

Reactivity of the Ru–O bond in $\eta^2(\text{O,P})$ -chelated mono(ether–phosphine)(pentamethylcyclopentadienyl) ruthenium(II) complexes [☆]

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Abstract

By treatment of the 16-electron starting compound $\text{Cp}^*\text{RuCl}(\text{P} \sim \text{O})$ (**1**) ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{P} \sim \text{O}$, $\eta^1(\text{P})$ -coordinated ether–phosphine ligand $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$) with $\text{L} = \text{CO}$ (**2a**) and $\text{P}(\text{OEt})_3$ (**2b**), the carbonyl and mixed bisphosphine ruthenium(II) complexes $\text{Cp}^*\text{RuCl}(\text{L})(\text{P} \sim \text{O})$ (**2a**, **2b**) are accessible. Chloride abstraction from **2a**, **2b** with NaBPh_4 leads to the chelated complexes $[\text{Cp}^*\text{Ru}(\text{L})(\text{P} \cap \text{O})][\text{BPh}_4]$ (**3a**, **3b**) ($\text{P} \cap \text{O}$, $\eta^2(\text{O,P})$ -coordinated ligand). Cleavage of the Ru–O bond in **3a**, **3b** with sulphur dioxide results in the formation of the $\eta^1\text{-SO}_2$ complexes $[\text{Cp}^*\text{Ru}(\text{L})(\text{P} \sim \text{O})(\eta^1\text{-SO}_2)][\text{BPh}_4]$ (**4a**, **4b**) in which the O_2SRu fragment adopts a trigonal planar geometry. In a similar way the Ru–O bond is easily ruptured when $[\text{Cp}^*\text{Ru}(\text{CO})(\text{P} \cap \text{O})][\text{BPh}_4]$ (**3a**) is reacted with ethene and phenylacetylene to give the adduct $[\text{Cp}^*\text{Ru}(\text{CO})(\text{P} \sim \text{O})(\eta^2\text{-C}_2\text{H}_4)][\text{BPh}_4]$ (**5a**) and the η^1 -vinylidene complex $[\text{Cp}^*\text{Ru}(\text{CO})(\text{P} \sim \text{O})(\text{C}=\text{CHPh})][\text{BPh}_4]$ (**6a**) respectively.

Keywords: Cyclopentadienyl; Group 8; Phosphine; Ruthenium; Sulphur dioxide; Vinylidene

1. Introduction

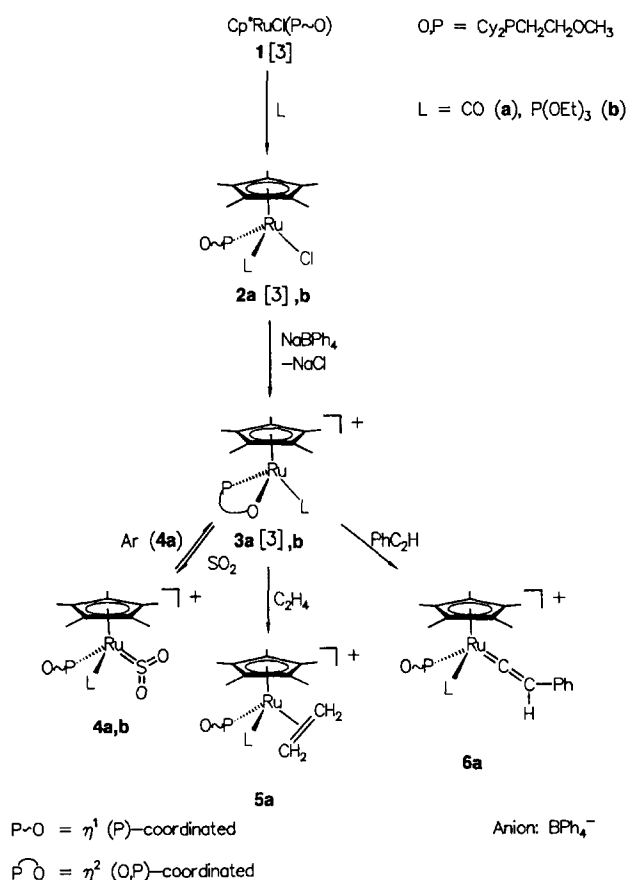
Recently we reported on the synthesis, dynamic behaviour, and reactivity of the cationic cyclopentadienyl-ruthenium complexes $[(\eta^5\text{-C}_5\text{R}_5)\text{Ru}(\text{P} \sim \text{O})(\text{P} \cap \text{O})]^+$ ($\text{P} \sim \text{O}$, $\eta^1(\text{P})$ -coordinated; $\text{P} \cap \text{O}$, $\eta^2(\text{O,P})$ -coordinated ligand; $\text{R} = \text{H}$, CH_3) containing hemilabile ether–phosphines [1]. These ligands are provided with a strongly coordinating phosphorus donor and moreover with an oxygen function incorporated in an open chain or cyclic ether moiety. The ether oxygen atom is able to stabilize undercoordinated transition metal complexes by formation of weak metal–oxygen interactions and the ether arm of such ligands may thus be regarded as an intramolecular solvent [2]. The reactivity of chelated (ether–phosphine)metal complexes is associated with a facile rupture of the metal–oxygen bond and hence is

