dec.). Λ 84 $cm^2\Omega^{-1}mol^{-1}$. IR (CH_2Cl_2): 1721 ($(C{=}O)_{uncoord}$), 1609 ($(C{=}O)_{coord}$), 1298 (P=O). ^{1}H-NMR (400 MHz, (D_6)acetone): 5.65 (*s*, C_6H_3); 4.14, 3.81 (2*s*, 2 MeO); 3.89 (*m*, PCH_2); 3.42 (*AB* of *ABX*; $\delta(H_A)$ 3.63, $\delta(H_B)$ 3.21, $^2J(P,H_A) = 12.2$, $^2J(P,H_B) = 8.3$, $^2J(H,H) = 17.9$, PCH_2); 2.56 (*m*, Me_2CH); 2.32 (*s*, 3 *Me*–C_6H_3); 1.50 (*dd*, $^3J(P,H) = 19.7$, $^3J(H,H) = 7.3$, 3 H, Me_2CH); 1.39 (*dd*, $^3J(P,H) = 15.7$, $^3J(H,H) = 7.1$, 3 H, Me_2CH): ^{13}C-NMR (100.6 MHz, (D_6)acetone): 188.9 (*d*, $^2J(P,C) = 11.7$, CO_{2coord}); 170.0 (*s*, $CO_{2uncoord}$); 109.5 (*s*, Me*C* of mes); 78.3 (*s*, CH of mes), 57.8, 53.6 (2*s*, 2 MeO); 32.0 (*d*, $^1J(P,C) = 27.7$, PCH_2); 29.2 (*d*, $^1J(P,C) = 17.2$, PCH_2); 19.4 (*s*, *Me*–C_6H_3); 18.6 (*d*, $^2J(P,C) = 2.8$, Me_2CH); 17.6 (*d*, $^2J(P,C) = 4.8$, 1 C, Me_2CH). ^{19}F-NMR (188.3 MHz, CD_3NO_2): −72.6 (*d*, $^1J(P,F) = 707.7$, PF_6^-); −80.1 (*AB* of *ABX*; $\delta(F_A)$ −78.7, $\delta(F_B)$ −81.5, $^1J(P,F_A) = 957.6$, $^1J(P,F_B) = 970.7$, $^2J(F,F) = 107.4$, O_2PF_2). ^{31}P-NMR (81.0 MHz, (D_6)acetone): 50.0 (*d*, $^3J(P,P) = 4.4$, ^{i}PrP), −12.7 (*ddd*, $^1J(P,F_A) = 957.6$, $^1J(P,F_B) = 970.7$, $^3J(P,P) = 4.4$, O_2PF_2), −142.7 (*sept.*, $^1J(P,F) = 707.7$, PF_6^-). Anal. calc. for $C_{18}H_{29}F_8O_6P_3Ru$ (687.4): C 31.45, H 4.25; found: C 31.37, H 4.27.

[Ru(mes){κ²-P,O-*ᵗBuP(CH₂C(O)OMe)(CH₂CO₂Me)}(κ*-O-*O₂PF₂)]PF₆* (**17**). As described for **15**, from **14** (100 mg, 0.19 mmol) and $AgPF_6$ (96 mg, 0.38 mmol): 121 mg (91%) of **17**. Orange-brown solid. M.p. 166° (dec.). Λ 82 $cm^2\Omega^{-1}mol^{-1}$. IR (CH_2Cl_2): 1722 ($(C{=}O)_{uncoord}$), 1609 ($(C{=}O)_{coord}$), 1302 (P=O). ^{1}H-NMR (400 MHz, (D_6)acetone): 5.67 (*s*, C_6H_3); 4.11, 3.75 (2*s*, 2 MeO); 3.93 (*m*, PCH_2); 3.46 (*AB* of *ABX*; $\delta(H_A)$ 3.61, $\delta(H_B)$ 3.30, $^2J(P,H_A) = 12.4$, $^2J(P,H_B) = 7.1$, $^2J(H,H) = 17.9$, PCH_2); 2.30 (*s*, 3 *Me*–C_6H_3); 1.41 (*d*, $^3J(P,H) = 16.3$, *t*-Bu). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 188.8 (*d*, $^2J(P,C) = 10.4$, CO_{2coord}); 169.6 (*s*, $CO_{2uncoord}$); 110.1 (*d*, $^2J(P,C) = 7.6$, Me*C* of mes); 77.7 (*d*, $^2J(P,C) = 3.8$, CH of mes); 57.8, 53.6 (2*s*, 2 MeO); 34.7 (*d*, $^1J(P,C) = 23.6$, Me_3C); 32.3 (*d*, $^1J(P,C) = 27.5$, PCH_2); 29.5 (*d*, $^1J(P,C) = 19.1$, PCH_2); 27.0 (*d*, $^2J(P,C) = 3.6$, Me_3C); 19.6 (*s*, *Me*–C_6H_3). ^{19}F-NMR (188.3 MHz, CD_2Cl_2): −74.8 (*d*, $^1J(P,F) = 707.7$, PF_6^-), −82.0 (*AB* of *ABX*; $\delta(F_A)$ −80.3, $\delta(F_B)$ −83.8, $^1J(P,F_a) = 963.6$, $^1J(P,F_B) = 972.5$, $^2J(F,F) = 109.5$, O_2PF_2). ^{31}P-NMR (81.0 MHz, (D_6)acetone): 52.7 (*d*, $^3J(P,P) = 2.9$, ^{t}BuP); −13.1 (*ddd*, $^1J(P,F_A) = 963.6$, $^1J(P,F_B) = 972.5$, $^3J(P,P) = 2.9$, O_2PF_2); −142.7 (*sept.*, $^1J(P,F) = 707.7$, PF_6^-). Anal. calc. for $C_{19}H_{31}F_8O_6P_3Ru$ (701.4): C 32.53, H 4.45, Ru 14.41; found: C 32.85, H 4.46, Ru 14.77.

