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Areneruthenium(II) complexes containing bulky phosphines with various functionalities as ligands †

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The dimeric starting materials $[Ru(\eta^6\text{-arene})Cl_2]_2$ (arene = mes, C_6Me_6) react with the functionalized phosphines $Pr^i_2PCH_2X$ (X = CH_2OMe, CO_2Me) to give the mononuclear compounds $[Ru(\eta^6\text{-arene})(\kappa P\text{-}Pr^i_2PCH_2X)Cl_2]$ **3**–**6** which upon treatment with $AgPF_6$ afford the chelate complexes $[Ru(\eta^6\text{-arene})(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)Cl]PF_6$ **7**, **8** and $[Ru(\eta^6\text{-arene})\{\kappa^2P,O\text{-}Pr^i_2PCH_2C(O)OMe\}Cl]PF_6$ **9**, **10**, respectively. Complexes **7** and **8** react with CO and $CNBu^t$ to yield the chiral-at-metal compounds $[Ru(\eta^6\text{-arene})(\kappa P\text{-}Pr^i_2PCH_2CH_2OMe)(L)Cl]PF_6$ **11**–**14**. Treatment of **8** (arene = C_6Me_6) with Na_2CO_3 in the presence of water produces the carbonatoruthenium(II) derivative $[Ru(\eta^6\text{-}C_6Me_6)(\kappa^2O,O\text{-}O_2C{=}O)(\kappa P\text{-}Pr^i_2PCH_2CH_2OMe)]$ **17**. The reaction of **9** (arene = mes) with $KOBu^t$ leads to the formation of the uncharged phosphinoester enolate complex $[Ru(\eta^6\text{-mes})(\kappa^2P,O\text{-}Pr^i_2PCH{=}C(O)OMe)Cl]$ **18** which in benzene at room temperature smoothly rearranges to the phosphinomethanide isomer $[Ru(\eta^6\text{-mes})(\kappa^2P,C\text{-}Pr^i_2PCHCO_2Me)Cl]$ **19**. The corresponding phosphinoacetate complexes $[Ru(\eta^6\text{-arene})\{\kappa^2P,O\text{-}Pr^i_2PCH_2C(=O)O\}Cl]$ **21**, **22** were obtained as the major products from **5** or **6** and NaH/Al_2O_3 in THF. Compound **18** reacts with water by ester hydrolysis to form **21** and with phenylisocyanate and diphenylketene to afford **24** and **25** by insertion of the heterocumulene into the enolate C–H bond. The molecular structures of **19** and **25** were determined crystallographically.

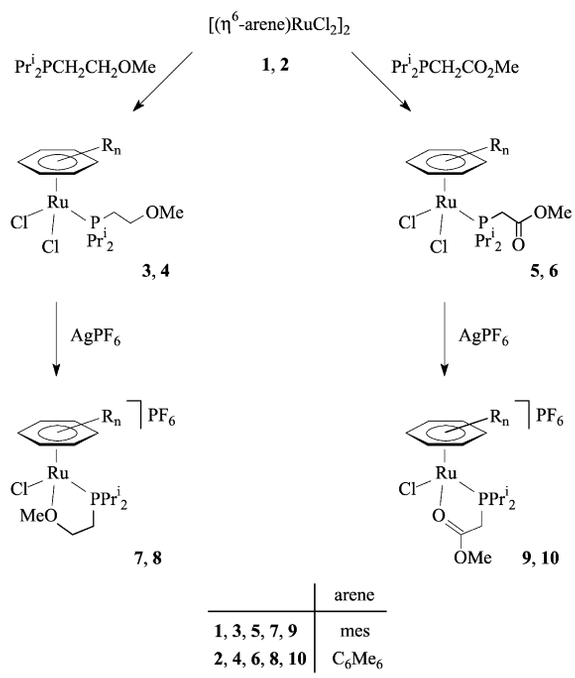
Recently, we have been interested in the synthesis and reactivity of transition-metal complexes containing phosphino-ethers, -amines and -esters as ligands.[1] The characteristic feature of these ligands is that they behave as hemilabile chelating units and even under mild conditions are able to create a free coordination site to which a reactive substrate can be added.[2] Moreover, phosphino-esters and -ketones are easily converted in the coordination sphere of a transition-metal to phosphino-enolates, the metal complexes of which play an important role in homogeneous catalysis.[3]

As a continuation of our work on half-sandwich-type compounds with functionalized phosphines,[4] we describe in this paper the preparation of a series of neutral and cationic η^6-mesitylene- and η^6-hexamethylbenzeneruthenium(II) complexes with $Pr^i_2PCH_2CH_2OMe$ and $Pr^i_2PCH_2CO_2Me$ as ligands. We also illustrate that the coordinated phosphinoester is not only easily deprotonated but that, quite unexpectedly, from the isomeric forms $Pr^i_2PCH{=}C(OR)O^-$ and $Pr^i_2PCHCO_2R^-$ the second one, forming a three-membered chelate ring with the metal, is the more stable. Some preliminary results of this work have already been communicated.[5]

Results and discussion

Neutral and cationic complexes with $Pr^i_2PCH_2CH_2OMe$ and $Pr^i_2PCH_2CO_2Me$ as mono- and bi-dentate ligands

Similarly to PPr^i_3 and other tertiary phosphines, the chloro-bridged dimers **1** and **2** also react with $Pr^i_2PCH_2CH_2OMe$ and $Pr^i_2PCH_2CO_2Me$ by bridge-splitting to give the mononuclear products **3**, **4** and **5**, **6** in excellent yields (Scheme 1). These are orange to red solids which are practically air-stable and readily soluble in polar organic solvents such as CH_2Cl_2, THF or nitromethane. While the ^1H and ^{31}P NMR data of **3**–**6** deserve no further comment, we note that the single resonance in the ^{31}P NMR spectra is shifted *ca*. 30–40 ppm downfield compared with the free phosphines $Pr^i_2PCH_2CH_2OMe$ and $Pr^i_2PCH_2CO_2Me$, respectively.



	arene
1, **3**, **5**, **7**, **9**	mes
2, **4**, **6**, **8**, **10**	C_6Me_6

Scheme 1

Treatment of the dichloro compounds **3**–**6** with an equimolar amount of $AgPF_6$ in CH_2Cl_2 results in the abstraction of one chloride to give the cationic complexes **7**–**10** in 80–90% isolated yield. The composition of the slightly air-sensitive solids has been confirmed not only by elemental analysis but also by conductivity measurements. In contrast to **7**, in the ^1H NMR spectrum of **8** at room temperature the signals for the methine and methyl protons of the isopropyl groups and for the PCH_2CH_2 methylene protons are significantly broadened and neither a P,H nor a H,H coupling can be observed. However, at 248 K the ^1H NMR spectrum of **8** displays two septets for the PC*H* and four doublets-of-doublets for the $CHCH_3$ protons which is in agreement with the rigid structure shown in Scheme 1. By

† Dedicated with great sympathy to Professor Peter M. Maitlis on the occasion of his 70th birthday.

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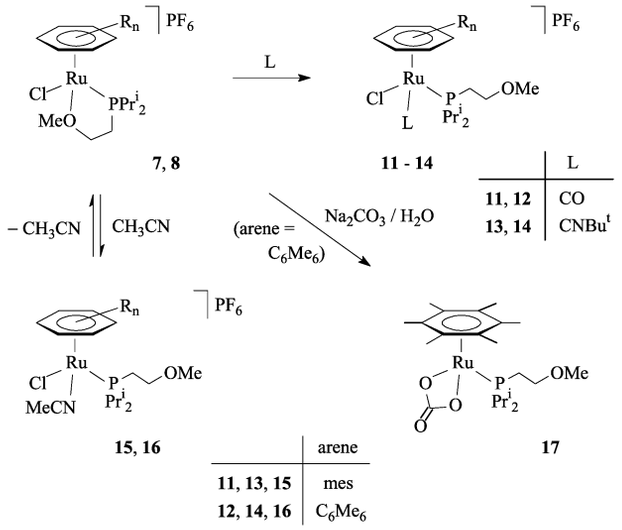
increasing the temperature to 350 K only one resonance for the PC*H* and two resonances for the CHCH_3 protons appear. The most reasonable explanation for the temperature dependence of the ^{1}H NMR spectrum of **8** is that the compound is fluxional in solution. At room temperature and above, a rapid opening and re-closing of the chelate ring occurs, thereby creating on average an effective mirror plane that makes the PC*H* and half of the CHCH_3 protons become equivalent. This behaviour is not unusual and has been observed in various cases in particular by Lindner,[2] Braunstein,[7] and also by us.[1]

The hemilabile nature of the phosphine ligand in compounds **7** and **8** is illustrated by the reactions summarized in Scheme 2.



