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Different reactivity of the Ru–O bond in the chelated [(methoxyethyl)diphenylphosphine]ruthenium(II) complexes $[(\eta^6\text{-}C_6Me_6)Ru(P^{\frown}O)X][BR_4]$ in dependence on X = Cl and CH_3

Ekkehard Lindner *, Stefan Pautz, Riad Fawzi, Manfred Steimann

Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-72076, Tübingen, Deutschland

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Abstract

Treatment of the starting complexes $[(\eta^6\text{-}C_6Me_6)Ru(P\sim O)X_2]$ (X = Cl (**1**), CH_3 (**2**); P~O = η^1 (P)-coordinated ether-phosphine ligand $Ph_2PCH_2CH_2OCH_3$) with $NaBPh_4$ and HBF_4, respectively, lead to the chelated complexes $[(\eta^6\text{-}C_6Me_6)Ru(P^{\frown}O)X][BR_4]$ (X = Cl (**3a**), CH_3 (**3b**); R = Ph (**3a**), F (**3b**); P⌒O = η^2 (O,P)-coordinated ligand). The rupture of the Ru–O bond in **3a**,**b** with carbon monoxide and acetonitrile results in the formation of the corresponding complexes $[(\eta^6\text{-}C_6Me_6)Ru(CO)(P\sim O)X][BR_4]$ (**4a**,**b**) and $[(\eta^6\text{-}C_6Me_6)Ru(CH_3CN)(P\sim O)X]$ $[BR_4]$ (**5a**,**b**). The structure of **4a** was determined by single-crystal X-ray diffraction. In a similar way the cleavage of the Ru–O bond is achieved when **3a** is reacted with *tert*-butyl isocyanide and **3b** with ethene to give the adducts $[(\eta^6\text{-}C_6Me_6)Ru(CN^tBu)(P\sim O)Cl][BPh_4]$ (**6a**) and $[(\eta^6\text{-}C_6Me_6)Ru(\eta^2\text{-}C_2H_4)(CH_3)(P\sim O)][BF_4]$ (**7b**). All compounds are obtained in excellent yields and under mild conditions.

Keywords: Ruthenium complexes; Ether–phosphine ligands; Coordinated ligand

1. Introduction

The appropriation of empty coordination sites in the form of coordinatively unsaturated and hence very reactive metal complexes represents an important step in stoichiometric and catalytic reactions. A marked progress in the stabilization of such intermediates was achieved by the introduction of so-called hemilabile ligands [1–3]. These systems are provided with a strongly coordinating atom and additionally with a hard donor site forming only a weak contact to the metal center. In this context we investigated ruthenium, rhodium, and palladium complexes containing ether-phosphines (O,P) acting as monodentate (P~O) and bidentate (P⌒O) ligands (P~O = η^1 (P)-coordinated ligand; P⌒O = η^2 (O,P)-coordinated ligand) [2,4]. Due to the hemilabile character, the ether-oxygen atom is able to generate or to occupy vacant coordination sites. Therefore such ligands may both enhance the reactivity and avoid decomposition of complexes [2,4]. In a preceding investigation we reported on the synthesis of the complexes $[(\eta^6\text{-}C_6Me_6)RuH(P^{\frown}O)][BF_4]$ (P⌒O = diphenyl(ether-phosphine)) and their behavior toward small molecules in dependence on the employed ether moiety [5]. In this work we demonstrate the influence of the ligand X on the reactivity of the Ru–O bond in reactions of the η^2 (O,P)-chelated complexes $[(\eta^6\text{-}C_6Me_6)Ru(P^{\frown}O)X][BR_4]$ (X = Cl (**a**), CH_3 (**b**); R = Ph (**a**), F (**b**)) with small molecules such as carbon monoxide, acetonitrile, *tert*-butyl isocyanide, and ethene.

2. Results and discussion

2.1. Synthesis of the η^2 (O,P)-chelated complexes $[(\eta^6\text{-}C_6Me_6)Ru(P^{\frown}O)X][BR_4]$ (3a,b)

One of both starting complexes (**2**) (Scheme 1) is accessible by treatment of the previously described

* Corresponding author. Tel.: +49 707 1295306.