[Ru(mes){κ³-P,C,O-*ⁱPrP(CHCO₂Me)(CH=C(O)OMe)}]* (**18**). A suspension of **13** (220 mg, 0.30 mmol) in 20 ml of *t*-BuOH/toluene (1:1) was treated with KO^{t}Bu (68 mg, 0.60 mmol) and irradiated in an ultrasound bath for 15 min. The solvent was evaporated *in vacuo*, the residue was extracted with 15 ml of Et_2O, and the extract was brought to dryness *in vacuo*. To the oily residue 10 ml of hexane was added, and the mixture was stirred for 12 h at r.t. A yellow solid was obtained which was filtered, washed twice with small quantities of hexane, and dried: 79 mg (60%) of **18**. M.p. 93° (dec.). IR (C_6H_6): 1661 (C=O). ^{1}H-NMR (400 MHz, C_6D_6): 4.46 (*s*, C_6H_3); 3.51, 3.42 (2*s*, 2 MeO); 3.45 (*d*, $^2J(P,H) = 12.9$, $PCH_{enolate}$), 2.84 (*m*, Me_2CH); 1.95 (*s*, 3 *Me*–C_6H_3); 1.67 (*s*, $PCH_{methanide}$); 1.31 (*dd*, $^3J(P,H) = 21.2$, $^3J(H,H) = 7.2$, 3 H, Me_2CH); 1.28 (*dd*, $^3J(P,H) = 15.5$, $^3J(H,H) = 7.2$, 3 H, Me_2CH). ^{13}C-NMR (100.6 MHz, (D_8)toluene): 179.7 (*d*, $^2J(P,C) = 7.6$, CO_{2ester}); 179.1 (*d*, $^2J(P,C) = 25.2$, $CO_{2enolate}$); 99.8 (*s*, Me*C* of mes); 78.9 (*d*, $^2J(P,C) = 3.3$, CH of mes); 52.3 (*d*, $^4J(P,C) = 2.1$, MeO); 50.0 (*d*, $^4J(P,C) = 1.3$, MeO); 44.6 (*d*, $^1J(P,C) = 74.6$, $PCH_{enolate}$); 20.6 (*d*, $^2J(P,C) = 8.4$, 1 C, Me_2CH); 19.6 (*d*, $^1J(P,C) = 33.5$, Me_2CH); 19.5 (*s*, *Me*–C_6H_3); 18.0 (*d*, $^2J(P,C) = 5.1$, 1 C, Me_2CH); 4.9 (*d*, $^1J(P,C) = 9.8$, $PCH_{methanide}$). ^{31}P-NMR (81.0 MHz, C_6D_6): 50.5 (*s*). EI-MS: 440 (47, M^+), 397 (85, $[M - C_3H_7]^+$). Anal. calc. for $C_{18}H_{27}O_4PRu$ (439.5): C 49.20, H 6.19; found: C 49.23, H 6.09.