Scheme 2

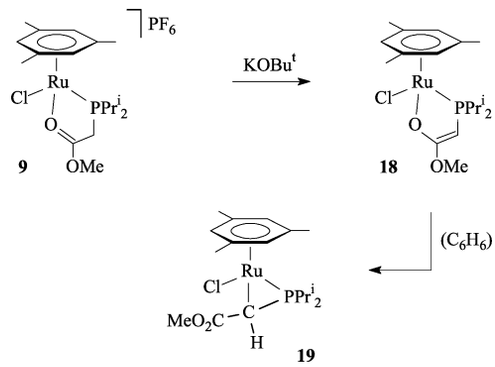
Treating solutions of the starting materials in acetone or dichloromethane with CO or CNBu^t leads to a smooth cleavage of the Ru–O bond and gives the 1 : 1 adducts **11**–**14** containing a monodentate phosphine as light yellow solids in 84–91% yield. Similarly to the related carbonylosmium complex [Os(η^6-mes)(κ*P*-Pr$^i_2$PCH$_2$CH$_2$OMe)(CO)Cl]PF$_6$,[6] both the ruthenium counterpart **11** and the hexamethylbenzene analogue **12** are relatively labile; they decompose in solution within 1–2 hours in the absence of a CO atmosphere. In contrast, the related isocyanide derivatives **13** and **14** are quite stable and can be stored under argon for weeks. We assume that the increase in the thermodynamic stability when CO is replaced by CNBu^t is attributed to the stronger donor ability of the isocyanide, which is also reflected in the shift of the phosphorus resonance by 10–20 ppm to higher field in the ^{31}P NMR spectra of **13**, **14** compared to those of **11** and **12**.

Compared with CO and *tert*-butylisocyanide, acetonitrile behaves differently toward **7** and **8**. If a solution of the corresponding chelate complex in CH_2Cl_2 is treated with excess CH_3CN, stirred for 5 min and the solvent is then removed rather quickly, the ^{1}H and ^{13}C NMR spectra confirm the presence of mixtures of **7** and **15** or of **8** and **16**, respectively. Attempts to separate the two components by column chromatography or re-crystallization from CH_2Cl_2/hexane led to the re-isolation of the starting material. Since a re-conversion of **15** to **7** and of **16** to **8** also occurs by storing the mixtures under argon, we conclude that the entropic contribution due to chelation and not the donor capability of N *versus* O is the dominating component. That in the reaction mixtures of **7**/**15** and **8**/**16** the acetonitrile compounds are present, is indicated both by the NMR and IR spectra, the latter displaying a strong ν(C≡N) band at 2260 (**15**) and 2264 cm^{-1} (**16**), respectively.

The reaction of **8** with Na_2CO_3, undertaken to find out whether a deprotonation of the PCH_2 unit or of one of the methyl groups of the six-membered ring is possible, affords instead the carbonatoruthenium(II) complex **17** (see Scheme 2). The light yellow air-stable solid was isolated in 67% yield. Since in contrast to the cationic precursor **8** the neutral molecule **17** is not chiral, the ^{1}H NMR spectrum shows only one signal for the PC*H* and two signals (doublets-of-doublets) for the CHCH_3 protons of the isopropyl groups.

Phosphinomethanide *versus* phosphinoenolate: thermodynamic preference of the three-membered chelate ring

Similarly to structurally related areneosmium complexes,[6] the cationic species **9** also reacts with KOBu^t in THF to give the phosphinoenolate compound **18** as a light red, slightly air-sensitive solid in 78% yield (Scheme 3). The composition of **18**



Scheme 3

was confirmed by elemental analysis and the mass spectrum. The most characteristic feature of the ^{1}H NMR spectrum of **18** is the signal at δ 3.19 for the vinylic proton which is split into a doublet due to P,H coupling. The ^{13}C NMR spectrum of **18** displays two resonances for the O–C–C–P carbon atoms of the chelate ring at δ 180.5 (O–C) and 44.5 (C–P), the chemical shift and the P,C coupling constant of which are similar to those of other phosphinoester enolate-metal derivatives.[6–8]

While most of the phosphinoenolate complexes, such as those used for the oligomerization and polymerization of alkenes,[3,9] seem to be quite stable, compound **18** is thermally labile and slowly (3 d) rearranges in benzene at room temperature to give the isomer **19**. The ^{1}H NMR spectrum of **19** (which is a yellow air-stable solid) shows a doublet at δ 2.71 for the C*H*CO$_2$Me proton and the ^{13}C NMR spectrum a singlet at δ 10.0 for the carbon atom of the RuCP ring.

The structural proposal for **19** outlined in Scheme 3 was confirmed by an X-ray crystal structure analysis. As the ORTEP drawing (Fig. 1) reveals, the ruthenium atom is coordinated by the mesitylene ring, one chloride and the P,C-bonded phosphinomethanide ligand, the CO_2Me substituent of which is pointing away from the Ru–Cl axis. As anticipated, the bond angle P–Ru–C(1) is significantly smaller than the bond angles P–Ru–Cl and Cl–Ru–C(1), the values being similar to those found in various M(κ^2*P*,*C*-R$_2$PCH$_2$) derivatives.[10] The distance P–C(1) is shorter, by *ca*. 0.08 Å, than the distances P–C(4) and P–C(7) (see Table 1) which indicates a substantial double-bond character of the phosphorus–carbon bond in the RuCP unit.

The phosphinomethanide- and not the isomeric phosphinoesterenolate-ruthenium(II) complex is also formed, although as the minor component, on treatment of **5** with NaH/Al_2O_3 in THF (Scheme 4). The hexamethylbenzene derivative **6** behaves analogously. In both cases, the main product of the reaction is the corresponding phosphinocarboxylate compound **21** or **22**, respectively. The IR and ^{1}H NMR data of **21** and **22** are similar to those of the half-sandwich-type complex [Ru(η^6-mes)-{κ^2*P*,*O*-Ph$_2$PCH$_2$C(=O)*O*}Cl] which was generated by acid hydrolysis of [Ru(η^6-mes)(κ*P*-Ph$_2$PCH$_2$CO$_2$But)Cl$_2$].[11] In this context we note that in contrast to **5** the related osmium compound [Os(η^6-mes)(κ*P*-Pr$^i_2$PCH$_2$CO$_2$Me)Cl$_2$] reacts with NaH/

Table 1 Selected bond lengths (Å) and angles (°) for compound **19**

Ru–C(1)	2.201(2)	Ru–C(13)	2.242(2)
Ru–P	2.2694(8)	Ru–C(14)	2.188(2)
Ru–Cl	2.4101(8)	Ru–C(15)	2.168(2)
Ru–C(10)	2.230(2)	P–C(1)	1.761(2)
Ru–C(11)	2.243(2)	C(1)–C(2)	1.455(3)
Ru–C(12)	2.259(2)	C(2)–O(1)	1.208(3)
Cl–Ru–P	88.97(3)	Ru–C(1)–P	68.86(7)
Cl–Ru–C(1)	84.97(6)	C(1)–C(2)–O(1)	128.6(2)
P–Ru–C(1)	46.37(6)	C(1)–C(2)–O(2)	110.0(2)
Ru–P–C(1)	64.77(7)	O(1)–C(2)–O(2)	121.3(2)

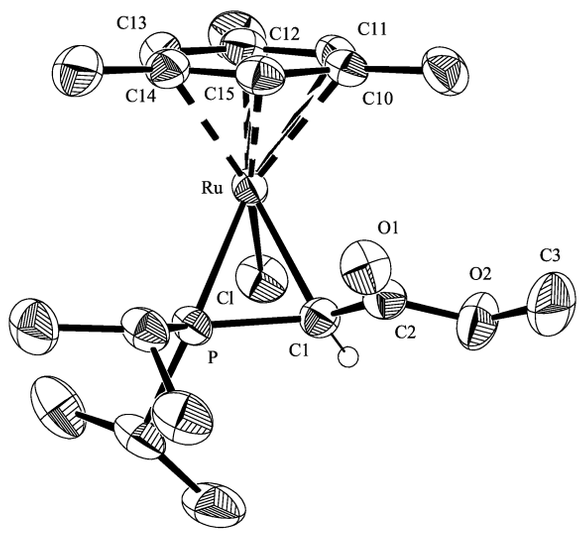
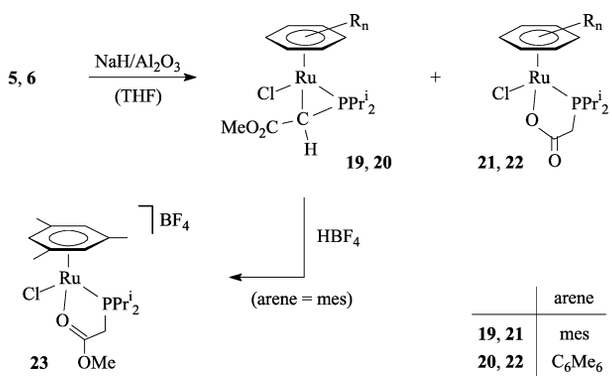


Fig. 1 An ORTEP plot of compound **19**.[21]