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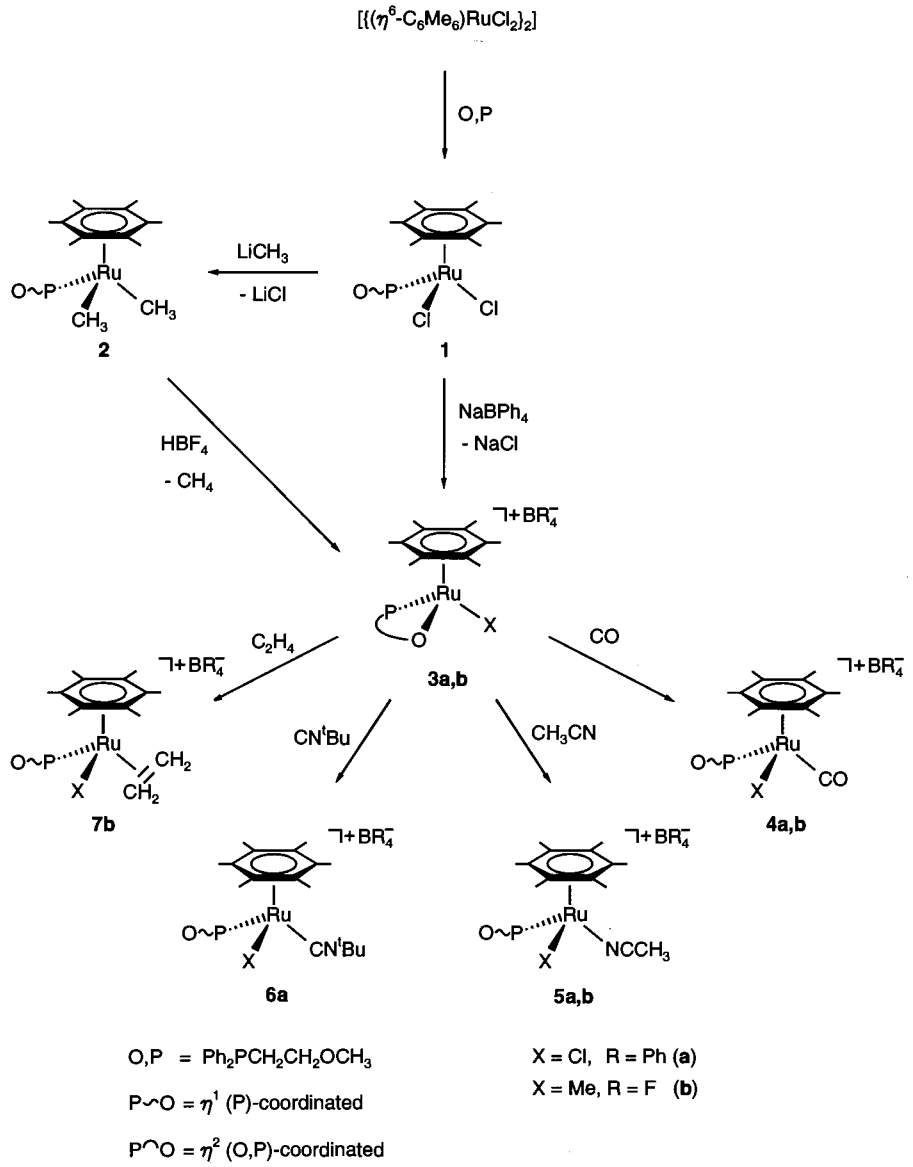

Scheme 1. Reaction scheme showing the production of the chelates **3a,b** from $[\{(\eta^6\text{-}C_6Me_6)RuCl_2\}_2]$, followed by further reaction to form the complexes **4a,b**, **5a,b**, **6a** and **7b**.

dichlororuthenium complex **1** [5] with two equivalents of methyl lithium in THF [6].

The intramolecular coordination of the ether-moiety succeeded by reaction of **1** and **2** with $NaBPh_4$ and HBF_4, respectively, leading to the chelates **3a,b** (Scheme 1). Whereas red **3a** represents a stable compound, the dark yellow congener **3b** decomposes even under an atmosphere of argon. The $^{31}P\{^1H\}$ NMR spectra of **3a,b** display each a singlet at 51.2 and 58.3 ppm. Due to the ring contribution Δ_R [7] this resonance is shifted to lower field compared to the corresponding ^{31}P signal of **1** and **2**. A further evidence for the existence of a η^2 (O,P)-coordination mode in **3a,b** can be derived from the $^{13}C\{^1H\}$ NMR spectra. The signals of the carbon atoms in the α-position to the ether-oxygen atoms are shifted to lower field as well. Typical doublets at 4.7 ppm ($^2J(PC) = 15.0$ Hz) in the $^{13}C\{^1H\}$ and at -0.4 ppm ($^3J(PH) = 7.2$ Hz) in the ^1H-NMR spectra of **3b** are attributed to the metal bound methyl group.

It should be mentioned that the comparable complexes $[(\eta^6\text{-arene})RuCl(P\frown O)][BPh_4]$ (arene = cymene, mesitylene) are accessible in a similar manner [8]. However, these species release the arene moiety when reacted with carbon monoxide.

2.2. Reactivity of *3a,b* toward carbon monoxide, acetonitrile, isocyanide, and ethene

In order to get an insight into the reactivity of the Ru–O bond the behavior of **3a,b** toward carbon monoxide, acetonitrile, and ethene was verified.

When a dichloromethane solution of **3a**,**b** is stirred under an atmosphere of carbon monoxide with cleavage of the Ru–O bonds the yellow carbonyl complexes **4a**,**b** (Scheme 1) are obtained, which dissolve readily in polar organic solvents. While the formation of **4b** is quantitative within 30 min, the completion of the reaction in the case of **4a** requires 16 h. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra are in accordance with a η^1 (P)-coordination of the ether-phosphines. Moreover the $^{13}C\{^1H\}$ NMR spectra of **4a**,**b** reveal each a low intensity doublet at 196.7 and 200.6 ppm which is assigned to the carbonyl groups. The IR spectra of **4a**,**b** exhibit typical absorptions at 2001 and 1961 cm^{-1} for the C≡O stretching vibrations [9]. Remarkably the CO band of **4a** appears at higher energy compared to **4b**. This fact points to an increased electron density at the ruthenium center in **4b**.