[Ru(mes){κ³-P,C,O-ᵗBuP(CHCO₂Me)(CH=C(O)OMe)}] (**19**). As described for **18**, from **14** (224 mg, 0.30 mmol) and KO^{t}Bu (68 mg, 0.60 mmol): yield 89 mg (65%) of **19**. Yellow solid. M.p. 99° (dec.). IR (C_6H_6): 1687 ($(C=O)_{ester}$), 1646 ($(C=O)_{enolate}$). ^{1}H-NMR (400 MHz, C_6D_6): 4.32 (*s*, C_6H_3); 3.64, 3.55 (2*s*, 2 MeO); 3.54 (*d*, ^2J(P,H) = 11.2, $PCH_{enolate}$); 1.94 (*s*, 3 *Me*−C_6H_3); 1.69 (*d*, ^2J(P,H) = 15.3, $PCH_{methanide}$); 1.10 (*d*, ^3J(P,H) = 16.3, *t*-Bu). ^{13}C-NMR (100.6 MHz, (D_6)acetone): 179.6 (*d*, ^2J(P,C) = 24.1, $CO_{2enolate}$); 179.5 (*d*, ^2J(P,C) = 4.8, CO_{2ester}); 101.6 (*d*, ^2J(P,C) = 1.8, Me*C* of mes); 77.5 (*d*, ^2J(P,C) = 2.7, CH of mes); 52.7 (*d*, ^4J(P,C) = 2.0, MeO); 49.8 (*s*, MeO); 44.0 (*d*, ^1J(P,C) = 72.8, $PCH_{enolate}$); 28.9 (*d*, ^1J(P,C) = 35.0, Me_3C); 27.3 (*d*, ^2J(P,C) = 3.6, Me_3C); 20.2 (*s*, *Me*−C_6H_3); −8.7 (*d*, ^1J(P,C) = 3.3, $PCH_{methanide}$). ^{31}P-NMR (81.0 MHz, C_6D_6): 62.5 (*s*). EI-MS: 454 (16, M^+), 397 (100, $[M-C_4H_9]^+$). Anal. calc. for $C_{19}H_{29}O_4PRu$ (453.5): C 50.32, H 6.45; found: C 49.99, H 6.37.

Reactions of Compounds **18** *and* **19** *with HCl.* A slow stream of gaseous HCl was passed through a soln. of **18** or **19** (0.09 mmol) in 10 ml of toluene for 20 s at r.t. A quick change of color from yellow to brown occurred. After stirring the soln. for 10 min, the solvent was evaporated *in vacuo*. The ^{1}H-NMR spectrum of the residue confirmed that compounds **6** or **7** were obtained in quantitative yields.

*[Ru(*p*-cym){κ³-P,O,O-ⁱPrP(CH₂C(O)O)₂]]* (**20**). A suspension of **4** (190 mg, 0.36 mmol) in 20 ml of *t*-BuOH/toluene 1:1 was treated with KO^{t}Bu (81 mg, 0.72 mmol) and stirred for 1 h at r.t. The solvent was evaporated *in vacuo*, the residue was dissolved in 2 ml of MeOH, and the soln. was chromatographed on Al_2O_3 (basic, activity grade III, height of column 5 cm). With MeOH, an orange fraction was eluted, which was brought to dryness *in vacuo*. The remaining orange-yellow solid was washed three times with 5-ml portions of Et_2O and dried: 54 mg (35%) of **20**. M.p. 86° (dec.). IR (CH_2Cl_2): 1637 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 5.72 (*m*, C_6H_4), 2.66 (*AB* of *ABX*; $\delta(H_A)$ 2.78, $\delta(H_B)$ 2.54, ^2J(P,H_A) = 7.0, ^2J(P,H_B) = 8.7, ^2J(H,H) = 17.2, 2 PCH_2); 2.66 (*m*, Me_2CH); 1.97 (*s*, *Me*−C_6H_4); 1.34 (*dd*, ^3J(P,H) = 17.3, ^3J(H,H) = 7.0, Me_2CHP); 1.12 (*d*, ^3J(H,H) = 6.8, Me_2CH); signal of 1 Me_2 not exactly located. ^{13}C-NMR (100.6 MHz, $CDCl_3$): 177.2 (*d*, ^2J(P,C) = 11.4, CO_2), 102.2, 97.4 (2*s*, *ipso*-C of C_6H_4); 86.3 (*d*, ^2J(P,C) = 4.1, C_6H_4), 86.1 (*d*, ^2J(P,C) = 3.4, C_6H_4); 30.7 (*s*, Me_2CH); 30.2 (*d*, ^1J(P,C) = 29.8, PCH_2); 25.0 (*d*, ^1J(P,C) = 31.0, Me_2CHP); 22.4 (*s*, Me_2CH); 18.0 (*d*, ^2J(P,C) = 1.5, Me_2CHP); 17.9 (*s*, *Me*−C_6H_4). ^{31}P-NMR (81.0 MHz, $CDCl_3$): 38.2 (*s*). Anal. calc. for $C_{17}H_{25}O_4PRu$ (425.4): C 48.00, H 5.92; found: C 47.67, H 6.16.