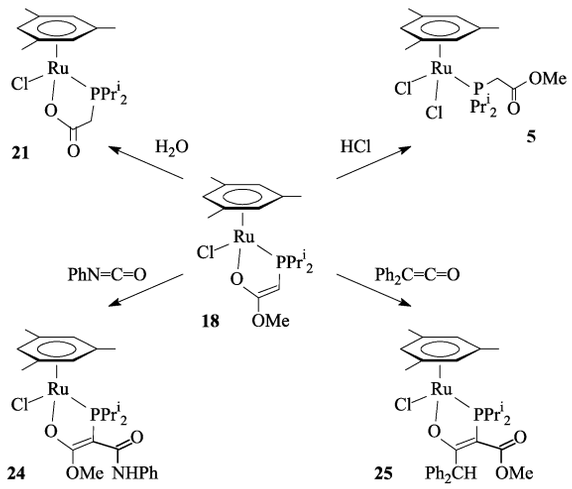
Scheme 4

Al_2O_3 in THF to give the corresponding phosphinomethanide complex almost quantitatively.[12]

Treatment of **19** with HBF_4 in ether leads to the cleavage of the Ru-C bond and affords the tetrafluoroborate of the cationic chelate compound **23**. The analogous PF_6^- salt was prepared prior to this experiment from **5** and $AgPF_6$ (see Scheme 1). Addition of excess $[HNEt_3]Cl$ to a solution of **23** in dichloromethane re-generates the dichlororuthenium(II) derivative **5**.

Reactions of the phosphinoester enolate complex 18

The phosphinocarboxylate compound **21**, being the major product in the reaction of **5** with NaH/Al_2O_3 (see Scheme 4), is formed exclusively upon hydrolysis of the ester enolate function of **18** in acetone solution. A similar metal-assisted transformation of a phosphinoester enolate to a corresponding phosphinoacetate was recently observed by us[13] as well as by Braunstein *et al.*[14] in the case of square-planar iridium(I) and palladium(II) derivatives. Treatment of **18** with HCl in benzene does not lead to cleavage of the O–CH_3 bond of the ester enolate moiety but produces instead by protonation of the PCH carbon atom the dichloro complex **5** quantitatively (Scheme 5).



Scheme 5

While the chelate compound **18** is inert toward CO_2, it reacts with phenylisocyanate in benzene to yield a mixture of products, among which the functionalized enolate complex **24** is the dominating species. This derivative of **18** formally results from the addition of the C–H bond of the phosphinoester enolate across the C=N bond of the substrate. Insertion reactions of this type are not without precedent and have been studied in detail, particularly by Braunstein, Matt and their coworkers.[15] Typical spectroscopic features of **24** are the N–H stretching mode at 3390 cm^{-1} in the IR and the signal for the N–H proton at δ 9.01 in the ^1H NMR spectrum.

Not only phenylisocyanate but also diphenylketene reacts with the enolate complex **18** in hexane/dichloromethane at room temperature to afford the 1 : 1 adduct **25** in 67% isolated yield (see Scheme 5). The composition of the orange, slightly air- and moisture-sensitive solid has been substantiated not only by elemental analysis but also by X-ray crystallography. The presence of the un-coordinated CO_2Me group is indicated by the ν(C=O) absorption at 1677 cm^{-1} in the IR spectrum and by the singlet resonance at δ 191.0 in the ^{13}C NMR spectrum. The signal for the C–O enolate carbon atom appears at δ 181.6 and is split into a doublet due to P,C coupling.

The result of the single-crystal X-ray structure analysis of **25** is shown in Fig. 2 with selected bond lengths and angles in Table 2. As the ORTEP drawing reveals the molecule possesses a similar piano-stool configuration as the phosphinomethanide complex **19**. However, due to the existence of a five-membered

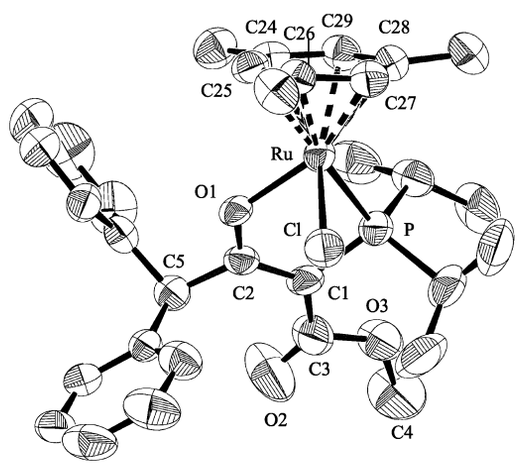


Fig. 2 An ORTEP plot of compound **25**.[21]

Table 2 Selected bond lengths (Å) and angles (°) for compound **25**

Ru–P	2.3349(19)	Ru–C(27)	2.184(7)
Ru–Cl	2.404(2)	Ru–C(28)	2.233(6)
Ru–O(1)	2.057(4)	Ru–C(29)	2.198(6)
Ru–C(24)	2.189(6)	P–C(1)	1.784(7)
Ru–C(25)	2.249(6)	O(1)–C(2)	1.277(6)
Ru–C(26)	2.298(6)	C(1)–C(2)	1.392(8)
Cl–Ru–P	89.49(8)	P–C(1)–C(2)	112.8(5)
Cl–Ru–O(1)	84.04(11)	P–C(1)–C(3)	123.6(5)
P–Ru–O(1)	79.71(11)	O(1)–C(2)–C(1)	122.3(6)
Ru–P–C(1)	101.4(2)	O(1)–C(2)–C(5)	114.4(5)
Ru–O(1)–C(2)	123.7(4)	C(1)–C(2)–C(5)	123.3(6)

chelate ring, the three bond angles between the three "legs" deviate much less from the 90° value than in the case of **19**. The cyclic phosphinoenolate-metal unit is almost planar, with the carbon atoms C(3) and C(5) of the substituents lying in the ring plane. While the bond length C(1)–C(2) [1.392(8) Å] is only somewhat elongated compared to a normal C=C bond, the distance C(2)–O(1) [1.277(6) Å] lies between that of a C–O single and a C=O double bond, indicating some electron delocalization within the enolate fragment.

Conclusions

The work presented in this paper has shown that bulky functionalized phosphines of the general composition $Pr^i_2PCH_2X$ with X = CH_2OMe and CO_2Me can behave in half-sandwich-type areneruthenium(II) compounds as mono- as well as bidentate ligands. Not unexpectedly, the interaction between the functional group X of the phosphine and the metal is more labile for M = Ru than for M = Os which is illustrated in the rapid and complete conversion of **7** and **8** to the carbonyl complexes **11** and **12** and in the (reversible) formation of **15** and **16**, respectively. The related osmium precursor [Os(η⁶-mes)(κ²*P*,*O*-$Pr^i_2PCH_2CH_2OMe$)Cl]PF_6 is inert toward acetonitrile.[16]

However, the most remarkable result of our investigations is that, regarding the compounds **18** and **19**, the complex with the three-membered chelate ring is thermodynamically more stable than the isomer with the five-membered ring. There is, to the best of our knowledge, no precedence for a reaction like that from **18** to **19** which also has no analogy in osmium chemistry.[12] We assume that the driving force for the unusual isomerization process is the re-formation of the intact CO_2Me unit.

Experimental

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1**,[17] **2**,[18] $Pr^i_2PCH_2CH_2OMe$,[1a] and $Pr^i_2PCH_2CO_2Me$,[1a] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments, IR spectra on a Perkin-Elmer 1420 or an IFS 25 FT-IR spectrometer, and mass spectra on a Finnigan 90 MAT instrument (70 eV). Melting points were measured by DTA. The conductivity *Λ* was determined in nitromethane with a Schott Konduktometer CG 851. Abbreviations used: s, singlet; d, doublet; sept, septet; m, multiplet; br, broadened signal; coupling constants *J* in Hz.

Preparations

[Ru(η⁶-mes)(κ*P*-$Pr^i_2PCH_2CH_2OMe$)Cl_2] 3. A suspension of compound **1** (523 mg, 0.90 mmol) in CH_2Cl_2 (40 cm^3) was treated with $Pr^i_2PCH_2CH_2OMe$ (500 mg, 2.84 mmol) and stirred for 3 h at room temperature. The reaction mixture was filtered with Celite and the filtrate was concentrated to *ca*. 3 cm^3 *in vacuo*. After the solution was layered with hexane (15 cm^3), an orange–red microcrystalline solid precipitated which was separated from the mother liquor, washed twice with hexane (5 cm^3) and dried: yield 738 mg (88%); mp 140 °C (decomp.) (Found: C, 45.89; H, 6.93. $C_{18}H_{33}Cl_2OPRu$ requires C, 46.16; H, 7.10%). NMR ($CDCl_3$): δ_H (200 MHz) 5.06 (3 H, s, C_6H_3), 3.64 (2 H, m, CH_2OMe), 3.27 (3 H, s, OCH_3), 2.54 (2 H, m, $PCHCH_3$), 2.26 (2 H, m, PCH_2), 2.19 (9 H, s, CH_3 of mes), 1.30 [6 H, dd, ^3J(P,H) 14.2, ^3J(H,H) 7.3, $PCHCH_3$], 1.29 [6 H, dd, ^3J(P,H) 13.1, ^3J(H,H) 7.1, $PCHCH_3$]; δ_C (50.3 MHz) 101.5 [d, ^2J(P,C) 2.6, CCH_3 of mes], 84.7 [d, ^2J(P,C) 3.7, CH of mes], 69.1 (s, CH_2OMe), 58.2 (s, OCH_3), 27.0 [d, ^1J(P,C) 22.0, $PCHCH_3$], 20.8 [d, ^1J(P,C) 24.6, PCH_2], 19.9, 19.3 (both s, $PCHCH_3$), 18.8 (s, CH_3 of mes); δ_P (81.0 MHz) 34.1 (s).