For a full characterization of **4a** a crystal structure determination was performed. The ORTEP-drawing is depicted in Fig. 1. Complex **4a** adopts a three-legged piano stool configuration which is evidenced by near-90° angles between P(1)–Ru(1)–Cl(1), C(52)–Ru(1)–P(1), and C(52)–Ru(1)–C(1), respectively. The Ru–C–O unit shows the typical arrangement with bond lengths Ru(1)–C(52) = 1.878 (4) Å and Ru(1)–P(1) = 2.3365 (9) Å which are in good agreement with the corresponding distances in the complexes [Cp*Ru(CO)(P⌒O)][BPh_4] and [Cp*Ru(CO)(P~O)(PPh_3)][BPh_4] [4]b.

If dichloromethane solutions of the O,P-chelates **3a**,**b** are treated with acetonitrile and additionally **3a** also with *tert*-butyl isocyanide a spontaneous rupture of the Ru–O bond takes place and the yellow adducts [(η^6-C_6Me_6)Ru(L)(P~O)X][BR_4] (**5a**,**b**, **6a**: L = CH_3CN, *t*-BuNC, Scheme 1) are formed. In contrast to the complexes [(η^6-arene)RuCl(P⌒O)][PF_6] [10] which need an excess of the ligand L for a complete formation of the addition products, in the case of **5a** and **6a** a quantitative reaction was achieved with equimolar amounts of L. Moreover an equilibrium between the starting chelate and the final adduct was not observed in the present case which is in contrast to the observations of Demerseman [10]. However, **5a** eliminates acetonitrile in the solid state. Within a week **3a** is reformed in a yield of 30%.

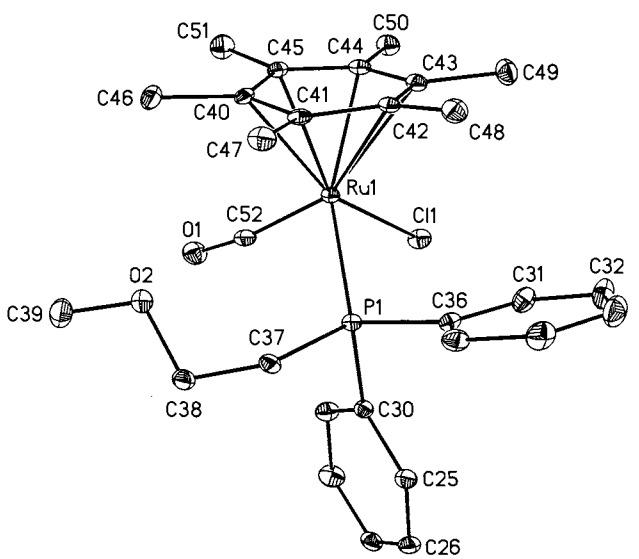

Fig. 1. ORTEP plot of complex **4a**. Selected interatomic distances (Å) and angles (°): Ru(1)–C(52) 1.878(4); Ru(1)–Cl(1) 2.3837(10); Ru(1)–P(1) 2.3365(9); O(1)–C(52) 1.111(4); C(52)–Ru(1)–P(1) 90.27(10); P(1)–Ru(1)–Cl(1) 86.67(3); C(52)–Ru(1)–Cl(1) 92.71(11); O(1)–C(52)–Ru(1) 171.7(3).

A single ^{31}P resonance in the $^{31}P\{^1H\}$ NMR spectra of **5a**,**b** (δ 27.1 (**5a**), δ 36.4 (**5b**)) and **6a** (δ 34.0) points to η^1 (P)-coordinated ether-phosphines. Compared to the educts **3a**,**b** these singlets are shifted characteristically to higher field [2]b; [7]. Besides the typical ^{13}C signals which are attributed to the hexamethylbenzene and phosphine ligands the $^{13}C\{^1H\}$ NMR spectra of **5a**,**b** and **6a** show resonances for the nitrile (δ 124.7 (**5b**)) and isocyanide (δ 142.2) carbon atoms which are slightly shifted to lower and higher field, respectively, compared to those of the uncoordinated ligands. These data correspond well with related results reported in the literature [11].

The action of ethylene on the (ether-phosphine)methylruthenium(II) complex **3b** affords the light yellow, thermally unstable η^2-ethene complex [(η^6-C_6Me_6)Ru(η^2-C_2H_4) (CH_3)(P~O)][BF_4] (**7b**) which dissolves readily in polar solvents, because of its ionic structure. Remarkably the Ru–O bond cleavage fails even at prolonged reaction times if the same reaction is carried out with **3a**. The $^{31}P\{^1H\}$ NMR spectrum of **7b** is in accordance with a η^1 (P)-coordinated phosphine. Two singlets at 51.5 and 46.2 ppm in the $^{13}C\{^1H\}$ NMR spectrum of **7b** are ascribed to the ethylene ligand. This result demonstrates that the rotation of C_2H_4 is slow with respect to the NMR time scale. Each a doublet in the $^{13}C\{^1H\}$ and the ^1H-NMR spectrum is assigned to the CH_3 group [9].