dependent on the strength of this interaction. Remarkably the sterically demanding $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$ ligand ($\text{Cy} = \text{cyclohexyl}$) affords the 16-electron complex $(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}(\text{P} \sim \text{O})$ ($\eta^5\text{-C}_5\text{Me}_5 = \text{Cp}^*$). Reaction with carbon monoxide and subsequent chloride abstraction yields the (O,P)-chelated complex $[\text{Cp}^*\text{Ru}(\text{CO})(\text{P} \cap \text{O})][\text{BPh}_4]$. To obtain an insight into the strength of the Ru–O bond this compound was treated with carbon monoxide, triphenylphosphine, and diphenyldiazomethane [3]. Very recently Braun et al. described the preparation and structure of half-sandwich ruthenium(II) complexes containing $^i\text{Pr}_2\text{PCH}_2\text{CO}_2\text{CH}_3$ as a hemilabile O,P ligand [4].

The mentioned 16-electron complex $\text{Cp}^*\text{RuCl}(\text{P} \sim \text{O})$ ($\text{O,P} = \text{Cy}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$) is a nice precursor for the introduction of different ligands L, in particular phosphines. We investigated the influence of the different metal basicities on both chloride abstraction from neutral complexes $\text{Cp}^*\text{RuCl}(\text{L})(\text{P} \sim \text{O})$ with $\text{L} = \text{CO}$ (**2a**), $\text{P}(\text{OEt})_3$ (**2b**) and the ease of the Ru–O bond cleavage in the cations of the complexes $[\text{Cp}^*\text{Ru}$

[☆] Dedicated to Professor Gerhard Thiele on the occasion of his 60th birthday.

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Scheme 1.

$(\text{L})(\text{P}^{\cap}\text{O})][\text{BPh}_4]$ (**3a**, **3b**) with small molecules such as sulphur dioxide, ethene, and phenylacetylene.

2. Results and discussion

2.1. Preparation of the neutral complexes $\text{Cp}^*\text{RuCl}(\text{L})(\text{P}\sim\text{O})$ (**2a**, **2b**)

While the carbon monoxide complex **2a** (Scheme 1) lately has been described in the literature [3], the corresponding congener **2b** with $\text{L} = \text{P}(\text{OEt})_3$ is accessible by treatment of the 16-electron starting compound **1** with an equimolar amount of $\text{P}(\text{OEt})_3$ in toluene. The reaction is accompanied by a spontaneous colour change from deep purple to orange and is quantitative within a few minutes. A byproduct of this reaction is $\text{Cp}^*\text{RuCl}(\text{P}(\text{OEt})_3)_2$ which can be separated by column chromatography [5]. Compound **2b** was obtained as an orange oil which resists persistent efforts for a crystallization. The $^{31}\text{P}(\text{H})$ NMR spectrum of **2b** exhibits an AX pattern resulting from two different phosphorus atoms. The high field doublet is assigned to the etherphosphine and is in the typical range of an $\eta^1(\text{P})$ -coordinated O,P ligand [3]. This coordination mode was

supported by a $^{13}\text{C}(\text{H})$ NMR spectrum of **2a** which displays characteristic resonances for the carbon atoms in the α position of the ether oxygen [3].