[Ru(η⁶-C_6Me_6)(κ*P*-$Pr^i_2PCH_2CH_2OMe$)Cl_2] 4. This compound was prepared as described for **3** from **2** (663 mg, 0.99 mmol) and $Pr^i_2PCH_2CH_2OMe$ (500 mg, 2.84 mmol) in CH_2Cl_2 (40 cm^3). Light red solid: yield 815 mg (80%), mp 130 °C (decomp.) (Found: C, 48.85; H, 7.41. $C_{21}H_{39}Cl_2OPRu$ requires C, 49.41; H, 7.10%). NMR ($CDCl_3$): δ_H (200 MHz) 3.59 (2 H, m, CH_2OMe), 3.30 (3 H, s, OCH_3), 2.51 (2 H, m, $PCHCH_3$), 2.20 (2 H, s, PCH_2), 2.01 (18 H, s, CH_3 of C_6Me_6), 1.32 [6 H, dd, ^3J(P,H) 13.4, ^3J(H,H) 7.0, $PCHCH_3$], 1.24 [6 H, dd, ^3J(P,H) 13.1, ^3J(H,H) 7.0, $PCHCH_3$]; δ_P (81.0 MHz) 27.6 (s).

[Ru(η⁶-mes)(κ*P*-$Pr^i_2PCH_2CO_2Me$)Cl_2] 5. This compound was prepared as described for **3** from **1** (499 mg, 0.85 mmol) and $Pr^i_2PCH_2CO_2Me$ (450 mg, 2.37 mmol) in CH_2Cl_2 (40 cm^3). Orange–red solid: yield 745 mg (91%), mp 160 °C (decomp.) (Found: C, 45.13; H, 6.73. $C_{18}H_{31}Cl_2O_2PRu$ requires C, 44.82; H, 6.48%). IR (KBr): ν(C=O) 1719 cm^{-1}. NMR ($CDCl_3$): δ_H (200 MHz) 5.21 (3 H, s, C_6H_3), 3.58 (3 H, s, OCH_3), 3.31 [2 H, d, ^2J(P,H) 10.6, PCH_2], 2.70 (2 H, m, $PCHCH_3$), 2.19 (9 H, s, CH_3 of mes), 1.35 [6 H, dd, ^3J(P,H) 15.5, ^3J(H,H) 7.2, $PCHCH_3$], 1.22 [6 H, dd, ^3J(P,H) 13.6, ^3J(H,H) 7.0, $PCHCH_3$]; δ_P (81.0 MHz) 41.6 (s).

[Ru(η⁶-C_6Me_6)(κ*P*-$Pr^i_2PCH_2CO_2Me$)Cl_2] 6. This compound was prepared as described for **3** from **2** (721 mg, 1.08 mmol) and $Pr^i_2PCH_2CO_2Me$ (700 mg, 3.68 mmol) in CH_2Cl_2 (40 cm^3). Light red solid: yield 1.005 g (89%), mp 144 °C (decomp.) (Found: C, 47.60; H, 6.72. $C_{21}H_{37}Cl_2O_2PRu$ requires C, 48.09; H, 7.11%). IR (KBr): ν(C=O) 1722 cm^{-1}. NMR ($CDCl_3$): δ_H (200 MHz) 3.58 (3 H, s, OCH_3), 3.28 [2 H, d, ^2J(P,H) 10.2, PCH_2], 2.57 (2 H, m, $PCHCH_3$), 2.05 (18 H, s, CH_3 of C_6Me_6), 1.30 [6 H, dd, ^3J(P,H) 15.3, ^3J(H,H) 7.3, $PCHCH_3$], 1.23 [6 H, dd, ^3J(P,H) 13.3, ^3J(H,H) 7.4, $PCHCH_3$]; δ_P (81.0 MHz) 38.8 (s).

[Ru(η⁶-mes)(κ²*P*,*O*-$Pr^i_2PCH_2CH_2OMe$)Cl]PF_6 7. A solution of compound **3** (303 mg, 0.65 mmol) in CH_2Cl_2 (15 cm^3) was treated with a solution of $AgPF_6$ (164 mg, 0.65 mmol) in CH_2Cl_2 (10 cm^3) and stirred for 45 min at room temperature. The reaction mixture was filtered with Celite and the filtrate was evaporated to dryness *in vacuo*. The oily residue was washed three times with ether (5 cm^3) and stored at −20 °C for 12 h. An orange microcrystalline solid was obtained: yield 338 mg (90%); mp 135 °C (decomp.) (Found: C, 37.05; H, 5.61; Ru, 17.44. $C_{18}H_{33}ClF_6OP_2Ru$ requires C, 37.41; H, 5.76; Ru, 17.49%). *Λ* 75 $cm^2\ \Omega^{-1}\ mol^{-1}$. NMR ($CDCl_3$): δ_H (400 MHz) 5.45 (3 H, s, C_6H_3), 3.90 (3 H, s, OCH_3), 3.39 (2 H, m, CH_2OMe), 2.84, 2.77 (1 H each, both m, $PCHCH_3$), 2.26 (9 H, s, CH_3 of mes), 1.78 (2 H, m, PCH_2), 1.47, 1.45, 1.30, 1.29 (3 H each, all m, $PCHCH_3$); δ_P (162.0 MHz) 67.4 (s, PPr^i_2), −144.3 [sept, ^1J(P,F) 712.7, PF_6^-].

[Ru(η⁶-C_6Me_6)(κ²*P*,*O*-$Pr^i_2PCH_2CH_2OMe$)Cl]PF_6 8. This compound was prepared as described for **7** from **4** (167 mg, 0.27 mmol) and $AgPF_6$ (68 mg, 0.27 mmol) in CH_2Cl_2 (35 cm^3). Light red solid: yield 149 mg (89%), mp 150 °C (decomp.) (Found: C, 40.26; H, 5.82. $C_{21}H_{39}ClF_6OP_2Ru$ requires C, 40.68; H, 6.34%). *Λ* 71 $cm^2\ \Omega^{-1}\ mol^{-1}$. NMR ($CDCl_3$): δ_H (400 MHz,

293 K) 3.57 (3 H, s, OCH_3), 3.44 (2 H, br, CH_2OMe), 2.77 (4 H, br, PCH_2 and PC$H$$CH_3$), 2.11 (18 H, s, CH_3 of C_6Me_6), 1.71 (3 H, br, PCHCH_3), 1.28 (9 H, br, PCHCH_3); δ_H (400 MHz, 248 K) 3.58 (3 H, s, OCH_3), 3.45 (2 H, m, CH_2OMe), 2.85 (2 H, m, PCH_2), 2.81, 2.72 (1 H each, both sept, ^3J(H,H) 7.0, PC$H$$CH_3$), 2.12 (18 H, s, CH_3 of C_6Me_6), 1.50 [3 H, dd, ^3J(P,H) 15.2, ^3J(H,H) 7.0, PCHCH_3], 1.37 [3 H, dd, ^3J(P,H) 14.7, ^3J(H,H) 7.0, PCHCH_3], 1.30 [3 H, dd, ^3J(P,H) 15.5, ^3J(H,H) 7.0, PCHCH_3], 1.22 [3 H, dd, ^3J(P,H) 13.9, ^3J(H,H) 7.0, PCHCH_3]; δ_C (100.6 MHz) 95.9 [d, ^2J(P,C) 2.5, $C$$CH_3$ of C_6Me_6], 75.9 (s, $C$$H_2$OMe), 68.5 (s, OCH_3), 25.4 (m, P$C$$HCH_3$), 22.0 [d, ^1J(P,C) 23.6, PCH_2], 19.8, 18.8, 15.8 (all s, PCH$C$$H_3$), 16.2 (s, CH_3 of C_6Me_6); δ_P (162.0 MHz) 58.4 (s, PPr^i_2), −144.4 [sept, ^1J(P,F) 712.8, PF_6^-].