Whereas the hydride complexes [(η^6-C_6Me_6)RuH(P⌒O)][BF_4] [5] exhibit a considerable catalytic activity in the ring opening polymerization of norbornene, the chelates **3a**,**b** lead only to poor yields of polynorbornene in this reaction.

3. Conclusions

A comparison of the related O,P-chelated complexes **3a**,**b** shows a considerable dependence of the reactivity of the Ru–O bond on the employed ligand X. This is reflected in the behavior of **3a**,**b** toward the π-acceptor ligands carbon monoxide and ethene. In contrast to the facile formation of the CO complex **4b**, the reaction

between **3a** and CO requires a longer time under the same conditions (temperature, CO pressure). Even a bigger difference is observed when **3a**,**b** are treated with ethene. Only in the case of **3b** a Ru–O bond rupture takes place and the empty coordination site is occupied by this incoming ligand. No difference is established when **3a**,**b** is reacted with ligands which are provided with predominantly σ-donor properties which was proved with the examples of acetonitrile and *tert*-butyl isonitrile. In the case of π-acceptor ligands the different reactivity of the Ru–O bond can be explained with an increased electron density in the methyl containing complex **3b**. This is indicated by the CO stretching frequencies in the IR spectra of **4a**,**b**.

4. Experimental section

4.1. General procedures

All manipulations were carried out under an atmosphere of argon by use of standard Schlenk techniques. Solvents were dried over appropriate reagents and stored under argon. IR data were obtained with a Bruker IFS 48 FT–IR instrument. FD mass spectra were taken on a Finnigan MAT 711 A instrument (8 kV, 60°C), modified by AMD; FAB mass spectra were recorded on a Finnigan MAT TSQ 70 (10 kV, 50°C). Elemental analyses were performed with a Carlo Erba 1106 analyzer; Cl and F analyses were carried out according to Schöniger [12], and were analyzed as described by Dirscherl and Erne [13], and Brunisholz and Michot [14], respectively. Ru was analyzed according to the literature [15]. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DRX 250 spectrometer at 250.13, 101.25, and 62.90 MHz, respectively. ^{1}H and ^{13}C chemical shifts were measured relative to partially deuterated solvent peaks and to deuterated solvent peaks, respectively. ^{31}P chemical shifts were measured relative to 85% H_3PO_4 ($\delta = 0$). HBF_4 was used as a 54 wt% solution in diethyl ether and methyl lithium as 1.6*N* solution in diethyl ether. $Ph_2PCH_2CH_2OCH_3$ [16] and the starting complex **1** [5] were prepared as previously described.

4.2. η^6-Hexamethylbenzene[(methoxyethyl) diphenylphosphine-P](dimethyl)ruthenium(II) (2)

A suspension of **1** (675 mg, 1.16 mmol) in 40 ml of THF was treated with methyl lithium (2.32 mmol) and stirred for 15 min at room temperature. The resulting yellow solution was transferred to a neutral alumina column (length of column: 5 cm) and eluted with THF. The solvent was removed completely and the residue was dried in vacuo to give 565 mg (90%) of **2** as a yellow powder; mp. 130°C (dec); MS (FD, 60°C): *m*/*e* 538 [M^+]. Anal. Calc. for $C_{29}H_{41}OPRu$ (537.68): C, 64.78%; H, 7.69%; Ru, 18.80%. Found: C, 64.49%; H, 7.64%; Ru, 18.72%. ^{31}P{^{1}H} NMR (101.25 MHz, C_6D_6, 22°C): $\delta = 43.6$ (s). ^{13}C{^{1}H} NMR (62.90 MHz, C_6D_6, 22°C): $\delta = 138.2$–128.0 (m, C–Ph), 97.2 (d, ^{2}J(PC) = 6.3 Hz, C_6Me_6), 70.1 (s, CH_2O), 58.2 (s, OCH_3), 29.2 (d, ^{1}J(PC) = 25.2 Hz, PCH_2), 14.8 (s, C_6Me_6), −2.5 (d, ^{2}J(PC) = 18.9 Hz, $RuCH_3$). ^{1}H-NMR (250.13 MHz, C_6D_6, 22°C): $\delta = -0.1$ (d, ^{3}J(PH) = 5.7 Hz, 6H, $RuCH_3$).