2.2. Chloride abstraction from $\text{Cp}^*\text{RuCl}(\text{L})(\text{P}\sim\text{O})$ (**2a**, **2b**) forming the complexes $[\text{Cp}^*\text{Ru}(\text{L})(\text{P}^{\cap}\text{O})][\text{BPh}_4]$ (**3a**, **3b**)

According to a previously published study in the case of **2a** $\rightarrow$ **3a** [3] the intramolecular coordination of the ether moiety in **2b** which leads to the $\eta^2(\text{O,P})$ -chelated complex $[\text{Cp}^*\text{Ru}(\text{P}^{\cap}\text{O})(\text{P}(\text{OEt})_3)][\text{BPh}_4]$ (**3b**) succeeded by chloride abstraction with NaBPh_4 in CH_2Cl_2 . Complex **3a** is a dark yellow compound which is easily soluble in polar but insoluble in non-polar solvents. While the formation of **3a** requires three days, the reaction **2b** $\rightarrow$ **3b** is finished within one-third of that time. This observation may be rationalized by an increased metal basicity of **2b** compared with the carbon monoxide complex **2a** weakening the Ru–Cl bond. The $^{31}\text{P}(\text{H})$ NMR spectrum of **3b** exhibits an AX pattern. Because of the ring contribution Δ_r [6] the doublet attributed to the O,P ligand is characteristically shifted to lower field compared with the corresponding resonance of **2b**. A further proof for the bidentately $\eta^2(\text{O,P})$ -coordinated ligand is deduced from the $^{13}\text{C}(\text{H})$ NMR spectrum. The signals of the carbon atoms adjacent to the ether oxygen are shifted to lower field as well. The high field shift of the ^{13}C signals of the C_5Me_5 ring atoms in the $^{13}\text{C}(\text{H})$ NMR spectra of **2b**, **3b** compared with those of **2a**, **3a** is consistent with a higher electron density at the ruthenium in **2b**, **3b**. The structure of **3b** was confirmed by an X-ray crystal structure analysis. Because of the deficient quality of the single crystals the standard deviations were extremely high [7].

2.3. Coordination of sulphur dioxide, ethene, and phenylacetylene to the complexes $[\text{Cp}^*\text{Ru}(\text{L})(\text{P}^{\cap}\text{O})][\text{BPh}_4]$ (**3a**, **3b**)

To obtain an insight into the strength of the Ru–O contact the complexes **3a** and **3b** were allowed to react with sulphur dioxide. Additionally complex **3a** was treated with ethene and phenylacetylene.

If sulphur dioxide is bubbled into dichloromethane solutions of **3a**, **3b** at ambient temperature the colour of the reaction mixtures brightens spontaneously. The formation of the complexes $[\text{Cp}^*\text{Ru}(\text{L})(\text{P}\sim\text{O})(\eta^1\text{-SO}_2)][\text{BPh}_4]$ (**4a**, **4b**) is quantitative after approximately 5 min. We observed a remarkably difference in the stability of **4a** and **4b**. On flushing CH_2Cl_2 solutions of **4a**, **4b** with argon, the educt **3a** is formed again quantitatively, while compound **4b** remains unchanged.

Even in the solid state **4a** eliminates SO₂. **4a** was precipitated from the CH₂Cl₂ reaction mixture with *n*-hexane as a pale yellow substance. Both **4a** and **4b** are soluble in dichloromethane or acetone but insoluble in non-polar solvents.

The ³¹P(¹H) NMR spectra exhibit a single resonance for **4a** and an AX pattern for **4b**. Compared with **3a**, **3b** the singlet in the spectrum of **4a** and the high field doublet in the spectrum of **4b** are shifted to higher field indicating an η¹(P) coordination of the ether–phosphines. According to Kubas it is possible to determine the SO₂-geometry by means of the SO₂ stretching modes [8]. The SO₂ stretching frequencies of **4a** and **4b** unequivocally point to an η¹-coplanar Ru–SO₂ geometry. Remarkably the SO₂ absorptions of **4a** are shifted to higher energy compared with the corresponding values of **4b**. This indicates a weaker back-donation of electrons from the central atom into the b₁ orbital of the sulphur dioxide ligand [9] due to a decreased electron density at the ruthenium centre of **4a** compared with **4b**.

Stirring a solution of **3a** for 30 min under an ethene atmosphere results in the formation of the η²-ethene complex [Cp* Ru(CO)(P ~ O)(η²-C₂H₄)] [BPh₄] (**5a**). The uptake of C₂H₄ is accompanied by a gradual colour change from yellow to almost colorless. Complex **5a** is a pale beige substance. Because of its ionic nature it is readily soluble in polar but insoluble in non-polar solvents. Compared with the related complexes [CpRu(L)₂(η²-C₂H₄)]⁺ (L = PMe₃, PPh₃) [10,11] the coordination of ethene in **5a** is less strong. However, **5a** is more stable than [Cp* Ru(P ~ O)₂(η²-C₂H₄)] [BPh₄] which binds ethene completely reversibly [1c]. The η¹(P)-coordinated ether–phosphine gives rise to a single resonance in the ³¹P(¹H) NMR spectrum. A singlet at 47.9 ppm in the ¹³C(¹H) NMR spectrum which is assigned to the equivalent carbon atoms of the ethene ligand corresponds well to related compounds [10].