[Ru(η⁶-mes){κ²*P*,*O*-Pr$^i_2$PCH$_2$C(*O*)OMe}Cl]PF$_6$ 9. This compound was prepared as described for **7** from **5** (280 mg, 0.58 mmol) and $AgPF_6$ (147 mg, 0.58 mmol) in CH_2Cl_2 (25 cm^3). Orange–red solid: yield 308 mg (90%), mp 89 °C (decomp.) (Found: C, 36.26; H, 5.11. $C_{18}H_{31}ClF_6O_2P_2Ru$ requires C, 36.53; H, 5.28%). Λ 68 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C=O) 1618 cm^{-1}. NMR ($CDCl_3$): δ_H (400 MHz) 5.36 (3 H, s, C_6H_3), 3.97 (3 H, s, OCH_3), 2.94 [2 H, AB part of ABX system, $\delta(H_A)$ 3.10, $\delta(H_B)$ 2.78, PCH_2], 2.82, 2.77 (1 H each, both m, PC$H$$CH_3$), 2.27 (9 H, s, CH_3 of mes), 1.36, 1.32, 1.31, 1.25 (3 H each, all m, PCHCH_3); δ_C (100.6 MHz) 186.2 [d, ^2J(P,C) 10.1, CO_2], 106.8 (s, $C$$CH_3$ of mes), 80.2 [d, ^2J(P,C) 4.0, CH of mes], 57.1 (s, OCH_3), 30.0 [d, ^1J(P,C) 28.8, PCH_2], 25.8 [d, ^1J(P,C) 25.5, P$C$$HCH_3$], 25.6 [d, ^1J(P,C) 18.2, P$C$$HCH_3$], 19.4 (s, CH_3 of mes), 19.0 (s, PCH$C$$H_3$), 18.4 [d, ^2J(P,C) 1.7, PCH$C$$H_3$], 17.3, 17.2 (both s, PCH$C$$H_3$); δ_P (162.0 MHz) 66.3 (s, PPr^i_2), −144.2 [sept, ^1J(P,F) 712.8, PF_6^-].

[Ru(η⁶-C$_6$Me$_6$){κ²*P*,*O*-Pr$^i_2$PCH$_2$C(*O*)OMe}Cl]PF$_6$ 10. This compound was prepared as described for **7** from **6** (102 mg, 0.19 mmol) and $AgPF_6$ (49 mg, 0.19 mmol) in CH_2Cl_2 (25 cm^3). Red solid: yield 98 mg (81%), mp 159 °C (decomp.) (Found: C, 39.06; H, 5.40. $C_{21}H_{37}ClF_6O_2P_2Ru$ requires C, 39.79; H, 5.88%). Λ 78 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C=O) 1616 cm^{-1}. NMR ($CDCl_3$): δ_H (400 MHz) 3.93 (3 H, s, OCH_3), 2.93 [2 H, AB part of ABX system, $\delta(H_A)$ 3.10, $\delta(H_B)$ 2.76, PCH_2], 2.73 (2 H, m, PC$H$$CH_3$), 2.16 (18 H, s, CH_3 of C_6Me_6), 1.31, 1.30, 1.26 (3 H each, all m, PCHCH_3), 1.13 [3 H, dd, ^3J(P,H) 16.5, ^3J(H,H) 7.2, PCHCH_3]; δ_C (100.6 MHz) 185.8 [d, ^2J(P,C) 9.1, CO_2], 96.4 [d, ^2J(P,C) 2.4, $C$$CH_3$ of C_6Me_6), 56.8 (s, OCH_3), 30.3 [d, ^1J(P,C) 28.4, PCH_2], 26.2 [d, ^1J(P,C) 25.4, P$C$$HCH_3$], 24.4 [d, ^1J(P,C) 18.1, P$C$$HCH_3$], 19.3 [d, ^2J(P,C) 3.5, PCH$C$$H_3$], 18.7 [d, ^2J(P,C) 1.6, PCH$C$$H_3$], 18.0 [d, ^2J(P,C) 1.7, PCH$C$$H_3$], 17.1 [d, ^2J(P,C) 5.7, PCH$C$$H_3$], 16.4 (s, C$C$$H_3$ of C_6Me_6); δ_P (162.0 MHz) 60.5 (s, PPr^i_2), −144.4 [sept, ^1J(P,F) 710.6, PF_6^-].

[Ru(η⁶-mes)(κ*P*-Pr$^i_2$PCH$_2$CH$_2$OMe)(CO)Cl]PF$_6$ 11. Passing a slow stream of CO for 10 min through a solution of **7** (48 mg, 0.08 mmol) in acetone (20 cm^3) led to a quick change of color from orange to yellow. After the solution was stirred for 30 min under a CO atmosphere, the solvent was evaporated *in vacuo*. The remaining light yellow solid was washed twice with ether (5 cm^3) and dried: yield 46 mg (91%), mp 107 °C (decomp.) (Found: C, 37.70; H, 5.71. $C_{19}H_{33}ClF_6O_2P_2Ru$ requires C, 37.66; H, 5.49%). Λ 78 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(CO) 1974 cm^{-1}. NMR ($CDCl_3$): δ_H (200 MHz) 6.78 (3 H, s, C_6H_3), 4.22 (3 H, s, OCH_3), 4.07 (2 H, m, CH_2OMe), 2.82 (2 H, m, PCH_2), 2.42, 2.20 (1 H each, both m, PC$H$$CH_3$), 2.26 (9 H, s, CH_3 of mes), 1.45, 1.40, 1.39, 1.36 (3 H each, all m, PCHCH_3); δ_P (81.0 MHz) 63.9 (s, PPr^i_2), −143.8 [sept, ^1J(P,F) 712.2, PF_6^-].

[Ru(η⁶-C$_6$Me$_6$)(κ*P*-Pr$^i_2$PCH$_2$CH$_2$OMe)(CO)Cl]PF$_6$ 12. This compound was prepared as described for **11** from **8** (110 mg, 0.18 mmol) and CO in acetone (10 cm^3). Orange solid: yield 103 mg (90%), mp 95 °C (decomp.) (Found: C, 40.31; H, 5.86. $C_{22}H_{39}ClF_6O_2P_2Ru$ requires C, 40.78; H, 6.07%). Λ 72 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(CO) 1999 cm^{-1}. NMR ($CDCl_3$): δ_H (400 MHz) 3.49 (2 H, m, CH_2OMe), 3.28 (3 H, s, OCH_3), 2.36 (4 H, m, PCH_2 and PC$H$$CH_3$), 2.24 (18 H, s, CH_3 of C_6Me_6), 1.31, 1.29, 1.25, 1.23 (3 H each, all m, PCHCH_3); δ_C (100.6 MHz) 198.0 [d, ^2J(P,C) 24.1, CO], 113.5 [d, ^2J(P,C) 2.0, $C$$CH_3$ of C_6Me_6), 67.0 (s, $C$$H_2$OMe), 58.4 (s, OCH_3), 28.6 [d, ^1J(P,C) 25.7, P$C$$HCH_3$], 28.0 [d, ^1J(P,C) 26.5, P$C$$HCH_3$], 22.0 [d, ^1J(P,C) 26.7, PCH_2], 20.5 (s, PCH$C$$H_3$), 19.5 [d, ^2J(P,C) 1.0, PCH$C$$H_3$], 19.2 [d, ^2J(P,C) 3.9, PCH$C$$H_3$], 19.1 [d, ^2J(P,C) 2.7, PCH$C$$H_3$], 16.6 (s, C$C$$H_3$ of C_6Me_6); δ_P (162.0 MHz) 52.0 (s, PPr^i_2), −144.7 [sept, ^1J(P,F) 712.8, PF_6^-].

[Ru(η⁶-mes)(κ*P*-Pr$^i_2$PCH$_2$CH$_2$OMe)(CNBu^t)Cl]PF$_6$ 13. A solution of **7** (98 mg, 0.17 mmol) in CH_2Cl_2 (10 cm^3) was treated with CNBu^t (15 mg, 0.18 mmol) and stirred for 5 min at room temperature. The solvent was evaporated *in vacuo* and to the remaining light yellow oil ether (5 cm^3) was added. After the suspension was stirred for 1 h, a light yellow solid was obtained which was washed twice with ether (5 cm^3) and dried: yield 94 mg (84%), mp 112 °C (decomp.) (Found: C, 41.69; H, 6.20; N, 2.83. $C_{23}H_{42}ClF_6NOP_2Ru$ requires C, 41.79; H, 6.40; N, 2.12%). Λ 70 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C≡N) 2164 cm^{-1}. NMR ($CDCl_3$): δ_H (400 MHz) 5.65 (3 H, s, C_6H_3), 3.55 (2 H, m, CH_2OMe), 3.30 (3 H, s, OCH_3), 2.46, 2.10 (1 H each, both m, PC$H$$CH_3$), 2.36 (2 H, m, PCH_2), 2.29 (9 H, s, CH_3 of mes), 1.57 (9 H, s, CH_3 of CNBu^t), 1.30, 1.26, 1.25, 1.21 (3 H each, all m, PCHCH_3); δ_P (162.0 MHz) 47.1 (s, PPr^i_2), −144.2 [sept, ^1J(P,F) 712.8, PF_6^-].