4.3. Chloro(η^6-hexamethylbenzene) [(methoxyethyl)diphenylphosphine-O,P]ruthenium(II) tetraphenylborate (3a)

A mixture of 800 mg (1.38 mmol) of **1** and 473 mg (1.38 mmol) of $NaBPh_4$ in 50 ml of CH_2Cl_2 was stirred for 16 h at room temperature. The solvent was removed under reduced pressure. The residue was redissolved in 20 ml of CH_2Cl_2 and the solution was filtered (G4) to separate NaCl. The solvent was evaporated to dryness in vacuo and the residue was washed with 20 ml of *n*-hexane to give a red precipitate which was collected by filtration (G3) and dried under reduced pressure: yield 1.19 g (90%); mp. 101°C (dec); MS (FD, 60°C): *m*/*e* 543 [M^+-BPh_4]. Anal. Calc. for $C_{51}H_{55}BClOPRu$ (862.30): C, 71.03%; H, 6.43%; Cl, 4.11%; Ru, 11.72%. Found: C, 70.98%; H, 6.47%; Cl, 4.11%; Ru, 12.03%. ^{31}P{^{1}H} NMR (101.25 MHz, CD_2Cl_2, 22°C): $\delta = 51.2$ (s). ^{13}C{^{1}H} NMR (62.90 MHz, CD_2Cl_2, 22°C): $\delta =$ 163.9 (q, ^{1}J(CB) = 49.1 Hz, *ipso*-C of BPh_4), 135.9–121.8 (m, C–Ph), 97.9 (d, ^{2}J(PC) = 2.1 Hz, C_6Me_6), 76.5 (s, CH_2O), 66.7 (s, OCH_3), 29.1 (d, ^{1}J(PC) = 27.7 Hz, PCH_2), 15.5 (s, C_6Me_6).

4.4. η^6-Hexamethylbenzene[(methoxyethyl) diphenylphosphine-O,P](methyl)ruthenium(II) tetrafluoroborate (3b)

A solution of **2** (200 mg, 0.37 mmol) in 10 ml of CH_2Cl_2 was treated with HBF_4 (0.37 mmol) at room temperature. The yellow color of the solution turns spontaneously to orange and the formation of methane is observed. After 15 min of stirring the solvent was removed under reduced pressure. The residue was washed with 10 ml of *n*-hexane to give a dark yellow precipitate, which was collected by filtration (G3) and dried in vacuo to yield 215 mg (95%) of **3b**; mp. 78°C (dec); MS (FD, 60°C): *m*/*e* 523 [M^+-BF_4]. Anal. Calc. for $C_{28}H_{38}BF_4OPRu$ (609.45): C, 55.18%; H, 6.28%; F, 12.47%; Ru, 16.58%. Found: C, 54.83%; H, 6.30; F, 12.38%; Ru, 16.35%. ^{31}P{^{1}H} NMR (101.25 MHz, CD_2Cl_2, 22°C): $\delta = 58.3$ (s). ^{13}C{^{1}H} NMR (62.90 MHz, CD_2Cl_2, 22°C): $\delta = 132.9$–128.9 (m, C–Ph), 97.8 (d, ^{2}J(PC) = 3.0 Hz, C_6Me_6), 78.1 (s, CH_2O), 65.3 (s, OCH_3), 29.0 (d, ^{1}J(PC) = 26.0 Hz, PCH_2), 15.3 (s,

C_6Me_6), 4.7 (d, $^2J(PC) = 15.0$ Hz, $RuCH_3$). ^{1}H-NMR (250.13 MHz, CD_2Cl_2, 22°C): $\delta = -0.4$ (d, $^3J(PH) = 7.2$ Hz, 3H, $RuCH_3$).

4.5. Carbonyl(chloro)(η⁶-hexamethylbenzene) [(methoxyethyl)diphenylphosphine-P]ruthenium(II) tetraphenylborate (**4a**)

A solution of **3a** (110 mg, 0.13 mmol) in 10 ml of CH_2Cl_2 was treated with carbon monoxide (1 bar) at room temperature. After 16 h the color of the orange solution changed to yellow. The solvent was removed and the residue was washed with 10 ml of *n*-hexane to give a yellow precipitate which was collected by filtration (G3) and dried under reduced pressure to yield 113 mg (100%) of **4a**; mp. 156°C; MS (FD, 60°C): *m/e* 571 [M^+-BPh_4]. Anal. Calc. for $C_{52}H_{55}BClO_2PRu$ (890.31): C, 70.15%; H, 6.23%; Cl, 3.98%; Ru, 11.35%. Found: C, 69.81%; H, 6.20%; Cl, 4.00%; Ru, 11.58%. IR (KBr): $\nu(CO) = 2001$ (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR (101.25 MHz, CD_2Cl_2, 22°C): $\delta = 35.7$ (s). $^{13}C\{^1H\}$ NMR (62.90 MHz, CD_2Cl_2, 22°C): $\delta = 196.7$ (d, $^2J(PC) = 25.1$ Hz, CO), 164.0 (q, $^1J(CB) = 50.3$ Hz, *ipso*-C of BPh_4), 137.8–121.8 (m, C–Ph), 113.5 (s, C_6Me_6), 66.9 (s, CH_2O), 58.1 (s, OCH_3), 30.6 (d, $^1J(PC) = 37.7$ Hz, PCH_2), 16.0 (s, C_6Me_6).