A couple of years ago and very recently a series of η¹-vinylidene complexes were reported accessible by the reaction of CpRuCl(PR₃)₂ [12] and Cp* RuCl(P[⊖]O) (O,P = ⁱPr₂PCH₂CO₂CH₃) [4] respectively with various 1-alkynes. In a primary step an unstable η²-ethyne intermediate was formed which rearranges rapidly into the corresponding η¹-vinylidene complex. Just by employment of small phosphines and acetylene the isolation of the mentioned intermediate was successful [13].

The action of a solution of **3a** with equimolar amounts of phenylacetylene at room temperature affords the quantitative formation of the η¹-vinylidene complex **6a**. As expected an η²-ethyne intermediate could not be observed. **6a** is a brownish orange compound which is easily soluble in polar solvents such as dichloromethane or acetone. Decomposition occurs within one day both in the solid state and in solution. The ³¹P(¹H) NMR spectrum displays a singlet at 53 ppm which is shifted

only slightly to higher field compared with the corresponding peak of **3a**. The η¹(P) coordination mode of the O,P ligand in **6a**, however, is unequivocally proved by the ¹³C(¹H) NMR spectrum. The resonances of the carbon atoms in the α position of the ether oxygen atom are shifted significantly to higher field in agreement with a non-chelated ether moiety. Moreover, the ¹³C(¹H) NMR spectrum exhibits a characteristic low intensity doublet at 368.2 ppm assigned to the α-carbon atom of the vinylidene unit [12]. Because of the coupling with phosphorus the ¹H NMR spectrum displays the vinylic proton as a doublet at 6.1 ppm. The absorption for the C=C stretching vibration at 1625 cm⁻¹ is in the typical range of η¹-vinylidene complexes [11].

2.4. Conclusion

Employment of P(OEt)₃ instead of CO in **2b** increases the electron density at the ruthenium centre. For this reason the chloride abstraction in the case of **2b** demands a significant shorter time than for the formation of **3a**. The increased metal basicity of **3b** seems also to be responsible for the higher stability of the SO₂ complex **4b**. The electron withdrawing effect of the carbon monoxide ligand in **3a** generates a relatively hard ruthenium centre which favours the Ru–O contact compared with the coordination of sulphur dioxide and ethene.

3. Experimental details

All manipulations were carried out under an atmosphere of argon by use of the standard Schlenk techniques. Solvents were dried over appropriate reagents and stored under argon. IR spectra were recorded on a Bruker IFS 48 FT-IR spectrometer. FD mass spectra were taken on a Finnigan MAT 711 A instrument (8 kV, 60°C), modified by AMD; FAB mass spectra were obtained on a Finnigan TSQ 70 (10 kV, 50°C). Elemental analyses were performed with a Carlo Erba 1106 analyser; Cl and S analyses were carried out according to Schöniger [14] and analysed as described by Dirschel and Erne [15] and Wagner [16]. Ru was determined according to the literature [17]. ³¹P(¹H) NMR spectra were obtained on a Bruker WP 80 spectrometer operating at 32.39 MHz, external standard (coaxial insert) 1% H₃PO₄ in acetone-*d*₆ for *T* ≤ 273 K. ¹H and ¹³C(¹H) NMR spectra were measured with Bruker AC 80 and Bruker AC 250 spectrometers at 80.13 and 20.15 MHz and at 250.13 and 62.90 MHz respectively. ¹H and ¹³C chemical shifts were measured relative to partially deuterated solvent peaks which are reported relative to TMS. Cy₂PCH₂CH₂OCH₃ [18] and the complexes **1**, **2a**, **3a** [3] were prepared as previously described.