[Ru(η⁶-C$_6$Me$_6$)(κ*P*-Pr$^i_2$PCH$_2$CH$_2$OMe)(CNBu^t)Cl]PF$_6$ 14. This compound was prepared as described for **13** from **8** (81 mg, 0.13 mmol) and CNBu^t (40 mg, 0.48 mmol) in CH_2Cl_2 (10 cm^3). Light yellow solid: yield 79 mg (86%), mp 120 °C (decomp.) (Found: C, 44.05; H, 6.75; N, 2.71. $C_{26}H_{48}ClF_6NOP_2Ru$ requires C, 44.41; H, 6.88; N, 1.99%). Λ 74 cm^2 Ω^{-1} mol^{-1}. IR (KBr): ν(C≡N) 2151 cm^{-1}. NMR ($CDCl_3$): δ_H (400 MHz) 3.43 (2 H, m, CH_2OMe), 3.25 (3 H, s, OCH_3), 2.78, 2.47 (1 H each, both m, PC$H$$CH_3$), 2.31 (2 H, m, PCH_2), 2.10 (18 H, s, CH_3 of C_6Me_6), 1.51 (9 H, s, CH_3 of CNBu^t), 1.20 (9 H, m, PCHCH_3), 1.12 [3 H, dd, ^3J(P,H) 15.0, ^3J(H,H) 7.3, PCHCH_3]; δ_C (100.6 MHz) 106.5 [d, ^2J(P,C) 2.0, $C$$CH_3$ of C_6Me_6), 97.8 (s, CN), 68.0 (s, $C$$H_2$OMe), 59.4 (s, $C$$CH_3$ of CNBu^t), 58.4 (s, OCH_3), 30.7 (s, C$C$$H_3$ of CNBu^t), 28.0 [d, ^1J(P,C) 24.1, P$C$$HCH_3$], 26.9 [d, ^1J(P,C) 24.9, P$C$$HCH_3$], 22.8 [d, ^1J(P,C) 25.3, PCH_2], 19.6, 19.2 (both s, PCH$C$$H_3$), 18.9 [d, ^2J(P,C) 2.8, PCH$C$$H_3$], 16.3 (s, C$C$$H_3$ of C_6Me_6), 16.0 (s, PCH$C$$H_3$); δ_P (162.0 MHz) 43.1 (s, PPr^i_2), −144.4 [sept, ^1J(P,F) 712.8, PF_6^-].

[Ru(η⁶-mes)(κ*P*-Pr$^i_2$PCH$_2$CH$_2$OMe)(NCMe)Cl]PF$_6$ 15. A solution of **7** (50 mg, 0.09 mmol) in CH_2Cl_2 (5 cm^3) was treated with acetonitrile (0.1 cm^3) and stirred for 5 min at room temperature. The solvent was evaporated *in vacuo*, the remaining orange solid washed twice with ether (5 cm^3) and dried. The IR and NMR spectra revealed that a mixture of the starting material and the product was obtained. Data for **15**: IR (KBr): ν(C≡N) 2260 cm^{-1}. NMR ($CDCl_3$): δ_H (400 MHz) 5.67 (s, C_6H_3), 3.45 (m, CH_2OMe), 3.32 (s, OCH_3), 2.44, 2.12 (both m, PC$H$$CH_3$), 2.36 (m, PCH_2), 2.30 (s, CH_3 of mes), 2.20 (s, CH_3CN), 1.32, 1.27, 1.25, 1.02 (all m, PCHCH_3); δ_P (81.0 MHz) 40.6 (s, PPr^i_2), −144.1 [sept, ^1J(P,F) 712.8, PF_6^-].

[Ru(η⁶-C$_6$Me$_6$)(κ*P*-Pr$^i_2$PCH$_2$CH$_2$OMe)(NCMe)Cl]PF$_6$ 16. This compound was prepared as described for **15** from **8** (45 mg, 0.07 mmol) and acetonitrile (0.1 cm^3) in CH_2Cl_2 (5 cm^3). Orange solid consisting of a mixture of **8** and **16**. Data for **16**: IR (KBr): ν(C≡N) 2264 cm^{-1}. NMR ($CDCl_3$): δ_H (400 MHz) 3.38 (m, CH_2OMe), 3.20 (s, OCH_3), 2.71, 2.47 (both m,

PC*H*CH_3), 2.29 (m, PCH_2), 2.15 (s, CH_3CN), 2.10 (s, CH_3 of C_6Me_6), 1.24, 1.22, 1.08 (all m, PCHC*H*$_3$); δ_P (81.0 MHz) 36.5 (s, PPr^i_2), −142.9 [sept, ^1J(P,F) 707.0, PF_6^-].

[Ru(η⁶-C_6Me_6)(κ²*O*,*O*-O_2C=O)(κ*P*-$Pr^i_2PCH_2CH_2OMe$)] 17. A solution of **8** (102 mg, 0.16 mmol) in acetone (25 cm^3) was treated with a saturated solution of Na_2CO_3 in water (1 cm^3) and irradiated for 30 min at room temperature in an ultrasound bath. The reaction mixture was filtered with Celite, and the filtrate was brought to dryness *in vacuo*. The residue was washed three times with ether (5 cm^3) and then extracted with a 1 : 1 mixture of CH_2Cl_2 and hexane (30 cm^3). The solvent from the extract was evaporated and the remaining light yellow solid dried *in vacuo*: yield 55 mg (67%), mp 142 °C (decomp.) (Found: C, 52.58; H, 7.62. $C_{22}H_{39}O_4PRu$ requires C, 52.89; H, 7.87%). IR (CH_2Cl_2): ν(C=O) 1659 cm^{-1}. NMR ($CDCl_3$): δ_H (400 MHz) 3.59 (2 H, m, C*H*$_2$OMe), 3.34 (3 H, s, OCH_3), 2.23 (2 H, m, PCH_2), 2.13 (2 H, m, PC*H*CH_3), 2.09 (18 H, s, CH_3 of C_6Me_6), 1.14 [6 H, dd, ^3J(P,H) 14.2, ^3J(H,H) 7.1, PCHC*H*$_3$], 1.11 [6 H, dd, ^3J(P,H) 14.9, ^3J(H,H) 7.1, PCHC*H*$_3$]; δ_C (100.6 MHz) 166.3 (s, CO_3), 95.0 [d, ^2J(P,C) 2.7, *C*CH_3 of C_6Me_6), 65.8 (s, *C*H_2OMe), 58.4 (s, OCH_3), 28.3 [d, ^1J(P,C) 21.6, P*C*HCH$_3$], 20.2 [d, ^1J(P,C) 26.0, PCH_2], 18.4, 15.2 (both s, PCH*C*H_3), 15.9 (s, C*C*H_3 of C_6Me_6); δ_P (162.0 MHz) 37.3 (s).

[Ru(η⁶-mes){κ²*P*,*O*-Pr^i_2PCH=C(*O*)OMe}Cl] 18. A solution of **9** (101 mg, 0.17 mmol) in THF (15 cm^3) was treated with a suspension of $KOBu^t$ (19 mg, 0.17 mmol) in THF (5 cm^3) and stirred for 15 min at room temperature. After the solvent was evaporated *in vacuo*, the residue was extracted with a 3 : 1 mixture of hexane/CH_2Cl_2 (10 cm^3). The extract was brought to dryness *in vacuo*, the remaining light red solid washed with small portions of hexane (0 °C) and dried: yield 59 mg (78%), mp 85 °C (decomp.) (Found: C, 48.07; H, 7.11. $C_{18}H_{30}ClO_2PRu$ requires C, 48.48; H, 6.78%). IR (KBr): ν(C=O)/ν(C=C) 1524 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 4.39 (3 H, s, C_6H_3), 3.55 (3 H, s, OCH_3), 3.19 [1 H, ^2J(P,H) 3.7, $PCHCO_2$], 2.49, 2.01 (1 H each, both m, PC*H*CH_3), 1.79 (9 H, s, CH_3 of mes), 1.27 [3 H, dd, ^3J(P,H) 16.0, ^3J(H,H) 7.7, PCHC*H*$_3$], 1.23 [3 H, dd, ^3J(P,H) 13.5, ^3J(H,H) 7.5, PCHC*H*$_3$], 1.03 [3 H, dd, ^3J(P,H) 12.1, ^3J(H,H) 6.9, PCHC*H*$_3$], 1.02 [3 H, dd, ^3J(P,H) 15.5, ^3J(H,H) 6.9, PCHC*H*$_3$]; δ_C (100.6 MHz) 180.5 [d, ^2J(P,C) 28.6, CO_2], 102.1 [d, ^2J(P,C) 1.9, *C*CH_3 of mes], 81.1 [d, ^2J(P,C) 3.8, CH of mes], 53.1 (s, OCH_3), 44.5 [d, ^1J(P,C) 70.6, P*C*HCO_2], 26.6 [d, ^1J(P,C) 22.9, P*C*HCH$_3$], 26.5 [d, ^1J(P,C) 35.3, P*C*HCH$_3$], 20.2 [d, ^2J(P,C) 3.8, PCH*C*H$_3$], 19.9 [d, ^2J(P,C) 4.8, PCH*C*H$_3$], 19.5 [d, ^2J(P,C) 1.9, PCH*C*H$_3$], 19.0 (s, C*C*H_3 of mes), 18.8 [d, ^2J(P,C) 5.7, PCH*C*H$_3$]; δ_P (81.0 MHz) 55.0 (s); MS (EI): *m*/*z* 446 (M^+, 62.0%).