4.6. Carbonyl(η⁶-hexamethylbenzene) [(methoxyethyl)diphenylphosphine-P] (methyl)ruthenium(II) tetrafluoroborate (**4b**)

Complex **4b** was synthesized and worked up in the same way as **4a** by reacting a solution of 100 mg (0.16 mmol) of **3b** in 10 ml of CH_2Cl_2 with carbon monoxide (1 bar) for 30 min: yield 104 mg (100%); mp. 63°C (dec); MS (FAB, 50°C): *m/e* 551 [M^+-BF_4]. Anal. Calc. for $C_{29}H_{38}BF_4O_2PRu$ (637.46): C, 54.64%; H, 6.01%; F, 11.92%; Ru, 15.86%. Found: C, 54.54%; H, 5.98%; F, 12.03%; Ru, 16.11%. IR (KBr): $\nu(CO) = 1961$ (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR (101.25 MHz, CD_2Cl_2, 22°C): $\delta = 39.5$ (s). $^{13}C\{^1H\}$ NMR (62.90 MHz, CD_2Cl_2, 22°C): $\delta = 200.6$ (d, $^2J(PC) = 35.1$ Hz, CO), 133.0–128.4 (m, C–Ph), 114.3 (d, $^2J(PC) = 6.3$ Hz, C_6Me_6), 67.2 (s, CH_2O), 58.3 (s, OCH_3), 30.2 (d, $^1J(PC) = 33.0$ Hz, PCH_2), 15.9 (s, C_6Me_6), −9.0 (d, $^2J(PC) = 10.0$ Hz, $RuCH_3$). ^{1}H-NMR (250.13 MHz, CD_2Cl_2, 22°C): $\delta = 0.4$ (d, $^3J(PH) = 4.5$ Hz, 3H, $RuCH_3$).

4.7. Acetonitrile(chloro)(η⁶-hexamethylbenzene) [(methoxyethyl)diphenylphosphine-P]ruthenium(II) tetraphenylborate (**5a**)

A solution of 100 mg (0.12 mmol) of **3a** in 10 ml of CH_2Cl_2 was reacted with 6.8 mg (0.12 mmol) of acetonitrile at ambient temperature. The color of the solution brightens spontaneously to yellow. After 5 min of stirring the solution was evaporated to dryness under reduced pressure and the residue was washed with 10 ml of *n*-hexane. The pale yellow precipitate was collected by filtration (G3) and dried in vacuo to yield 105 mg (100%) of **5a**; mp. 66°C (dec); MS (FD, 60°C): *m/e* 543 [M^+-BPh_4–CH_3CN]. Anal. Calc. for $C_{53}H_{58}BClNOPRu$ (903.35): C, 70.47%; H, 6.47%; Cl, 3.93%; N, 1.55%; Ru, 11.19%. Found: C, 70.26%; H, 6.71%; Cl, 4.23%; N, 1.60%; Ru, 11.06%. $^{31}P\{^1H\}$ NMR (101.25 MHz, CD_2Cl_2, 22°C): $\delta = 27.1$ (s). $^{13}C\{^1H\}$ NMR (62.90 MHz, CD_2Cl_2, 22°C): $\delta = 164.3$ (q, $^1J(CB) = 49.2$ Hz, *ipso*-C of BPh_4), 136.1–122.0 (m, C–Ph and CH_3CN), 100.4 (d, $^2J(PC) = 2.7$ Hz, C_6Me_6), 67.8 (d, $^2J(PC) = 3.4$ Hz, CH_2O), 58.3 (s, OCH_3), 28.4 (d, $^1J(PC) = 29.0$ Hz, PCH_2), 15.8 (s, C_6Me_6), 3.6 (s, CH_3CN).

Table 1
Crystal data and refinement details for **4a**

	Compound **4a**
Formula	$C_{52}H_{55}BClO_2PRu$
FW	890.3
Color	Yellow cubes
Crystal dimensions	$0.19 \times 0.15 \times 0.10$
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	11.693 (3)
b (Å)	21.279 (5)
c (Å)	17.934 (3)
β (°)	99.62 (2)
V (Å^3)	4400 (2)
Z	4
Calc. density (g cm^{-3})	1.344
T (°C)	−100
F(000), e	1856
μ(Mo–K_α), mm^{-1}	0.490
2θ limits (°)	4–50
No. of reflections measured	15 472
No. of unique data with $I \geq 2\sigma(I)$	7743
No. of variables	524
S	1.14
[a] R_1	0.033
[b] wR_2	0.061

[a] $R_1 = \Sigma \| F_0 | - | F_c \| / \Sigma | F_0 |$.
[b] $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[w(F_0^2)^2]\}^{0.5}$.