3.1. Chloro[dicyclohexyl(2-methoxyethyl)phosphine-*P*](pentamethylcyclopentadienyl)(triethylphosphite)ruthenium(II) (**2b**)

To a solution of **1** (240 mg, 0.45 mmol) in 20 ml of toluene $\text{P}(\text{OEt})_3$ (50 mg, 0.45 mmol) was added and the mixture was stirred for 15 min at ambient temperature. The orange solution was evaporated to dryness and redissolved in 10 ml of *n*-hexane. The reaction mixture was purified by column chromatography (length of the column 15 cm, silica gel 60 silanized, 70–230 mesh (Merck)). Non-coordinated O,P ligand and $\text{P}(\text{OEt})_3$ were eluted with 100 ml of *n*-hexane. The yellow fraction was eluted with *n*-hexane–diethylether (2:1) and was collected in two different samples, of which the first contained **2b** and $\text{Cp}^*\text{RuCl}(\text{P}(\text{OEt})_3)_2$ and the second sample contained **2b** in pure form. The solvent was removed completely and the residue was dried in vacuo to give 144 mg (46%) of **2b** as an orange oil; MS (FD, 60°C) $m/e = 594.1$ [M^+]. Anal. Calcd. for $\text{C}_{31}\text{H}_{59}\text{ClO}_4\text{P}_2\text{Ru}$: C, 53.64%; H, 8.57%; Cl, 5.11%; Ru, 14.55%. Found: C, 52.12%; H, 9.01%; Cl, 6.01%; Ru, 13.88%. $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, toluene, –30°C): $\delta = 139.2$ (d, $^2J(\text{PP}) = 75$ Hz, $\text{P}(\text{OEt})_3$), 32.7 (d, $^2J(\text{PP}) = 75$ Hz, $\text{P} \sim \text{O}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.90 MHz, CDCl_3 , 22°C): $\delta = 90.0$ (s, C_5Me_5), 70.1 (s, CH_2O of $\text{P} \sim \text{O}$), 61.0 (d, $^2J(\text{PC}) = 8.7$ Hz, OCH_2 of $\text{P}(\text{OEt})_3$), 58.0 (s, OCH_3), 38.8, 37.4 (d, $^1J(\text{PC}) = 18.5$ and 22.9 Hz, PCH), 29.5–26.6 (m, CH_2 of C_6H_{11}), 23.0 (d, $^1J(\text{PC}) = 16.6$ Hz, PCH_2), 16.3 (d, $^3J(\text{PC}) = 6.6$ Hz, CH_3 of $\text{P}(\text{OEt})_3$), 10.0 (s, C_5Me_5).

3.2. [Dicyclohexyl(2-methoxyethyl)phosphine-*O,P*](pentamethylcyclopentadienyl)(triethylphosphite)ruthenium(II) tetraphenylborate (**3b**)

A mixture of 500 mg (0.72 mmol) of **2b** and 246 mg (0.72 mmol) of NaBPh_4 in 40 ml of CH_2Cl_2 was stirred for 24 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*-pentane to give a dark yellow precipitate which was collected by filtration (G3) and dried under reduced pressure. Yield 577 mg (82%); mp. 63°C (dec); MS (FD, 60°C) $m/e = 658.7$ [$\text{M}^+ - \text{BPh}_4$]. Anal. Calcd. for $\text{C}_{55}\text{H}_{79}\text{BO}_4\text{P}_2\text{Ru}$: C, 67.55%; H, 8.14%; Ru, 10.33%. Found: C, 67.42%; H, 8.23%; Ru, 10.50%. $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, CH_2Cl_2 , –30°C): $\delta = 139.0$ (d, $^2J(\text{PP}) = 65.5$ Hz, $\text{P}(\text{OEt})_3$), 57.8 (d, $^2J(\text{PP}) = 65.5$ Hz, $\text{P} \sim \text{O}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.15 MHz, CD_2Cl_2 , 22°C): $\delta = 164.4$ (q, $^1J(\text{CB}) = 49.8$ Hz, *ipso*-C of BPh_4), 136.2–122.1 (m, C–Ph), 89.8 (s, C_5Me_5),

77.4 (s, CH_2O of $\text{P} \sim \text{O}$), 68.0 (s, OCH_3), 62.2 (d, $^2J(\text{PC}) = 8.3$ Hz, OCH_2 of $\text{P}(\text{OEt})_3$), 41.2, 34.9 (d, $^1J(\text{PC}) = 25.6$ and 16.9 Hz, PCH), 30.1–26.7 (m, CH_2 of C_6H_{11}), 21.5 (d, $^1J(\text{PC}) = 18.1$ Hz, PCH_2), 16.6 (d, $^3J(\text{PC}) = 6.9$ Hz, CH_3 of $\text{P}(\text{OEt})_3$), 11.2 (s, C_5Me_5).