[Ru(η⁶-mes)(κ²*P*,*C*-Pr^i_2P*C*HCO_2Me)Cl] 19. A solution of **18** (80 mg, 0.18 mmol) in benzene (5 cm^3) was stirred for 3 d at room temperature. The solution was concentrated to *ca*. 1 cm^3 *in vacuo* and hexane (10 cm^3) was added. A yellow solid precipitated which was filtered, washed with small portions of hexane (0 °C) and dried: yield 70 mg (88%), mp 174 °C (Found: C, 48.10; H, 6.75. $C_{18}H_{30}ClO_2PRu$ requires C, 48.48; H, 6.78%). IR (KBr): ν(C=O) 1661 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 4.48 (3 H, s, C_6H_3), 3.57 (3 H, s, OCH_3), 2.71 [1 H, ^2J(P,H) 3.1, $PCHCO_2$], 2.46, 2.36 (1 H each, both m, PC*H*CH_3), 1.93 (9 H, s, CH_3 of mes), 1.32 [3 H, dd, ^3J(P,H) 17.9, ^3J(H,H) 7.2, PCHC*H*$_3$], 1.27 [3 H, dd, ^3J(P,H) 16.5, ^3J(H,H) 7.4, PCHC*H*$_3$], 1.23 [3 H, dd, ^3J(P,H) 12.8, ^3J(H,H) 6.8, PCHC*H*$_3$], 1.11 [3 H, dd, ^3J(P,H) 18.1, ^3J(H,H) 7.6, PCHC*H*$_3$]; δ_C (50.3 MHz) 179.5 [d, ^2J(P,C) 1.6, CO_2], 101.3 (s, *C*CH_3 of mes), 81.3 [d, ^2J(P,C) 3.5, CH of mes], 50.3 (s, OCH_3), 26.2 [d, ^1J(P,C) 20.2, P*C*HCH$_3$], 21.5 [d, ^1J(P,C) 18.0, P*C*HCH$_3$], 21.5, 21.0, 20.8 (all s, PCH*C*H$_3$), 19.5 (s, C*C*H_3 of mes), 18.7 [d, ^2J(P,C) 4.8, PCH*C*H$_3$], 10.0 (s, P*C*HCO_2); δ_P (162.0 MHz) 31.3 (s); MS (EI): *m*/*z* 446 (M^+, 100%).

[Ru(η⁶-C_6Me_6)(κ²*P*,*C*-Pr^i_2PCHCO_2Me)Cl] 20 and [Ru(η⁶-C_6Me_6){κ²*P*,*O*-$Pr^i_2PCH_2C$(=O)*O*}Cl] 22. A solution of **6** (500 mg, 0.95 mmol) in THF (20 cm^3) was treated first with Al_2O_3 (200 mg) and then five times with 10 mg portions of NaH (50 mg, 2.08 mmol). After the reaction mixture was stirred for 45 min at room temperature, the solution was decanted and the residue extracted twice with THF (10 cm^3). The solution and the extracts were combined and the solvent was evaporated *in vacuo*. The residue was extracted with benzene (15 cm^3), the extract was concentrated to *ca*. 1 cm^3 *in vacuo*, and the solution was chromatographed on Al_2O_3 (basic, activity grade III). With benzene/CH_2Cl_2 (3 : 1) a yellow fraction was eluted, which contained compound **20**: yield 28 mg (6%). With acetone, a second yellow fraction was eluted which was brought to dryness *in vacuo*. The remaining light yellow solid **22** was washed with ether (5 cm^3) and dried: yield 350 mg (78%).

Data for **20**: mp 120 °C (decomp.) (Found: C, 51.42; H, 7.41. $C_{21}H_{36}ClO_2PRu$ requires C, 51.69; H, 7.44%). IR (CH_2Cl_2): ν(C=O) 1668 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 3.56 (3 H, s, OCH_3), 2.64 [1 H, ^2J(P,H) 4.1, $PCHCO_2$], 2.39, 2.33 (1 H each, both m, PC*H*CH_3), 1.89 [18 H, d, ^4J(P,H) 0.9, CH_3 of C_6Me_6], 1.31, 1.28 (3 H each, m, PCHC*H*$_3$), 1.23 [3 H, dd, ^3J(P,H) 15.9, ^3J(H,H) 7.3, PCHC*H*$_3$], 1.13 [3 H, dd, ^3J(P,H) 18.1, ^3J(H,H) 7.6, PCHC*H*$_3$]; δ_P (81.0 MHz) 29.1 (s).

Data for **22**: mp 202 °C (Found: C, 50.44; H, 6.99. $C_{20}H_{34}ClO_2PRu$ requires C, 50.68; H, 7.23%). IR (KBr): ν(C=O) 1631 cm^{-1}. NMR ($CDCl_3$): δ_H (400 MHz) 2.84 [1 H, dd, ^2J(P,H) 10.0, ^2J(H,H) 16.0, PCH_2], 2.73, 2.43 (1 H each, both m, PC*H*CH_3), 2.30 [1 H, dd, ^2J(P,H) 10.3, ^2J(H,H) 16.0, PCH_2], 2.07 [18 H, d, ^4J(P,H) 0.6, CH_3 of C_6Me_6], 1.26 [3 H, dd, ^3J(P,H) 16.0, ^3J(H,H) 7.4, PCHC*H*$_3$], 1.23 [3 H, dd, ^3J(P,H) 12.2, ^3J(H,H) 7.1, PCHC*H*$_3$], 1.18 [3 H, dd, ^3J(P,H) 13.5, ^3J(H,H) 7.4, PCHC*H*$_3$], 1.15 [3 H, dd, ^3J(P,H) 15.2, ^3J(H,H) 7.2, PCHC*H*$_3$]; δ_C (100.6 MHz) 179.7 [d, ^2J(P,C) 8.5, CO_2], 95.1 [d, ^2J(P,C) 2.8, *C*CH_3 of C_6Me_6], 29.6 [d, ^1J(P,C) 29.1, PCH_2], 25.9 [d, ^1J(P,C) 24.3, P*C*HCH$_3$], 24.4 [d, ^1J(P,C) 19.1, P*C*HCH$_3$], 19.3 [d, ^2J(P,C) 4.8, PCH*C*H$_3$], 18.6 [d, ^2J(P,C) 1.7, PCH*C*H$_3$], 18.3 [d, ^2J(P,C) 2.7, PCH*C*H$_3$], 17.6 [d, ^2J(P,C) 5.9, PCH*C*H$_3$], 16.2 (s, C*C*H_3 of C_6Me_6); δ_P (162.0 MHz) 45.8 (s); MS (EI): *m*/*z* 474 (M^+, 28.8%).

[Ru(η⁶-mes){κ²*P*,*O*-$Pr^i_2PCH_2C$(=O)*O*}Cl] 21. This compound was prepared as described for **22** from **5** (107 mg, 0.22 mmol), Al_2O_3 (200 mg) and NaH (50 mg, 2.08 mmol) in THF (30 cm^3). After the by-product **19** was separated by column chromatography (yield 15 mg; 15%), a light yellow solid was isolated: yield 76 mg (80%); mp 198 °C (Found: C, 47.56; H, 6.54; Ru, 23.62. $C_{17}H_{28}ClO_2PRu$ requires C, 47.28; H, 6.53; Ru, 23.40%). IR (KBr): ν(C=O) 1632 cm^{-1}. NMR ($CDCl_3$): δ_H (400 MHz) 4.92 (3 H, s, C_6H_3), 2.80 [1 H, dd, ^2J(P,H) 9.9, J(H,H) 16.1, PCH_2], 2.65, 2.39 (1 H each, both m, PC*H*CH_3), 2.24 [1 H, dd, ^2J(P,H) 10.4, ^2J(H,H) 16.1, PCH_2], 2.11 (9 H, s, CH_3 of mes), 1.23 [3 H, dd, ^3J(P,H) 16.4, ^3J(H,H) 7.4, PCHC*H*$_3$], 1.20 [3 H, dd, ^3J(P,H) 15.5, ^3J(H,H) 7.2, PCHC*H*$_3$], 1.17 [3 H, dd, ^3J(P,H) 14.3, ^3J(H,H) 7.7, PCHC*H*$_3$], 1.15 [3 H, dd, ^3J(P,H) 13.0, ^3J(H,H) 7.0, PCHC*H*$_3$]; δ_P (162.0 MHz) 50.0 (s).