*[Ru(*p*-cym){κ³-P,O,O-ᵗBuP(CH₂C(O)O)₂]]* (**21**). As described for **20**, from **5** (220 mg, 0.41 mmol) and KO^{t}Bu (91 mg, 0.81 mmol): 29 mg (23%) of **21**. Orange-yellow solid. 119° (dec.). IR (CH_2Cl_2): 1647 (C=O). ^{1}H-NMR (200 MHz, $CDCl_3$): 5.78 (*m*, C_6H_4); 2.63 (*AB* of *ABX*, $\delta(H_A)$ 2.78, $\delta(H_B)$ 2.49, ^2J(P,H_A) = 7.9, ^2J(P,H_B) = 12.1, ^2J(H,H) = 17.2, 2 PCH_2); 2.57 (*sept.*, ^3J(H,H) = 6.9, Me_2CH); 1.98 (*s*, *Me*−C_6H_4); 1.38 (*d*, ^3J(P,H) = 16.1, *t*-Bu); 1.14 (*d*, ^3J(H,H) = 6.9, Me_2CH). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 177.1 (*d*, ^2J(P,C) = 11.2, CO_2); 102.7, 95.4 (2*s*, *ipso*-C of C_6H_4); 87.4, 85.7 (2*d*, ^2J(P,C) = 4.0, C_6H_4); 30.7 (*s*, Me_2CH); 30.1 (*d*, ^1J(P,C) = 29.5, Me_3C); 30.0 (*d*, ^1J(P,C) = 28.1, PCH_2); 26.5 (*d*, ^2J(P,C) = 3.0, Me_3C); 22.3 (*s*, Me_2CH); 17.9 (*s*, *Me*−C_6H_4). ^{31}P-NMR (81.0 MHz, $CDCl_3$): 46.2 (*s*). Anal. calc. for $C_{18}H_{27}O_4PRu$ (439.5): C 49.20, H 6.19; found: C 49.45, H 5.78.

[Ru(mes){κ³-P,O,O-ⁱPrP(CH₂C(O)O)₂]] (**22**). A soln. of **18** (61 mg, 0.14 mmol) in 5 ml of acetone was treated with H_2O (*ca.* 100 µl) and stirred for 12 h at r.t. The workup procedure was the same as described for **20**: 47 mg (83%) of **22**. Yellow solid. M.p. 101° (dec.). IR (CH_2Cl_2): 1647 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 5.10 (*s*, C_6H_3); 2.69 (*AB* of *ABX*; $\delta(H_A)$ 2.79, $\delta(H_B)$ 2.58, ^2J(P,H_A) = 8.1, ^2J(P,H_B) = 12.4, ^2J(H,H) = 17.1, 2 PCH_2); 2.16 (*s*, 3 *Me*−C_6H_3); 1.33 (*dd*, ^3J(P,H) = 16.6, ^3J(H,H) = 7.1, Me_2CH); signal of Me_2CH not exactly located. ^{13}C-NMR (100.6 MHz, CD_3NO_2): 178.8 (*d*, ^2J(P,C) = 10.9, CO_2); 106.8 (*s*, Me*C* of mes); 81.2 (*d*, ^2J(P,C) = 3.9, CH of mes); 31.8 (*d*, ^1J(P,C) = 29.3, PCH_2); 23.3 (*d*, ^1J(P,C) = 29.7, Me_2CH); 19.2 (*s*, *Me*−C_6H_3); 18.1 (*d*, ^2J(P,C) = 2.7, Me_2CH). ^{31}P-NMR (81.0 MHz, $CDCl_3$): 36.2 (*s*). Anal. calc. for $C_{16}H_{23}O_4PRu$ (411.4): C 46.71, H 5.64; found: C 46.91, H 5.53.