4.8. Acetonitrile(η⁶-hexamethylbenzene) [(methoxyethyl)diphenylphosphine-P] (methyl)ruthenium(II) tetrafluoroborate (**5b**)

5b was prepared and worked up analogously to **5a** by treating a solution of 120 mg (0.2 mmol) of **3b** in 10 ml of CH_2Cl_2 with 8.1 mg (0.2 mmol) of CH_3CN: yield 128 mg (100%); mp. 51°C (dec); MS (FAB, 50°C): *m/e* 564 [M^+-BF_4]. Anal. Calc. for $C_{30}H_{41}BF_4NOPRu$ (650.51): C, 55.39%; H, 6.35%; F, 11.68%; Ru, 15.54%. Found: C, 55.27%; H, 6.59%; F, 12.03%; Ru, 15.50%. IR (CH_2Cl_2): $\nu(CN) = 2275$ (w) cm^{-1}. $^{31}P\{^1H\}$ NMR

(101.25 MHz, CD_2Cl_2, 22°C): $\delta = 36.4$ (s). $^{13}C\{^1H\}$ NMR (62.90 MHz, CD_2Cl_2, 22°C): $\delta = 133.4–128.9$ (m, C–Ph), 124.7 (s, CH_3CN), 101.7 (d, $^2J(PC) = 2.7$ Hz, C_6Me_6), 68.6 (s, CH_2O), 58.6 (s, OCH_3), 28.3 (d, $^1J(PC) = 26.3$ Hz, PCH_2), 15.4 (s, C_6Me_6), 4.4 (s, CH_3CN), −2.2 (d, $^2J(PC) = 16.2$ Hz, $RuCH_3$). ^1H-NMR (250.13 MHz, CD_2Cl_2, 22°C): $\delta = 0.4$ (d, $^3J(PH) = 6.3$ Hz, 3H, $RuCH_3$).

4.9. tert-Butyl-isocyanide(chloro)(η⁶-hexamethylbenzene)[(methoxyethyl)diphenylphosphine-P]ruthenium(II) tetraphenylborate (6a)

Addition of *t*-BuNC (12.5 mg, 0.15 mmol) to a solution of **3a** (130 mg, 0.15 mmol) in 10 ml of dichloromethane, followed by 5 min of stirring at room temperature, gave a yellow solution, which was evaporated to dryness. The residue was washed with 10 ml of *n*-hexane, and dried in vacuo yielding 142 mg (100%) of **6a**; mp. 56°C (dec); MS (FD, 60°C): *m/e* 627 [M^+-BPh_4]. Anal. Calc. for $C_{56}H_{64}BClNOPRu$ (945.43): C, 71.14%; H, 6.82%; Cl, 3.75%; N, 1.48%; Ru, 10.69%. Found: C, 70.98%; H, 7.02%; Cl, 3.80%; N, 1.64%; Ru, 10.57%. IR (KBr): $\nu(CN) = 2162$ (vs) cm^{-1}. $^{31}P\{^1H\}$ NMR (101.25 MHz, CD_2Cl_2, 22°C): $\delta = 34.0$ (s). $^{13}C\{^1H\}$ NMR (62.90 MHz, CD_2Cl_2, 22°C): $\delta = 164.5$ (q, $^1J(CB) = 49.4$ Hz, *ipso*-C of BPh_4), 142.2 (s, $CNCMe_3$), 135.9–121.7 (m, C–Ph), 106.9 (s, C_6Me_6), 67.5 (s, CH_2O), 59.5 (s, $CNCMe_3$), 58.0 (s, OCH_3), 30.4 (s, $CNCMe_3$), 30.3 (d, $^1J(PC) = 32.1$ Hz, PCH_2), 15.5 (s, C_6Me_6).

4.10. η²-Ethene(η⁶-hexamethylbenzene)[(methoxyethyl)diphenylphosphine-P](methyl)ruthenium(II) tetrafluoroborate (7b)

A solution of 100 mg (0.16 mmol) of **3b** in 10 ml of CH_2Cl_2 was treated with ethene (1 bar) at room temperature. After 3 h stirring the solvent was removed under reduced pressure. The residue was washed with 10 ml of *n*-hexane to give a yellow precipitate which was collected by filtration (G3) and dried in vacuo yielding 105 mg (100%) of **7b**; mp. 60°C (dec); MS (FAB, 50°C): *m/e* 534 [M^+-BF_4–CH_3]. Anal. Calc. for $C_{30}H_{42}BF_4OPRu$ (637.51): C, 56.52%; H, 6.64%; F, 11.92%; Ru, 15.85%. Found: C, 56.27%; H, 6.59%; F, 12.23%; Ru, 15.85%. $^{31}P\{^1H\}$ NMR (101.25 MHz, CD_2Cl_2, 22°C): $\delta = 41.0$ (s). $^{13}C\{^1H\}$ NMR (62.90 MHz, CD_2Cl_2, −30°C): $\delta = 135.1–128.5$ (m, C–Ph), 110.5 (s, C_6Me_6), 67.3 (s, CH_2O), 58.3 (s, OCH_3), 51.5, 46.2 (s, C_2H_4), 22.9 (d, $^1J(PC) = 31.0$ Hz, PCH_2), 15.4 (s, C_6Me_6), 1.4 (d, $^2J(PC) = 16.2$ Hz, $RuCH_3$). ^1H-NMR (250.13 MHz, CD_2Cl_2, 22°C): $\delta = 0.6$ (d, $^3J(PH) = 6.6$ Hz, 3H, $RuCH_3$).