Reaction of compound 18 with water

A solution of **18** (94 mg, 0.21 mmol) in acetone (10 cm^3) was treated with water (0.1 cm^3) and stirred for 10 min at room temperature. After the solvent was evaporated *in vacuo*, the remaining light yellow solid was washed three times with ether (5 cm^3) and dried: yield 86 mg (95%). The product was identified as **21** by comparison with the spectroscopic data of an authentic sample.

Reaction of compound 18 with HCl

A slow stream of dry HCl was passed through a solution of **18** (54 mg, 0.12 mmol) in benzene (15 cm^3) for *ca*. 20 s at room

Table 3 Crystallographic data for **19** and **25**

	19	**25**
Formula	$C_{18}H_{30}ClO_2PRu$	$C_{32}H_{40}ClO_3PRu$
M	445.91	640.13
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	9.195(3)	12.472(8)
b/Å	15.398(3)	14.435(7)
c/Å	14.193(5)	17.992(11)
β/°	94.69(2)	104.81(3)
V/Å^3	2002.7(10)	3132(3)
T/K	293(2)	293(2)
Z	4	4
D_c/g cm^{-3}	1.479	1.358
λ(Mo-Kα)/Å	0.71073	0.71073
μ/mm^{-1}	0.991	0.667
No. of reflections measured	3117	5126
No. of unique reflections	3117 [R(int) = 0.0000]	4880 [R(int) = 0.0677]
$R1$ [a]	0.0178	0.0483
$wR2$ [b]	0.0726	0.1155
Residual electron density/e Å^{-3}	0.245/−0.212	0.342/−0.491

[a] $R = \Sigma|F_o - F_c|/\Sigma F_o$ [for $F_o > 2\sigma(F_o)$] for the number of observed reflections [$I > 2\sigma(I)$], respectively. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.400P)^2 + 0.4395P]$ **19**, $w^{-1} = [\sigma^2(F_o^2) + (0.0476P)^2 + 0.0000P]$ **25**, where $P = (F_o^2 + 2F_c^2)/3$; for all data reflections, respectively.

temperature. The solution was stirred for 10 min and then the solvent was evaporated *in vacuo*. The remaining orange solid was identified as **5** by comparison with the spectroscopic data of an authentic sample. Yield quantitative.

[Ru(η^6-mes){κ^2*P*,*O*-Pr$^i_2$PC(C(=O)NHPh)=C(*O*)OMe}Cl] 24. A solution of **18** (74 mg, 0.17 mmol) in benzene (10 cm^3) was treated with PhNCO (27 mg, 0.23 mmol) and stirred for 2 h at room temperature. The solvent was evaporated *in vacuo* and the orange residue was washed three times with hexane (5 cm^3). The ^{1}H and ^{31}P NMR data revealed that the remaining solid consisted mainly of **24** (*ca*. 85%). Attempts to separate **24** from the un-identified by-products by chromatographic techniques or fractional crystallization failed. Data for **24**: IR (KBr): ν(NH) 3390, ν(C=O) 1630, ν(C=O)/ν(C=C) 1589 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 9.01 (1 H, s, NH), 7.82–6.46 (5 H, m, C_6H_5), 4.48 (3 H, s, C_6H_3), 3.58 (3 H, s, OCH_3), 2.42, 2.35 (1 H each, both m, PC*H*CH_3), 1.92 (9 H, s, CH_3 of mes), 1.32, 1.02 (3 H each, both m, PCHC*H*$_3$), 0.85 (6 H, m, PCHC*H*$_3$); δ_C (100.6 MHz) 176.5 [d, ^2J(P,C) 28.0, CO_2], 167.2 (s, *C*NHPh), 139.2, 132.0, 127.4, 119.3 (all s, C_6H_5), 100.9 [d, ^2J(P,C) 1.5, *C*CH_3 of mes], 72.1 [d, ^2J(P,C) 2.2, CH of mes], 70.8 [d, ^1J(P,C) 62.2, P*C*=C], 55.4 (s, OCH_3), 29.3 [d, ^1J(P,C) 28.9, P*C*HCH$_3$], 27.0 [d, ^1J(P,C) 33.2, P*C*HCH$_3$], 19.5 [d, ^2J(P,C) 3.2, PCH*C*H$_3$], 19.2 [d, ^2J(P,C) 2.4, PCH*C*H$_3$], 18.7 [d, ^2J(P,C) 5.0, PCH*C*H$_3$], 18.2 (s, C*C*H$_3$ of mes), 18.0, 17.4 (both s, PCH*C*H$_3$); δ_P (162.0 MHz) 64.6 (s).

[Ru(η^6-mes){κ^2*P*,*O*-Pr$^i_2$PC(CO$_2$Me)=C(*O*)CHPh$_2$}Cl] 25. A solution of **18** (187 mg, 0.42 mmol) in a 3 : 1 mixture of hexane/CH_2Cl_2 (10 cm^3) was treated with Ph_2CCO (175 mg, 0.90 mmol) and stirred for 1 h at room temperature. The solvent was evaporated *in vacuo*, the residue was washed twice with hexane (5 cm^3) and then dissolved in benzene (1 cm^3). The solution was chromatographed on Al_2O_3 (basic, activity grade III). With benzene, an orange fraction was eluted, which was brought to dryness *in vacuo*. The remaining orange solid was washed three times with hexane (5 cm^3) and dried: yield 180 mg (67%); mp 112 °C (decomp.) (Found: C, 59.72; H, 6.02. $C_{32}H_{40}ClO_3PRu$ requires C, 60.04; H, 6.30%). IR (KBr): ν(C=O) 1677, ν(C=O)/ν(C=C) 1610 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 7.89, 7.38, 7.22, 7.07, 6.91 (10 H, all m, C_6H_5), 4.21 (3 H, s, C_6H_3), 3.41 (3 H, s, OCH_3), 3.03, 2.35 (1 H each, both m, PC*H*CH_3), 2.15 (1 H, s, C*H*Ph_2), 1.58 [3 H, dd, ^3J(P,H) 14.9, ^3J(H,H) 7.0, PCHC*H*$_3$], 1.48 (9 H, s, CH_3 of mes), 1.36 [3 H, dd, ^3J(P,H) 12.2, ^3J(H,H) 7.1, PCHC*H*$_3$], 1.30 [3 H, dd, ^3J(P,H) 19.9, ^3J(H,H) 7.1, PCHC*H*$_3$], 0.95 [3 H, dd, ^3J(P,H) 15.8, ^3J(H,H) 7.0, PCHC*H*$_3$]; δ_C (100.6 MHz) 191.0 (s, CO_2), 181.6 [d, ^2J(P,C) 27.5, *C*(O)CHPh$_2$], 143.4, 142.9, 129.8, 129.7, 129.1, 128.5, 126.1, 125.8 (all s, C_6H_5), 102.3 [d, ^2J(P,C) 1.9, *C*CH_3 of mes], 83.2 [d, ^1J(P,C) 59.4, P*C*=C], 80.1 [d, ^2J(P,C) 3.4, CH of mes], 60.9 [d, ^3J(P,C) 3.8, *C*HPh$_2$], 53.2 (s, OCH_3), 32.2 [d, ^1J(P,C) 29.0, P*C*HCH$_3$], 23.9 [d, ^1J(P,C) 36.1, P*C*HCH$_3$], 19.7 [d, ^2J(P,C) 1.5, PCH*C*H$_3$], 19.2 [d, ^2J(P,C) 2.0, PCH*C*H$_3$], 19.0 [d, ^2J(P,C) 3.2, PCH*C*H$_3$], 18.8 (s, PCH*C*H$_3$), 17.6 (s, C*C*H$_3$ of mes); δ_P (162.0 MHz) 79.0 (s).

Crystallography

Single crystals of both, **19** and **25**, were grown from a saturated solution in hexane which was slowly cooled from 60 °C to room temperature. Crystal data collection parameters are summarized in Table 3. Intensity data were corrected for Lorentz and polarization effects. Empirical absorption corrections (ψ-scan method, minimal transmission 91.30 and 84.19%, respectively) were applied. Data reduction was performed with Enraf-Nonius CAD4 software. The structures were solved by direct methods (SHELXS-97).[19] Atomic coordinates and anisotropic thermal displacement parameters of the non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 (SHELXL-97).[20] The positions of all hydrogen atoms were calculated according to idealised geometries and were refined by using the riding method.

CCDC reference numbers 123242 (**19**) and 193365 (**25**).

See http://www.rsc.org/suppdata/dt/b2/b208891f/ for crystallographic data for **25** in CIF or other electronic format.

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