[Ru(mes){κ³-P,O,O-ᵗBuP(CH₂C(O)O)₂]] (**23**). As described for **22**, from **19** (54 mg, 0.12 mmol) and H_2O (*ca.* 100 µl). 41 mg (81%) of **23**. Yellow solid. M.p. 155° (dec.). IR (CH_2Cl_2): 1647 (C=O). ^{1}H-NMR (400 MHz, $CDCl_3$): 5.27 (*s*, C_6H_3); 2.65 (*AB* of *ABX*; $\delta(H_A)$ 2.79, $\delta(H_B)$ 2.50, ^2J(P,H_A) = 7.3, ^2J(P,H_B) = 12.3, ^2J(H,H) = 17.0, 2 PCH_2); 2.20 (*s*, 3 *Me*−C_6H_3); 1.36 (*d*, ^3J(P,H) = 15.7, *t*-Bu). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 177.4 (*d*, ^2J(P,C) = 10.5, CO_2); 101.8 (*d*, ^2J(P,C) = 1.7, Me*C* of mes); 83.2 (*d*, ^2J(P,C) = 2.3, CH of mes); 31.0 (*d*, ^1J(P,C) = 27.3, PCH_2); 29.7 (*d*, ^1J(P,C) = 26.9, Me_3C); 26.5 (*d*, ^2J(P,C) = 3.9, Me_3C); 19.4 (*s*, *Me*−C_6H_3). ^{31}P-NMR (81.0 MHz, $CDCl_3$): 42.2 (*s*). Anal. calc. for $C_{17}H_{25}O_4PRu$ (425.4): C 48.00, H 5.92; found: C 47.84, H 6.15.

[Ru(mes){κ³-P,C,O-ᵗBuP(CHCO₂Me)(C(C(O)NHPh)=C(O)OMe)}] (**24**). A soln. of **19** (63 mg, 0.14 mmol) in 10 ml of toluene was treated with PhNCO (33 mg, 0.28 mmol) and stirred for 2 h at r.t. The solvent was evaporated *in vacuo*, the remaining yellow solid was washed three times with small quantities of hexane, and dried: 56 mg (70%) of **24**. M.p. 124° (dec.). IR (C_6H_6): 3380 (NH), 1679 ($(C=O)_{ester}$), 1628 ($(C=O)_{enolate}$). ^{1}H-NMR (400 MHz, $CDCl_3$): 9.10 (*s*, NH); 7.87–6.84 (*m*, C_6H_5), 4.35 (*s*, C_6H_3); 3.43, 3.39 (2*s*,

2 MeO); 1.84 (*s*, 3 *Me*–C_6H_3); 1.76 (*d*, ^2J(P,H) = 14.8, $PCH_{methanide}$); 1.58 (*d*, ^3J(P,H) = 18.1, *t*-Bu). ^{13}C-NMR (100.6 MHz, C_6D_6): 176.2 (*d*, ^2J(P,C) = 28.0, $CO_{2enolate}$); 173.9 (*s*, C(O)R); 141.3, 128.9, 122.1, 119.6 (4*s*, C_6H_5); 100.7 (*s*, MeC of mes); 78.7 (*d*, ^2J(P,C) = 1.7, CH of mes); 69.3 (*d*, ^1J(P,C) = 67.0, $PCH_{enolate}$); 52.3, 50.4 (2*s*, 2 MeO); 33.0 (*d*, ^1J(P,C) = 30.4, Me_3C); 29.5 (*d*, ^2J(P,C) = 4.8, Me_3C); 19.7 (*s*, *Me*–C_6H_3); −3.5 (*d*, ^1J(P,C) = 2.8, $PCH_{methanide}$). ^{31}P-NMR (81.0 MHz, (D_8)toluene): 56.7 (*s*). EI-MS: 573 (1, M^+), 516 (9, $[M - C_4H_9]^+$). Anal. calc. for $C_{26}H_{24}NO_5PRu$ (572.6): C 54.54, H 5.99, N 2.45; found: C 53.96, H 5.77, N 2.89.