Table 2
Atomic coordinates ($\times 10^4$) of **4a** with equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)[a]

Atom	*x*	*y*	*z*	*U*(eq)
Ru(1)	1626(1)	619(1)	2362(1)	19(1)
Cl(1)	1651(1)	−309(1)	1621(1)	31(1)
P(1)	3123(1)	988(1)	1763(1)	21(1)
O(1)	3261(2)	101(1)	3672(2)	40(1)
B(1)	8249(3)	−2117(2)	3773(2)	25(1)
C(1)	9915(3)	−1872(2)	2957(2)	39(1)
C(2)	11002(4)	−1645(2)	2853(3)	53(1)
C(3)	11762(4)	−1412(2)	3452(3)	61(2)
C(4)	11455(3)	−1417(2)	4160(3)	55(1)
C(5)	10376(3)	−1654(2)	4267(3)	41(1)
C(6)	9563(3)	−1884(2)	3662(2)	32(1)
C(7)	7121(3)	−2321(2)	2365(2)	37(1)
C(8)	6740(3)	−2696(2)	1735(2)	50(1)
C(9)	6936(3)	−3334(2)	1764(2)	45(1)
C(10)	7499(3)	−3593(2)	2428(2)	38(1)
C(11)	7872(3)	−3221(2)	3058(2)	30(1)
C(12)	7708(3)	−2565(2)	3045(2)	28(1)
C(13)	7368(3)	−2619(2)	4924(2)	28(1)
C(14)	7359(3)	−3039(2)	5519(2)	38(1)
C(15)	8332(4)	−3397(2)	5779(2)	42(1)
C(16)	9298(3)	−3324(2)	5438(2)	42(1)
C(17)	9288(3)	−2913(2)	4833(2)	36(1)
C(18)	8317(3)	−2545(2)	4547(2)	26(1)
C(19)	7862(3)	−915(2)	4106(2)	30(1)
C(20)	7161(3)	−406(2)	4216(2)	39(1)
C(21)	5970(3)	−460(2)	4061(2)	41(1)
C(22)	5496(3)	−1027(2)	3781(2)	41(1)
C(23)	6209(3)	−1532(2)	3668(2)	31(1)
C(24)	7419(3)	−1501(2)	3836(2)	26(1)
C(25)	4839(3)	579(2)	981(2)	31(1)
C(52)	2719(3)	295(2)	3155(2)	28(1)
C(48)	−17(3)	1796(2)	1181(2)	36(1)
C(45)	289(2)	619(2)	3172(2)	25(1)
C(41)	858(3)	1577(2)	2550(2)	24(1)
C(43)	−319(3)	773(1)	1805(2)	25(1)
C(50)	−829(3)	−250(2)	2423(2)	34(1)
C(29)	4586(3)	−78(2)	2021(2)	34(1)
C(42)	197(3)	1365(2)	1851(2)	23(1)
C(28)	5514(3)	−442(2)	1890(2)	39(1)
C(30)	4232(3)	438(1)	1565(2)	24(1)
C(40)	880(3)	1211(2)	3213(2)	24(1)
C(36)	2524(3)	1307(2)	837(2)	25(1)
C(35)	2680(3)	1935(2)	643(2)	33(1)
C(31)	1844(3)	922(2)	311(2)	34(1)
C(27)	6099(3)	−305(2)	1306(2)	35(1)
C(46)	1440(3)	1472(2)	3961(2)	37(1)
C(49)	−1001(3)	544(2)	1062(2)	40(1)
C(34)	2169(3)	2163(2)	−57(2)	42(1)
C(26)	5760(3)	204(2)	851(2)	36(1)
C(47)	1366(3)	2235(2)	2614(2)	35(1)
C(44)	−256(3)	385(2)	2472(2)	26(1)
C(32)	1327(4)	1157(2)	−383(2)	43(1)
C(51)	268(3)	248(2)	3893(2)	40(1)
C(33)	1494(4)	1780(2)	−564(2)	46(1)
O(2)	4039(2)	1497(1)	3539(1)	39(1)
C(37)	4034(3)	1625(2)	2218(2)	27(1)
C(38)	4762(3)	1482(2)	2983(2)	33(1)
C(39)	4685(4)	1419(2)	4276(2)	49(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

4.11. Crystallographic analysis

Single crystals of **4a** were obtained by slow diffusion of diethyl ether into a concentrated solution of **4a** in CH_2Cl_2. The crystals were mounted on a glass fiber and transferred to a P4 Siemens diffractometer, using graphite-monochromated Mo–K_α radiation. A rotation photograph was taken and a photo search was performed to find a suitable reduced cell. The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. The final cell parameters for **4a** are summarized in Table 1. The atomic coordinates and equivalent isotropic displacement parameters for **4a** are given in Table 2. Intensities were collected with the ω-scan technique with scan speed varying from 6.5 to 29.3° min^{-1} in ω. Scan range for **4a** was 1.0 and absorption correction was applied (Ψ-scan, maximum and minimum transmission: 0.693, 0.654). The structure was solved by Patterson methods [17] and refined by least squares with anisotropic thermal parameters for all non-hydrogen atoms (based on F^2). Hydrogen atoms were included in calculated positions (riding model). Maximum and minimum peaks in the final difference synthesis were 0.303 and -0.352 e $Å^{-3}$. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-407707, the names of the authors and the journal citation.

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