[Ru(mes){κ³-P,S,S-tBuP(C(C(=NHPh)S)₂CO₂Me)(CH₂CO₂Me)}] (**25**). A soln. of **19** (72 mg, 0.16 mmol) in 10 ml of toluene was treated with PhNCS (200 µl, 1.67 mmol) and stirred for 6 h at r.t. The solvent was evaporated *in vacuo*, the remaining brown solid was washed three times with small quantities of hexane, and dried: 87 mg (76%) of **25**. M.p. 93° (dec.). IR (C_6H_6): 1726 (C=O), 1577 (C=N). ^{1}H-NMR (400 MHz, $CDCl_3$): 7.27–6.85 (*m*, 2 Ph); 5.02 (*s*, C_6H_3); 3.95 (*m*, 1 H, PCH_2); 3.81, 3.58 (2*s*, 2 MeO); 2.98 (*dd*, ^2J(P,H) = 8.6, ^2J(H,H) = 13.1, 1 H, PCH_2); 2.11 (*s*, 3 *Me*–C_6H_3); 1.42 (*d*, ^3J(P,H) = 14.3, *t*-Bu). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.9 (*d*, ^2J(P,C) = 9.9, CO_2); 169.9 (*s*, C(=NPh)S); 169.0 (*d*, ^2J(P,C) = 16.7, C(=NPh)S); 167.2 (*d*, ^2J(P,C) = 3.7, CO_2); 153.0, 151.9, 128.4, 128.1, 122.6, 122.3, 121.2, 120.3 (8*s*, Ph); 108.0 (*d*, ^2J(P,C) = 1.7, Me*C* of mes), 87.2 (*d*, ^2J(P,C) = 3.9, CH of mes); 81.6 (*d*, ^1J(P,C) = 34.7, *C*CO_2Me); 52.5, 52.0 (2*s*, 2 MeO); 37.7 (*d*, ^1J(P,C) = 15.0, Me_3C); 30.8 (*d*, ^1J(P,C) = 11.5, PCH_2); 28.9 (*d*, ^2J(P,C) = 3.1, Me_3C); 19.0 (*s*, *Me*–C_6H_3). ^{31}P-NMR (162.0 MHz, $CDCl_3$): 87.6 (*s*). Anal. calc. for $C_{33}H_{39}N_2O_4PS_2Ru$ (723.9): C 54.76, H 5.43, N 3.87, S 8.86; found: C 54.92, H 5.40, N 3.84, S 9.17.

X-Ray Structure Determination of Compounds **17** *and* **18**. Single crystals of **17** were grown from a sat. soln. in toluene at r.t., and those of **18** by diffusion of Et_2O into a sat. soln. in CH_2Cl_2 at r.t. Crystal-data collection

Table 1. *Crystal-Structure Data of Compounds* **17** *and* **18**

	17	**18**
Formula	$C_{19}H_{31}F_8O_6P_3Ru$	$C_{18}H_{27}O_4PRu$
Mol. mass	701.42	439.44
Crystal size [mm]	0.60 × 0.33 × 0.23	0.30 × 0.20 × 0.15
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a [Å]	17.001(5)	7.913(8)
b [Å]	10.6463(14)	10.195(11)
c [Å]	17.221(5)	13.475(18)
α [°]	90.0	99.47(7)
β [°]	117.693(12)	103.91(7)
γ [°]	90.0	111.92(5)
V [Å^3]	2760.0(12)	1706.3(4)
Z	4	2
d_{calcd} [g cm^{-1}]	1.688	1.554
Diffractometer	*Enraf-Nonius CAD4*	*Enraf-Nonius CAD 4*
Radiation (graphite-monochromated)	MoK_α (0.71073 Å)	MoK_α (0.71073 Å)
T [K]	293(2)	293(2)
μ [mm^{-1}]	0.820	0.925
transmission min. [%]	97.00	no absorption correction
Scan method	ω/θ	ω
$2\theta_{(max)}$ [°]	51.82	53.08
Total reflections	5592	3456
Unique reflections	5399	3181
Observed reflections	4188	2784
	$[I > 2\sigma(I)]$	$[I > 2\sigma(I)]$
Parameters refined	360	224
R_1	0.0418	0.0283
wR_2	0.1129	0.0764
GOF	1.086	1.108
Reflection/parameter ratio	15.0	14.2
Residual electron density [eÅ^{-3}]	+0.473/−0.551	+0.487/−0.573

parameters are summarized in the *Table*. Intensity data were corrected for *Lorentz* and polarization effects, and an empirical absorption correction was applied for **17** (ψ-scans). The structures were solved by direct methods (SHELXS-97) [25]. Atomic coordinates and anisotropic thermal parameters of the non-H-atoms were refined by the full-matrix least-squares method (SHELXL-97) [26]. The positions of all H-atoms were calculated according to ideal geometry (distance C–H = 0.95 Å) and used only in structure-factor calculation. Crystallographic data (excluding structure factors) for **17** have been deposited with the *Cambridge Crystallographic Data Centre* (*CCDC*) as deposition No. CCDC-166427. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk). Ref. code for **18** ZIQBAC, Cambridge Structural Database System, 2001.

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