3.3. Carbonyl[dicyclohexyl(2-methoxyethyl)phosphine-*P*](pentamethylcyclopentadienyl)(η^1 -*S*-sulphur dioxide)ruthenium(II) tetraphenylborate (**4a**)

Sulphur dioxide was bubbled for 5 min into a solution of **3a** (200 mg, 0.24 mmol) in 5 ml of CH_2Cl_2 at ambient temperature. Precipitation with *n*-hexane (20 ml) gives a pale yellow solid. The precipitate was collected by filtration (G3) and dried under a stream of argon. Yield 206 mg (95%); MS (FAB, 50°C) $m/e = 584.9$ [$\text{M}^+ - \text{BPh}_4$]. Anal. Calcd. for $\text{C}_{50}\text{H}_{64}\text{BO}_4\text{PRuS} \cdot \text{CH}_2\text{Cl}_2$: C, 61.28%; H, 6.65%; Ru, 10.10%; S, 3.21%. Found: C, 60.97%; H, 7.11%; Ru, 9.84%; S, 2.82%. IR (KBr): $\nu(\text{CO}) = 2016$ cm^{-1} (vs), $\nu(\text{SO}_2) = 1310$ (m), 1131 (s), 1124 (s) cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, CH_2Cl_2 , –30°C): $\delta = 39.9$ (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (62.90 MHz, CD_2Cl_2 , 22°C): $\delta = 199.6$ (d, $^2J(\text{PC}) = 16.2$ Hz, CO), 165.2 (q, $^1J(\text{CB}) = 49.4$ Hz, *ipso*-C of BPh_4), 136.7–122.5 (m, C–Ph), 106.6 (s, C_5Me_5), 68.1 (d, $^2J(\text{PC}) = 3.6$ Hz, CH_2O), 58.5 (s, OCH_3), 40.4, 39.7 (d, $^1J(\text{PC}) = 22.4$ and 22.1 Hz, PCH), 30.3–26.2 (m, CH_2 of C_6H_{11}), 23.5 (d, $^1J(\text{PC}) = 26$ Hz, PCH_2), 10.4 (s, C_5Me_5).

3.4. [Dicyclohexyl(2-methoxyethyl)phosphine-*P*](pentamethylcyclopentadienyl)(η^1 -*S*-sulphur dioxide)(triethylphosphite)ruthenium(II) tetraphenylborate (**4b**)

Sulphur dioxide was passed through a solution of **3b** (250 mg, 0.26 mmol) in 20 ml of CH_2Cl_2 at room temperature. After 5 min of stirring the solvent was removed under reduced pressure. The residue was washed with 10 ml of *n*-pentane to give a yellow precipitate, which was collected by filtration (G3) and dried in vacuo to yield 270 mg (100%) of **4b**; mp. 88°C (dec); MS (FD, 60°C) $m/e = 722.9$ [$\text{M}^+ - \text{BPh}_4$]. Anal. Calcd. for $\text{C}_{55}\text{H}_{79}\text{BO}_6\text{P}_2\text{RuS}$: C, 63.39%; H, 7.64%; Ru, 9.69%; S, 3.08%. Found: C, 63.72%; H, 7.81%; Ru, 9.83%; S, 3.63%. IR (KBr): $\nu(\text{SO}_2) = 1273$ (m), 1112 (vs) cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ NMR (32.39 MHz, CH_2Cl_2 , –30°C): $\delta = 128.0$ (d, $^2J(\text{PP}) = 50$ Hz, $\text{P}(\text{OEt})_3$), 31.5 (d, $^2J(\text{PP}) = 50$ Hz, $\text{P} \sim \text{O}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (20.15 MHz, CD_2Cl_2 , 22°C): $\delta = 164.3$ (q, $^1J(\text{CB}) = 49.4$ Hz, *ipso*-C of BPh_4), 136.2–122.0 (m, C–Ph), 104.9 (s, C_5Me_5), 68.6 (d, $^2J(\text{PC}) = 5.4$ Hz, CH_2O of $\text{P} \sim \text{O}$), 64.9 (d, $^2J(\text{PC}) = 10.7$ Hz, OCH_2 of $\text{P}(\text{OEt})_3$), 58.7 (s, OCH_3), 37.3 (d, $^1J(\text{PC}) = 23.8$ Hz, PCH), 30.1–26.3 (m, CH_2 of C_6H_{11}), 23.7 (d, $^1J(\text{PC}) = 23.4$ Hz, PCH_2), 15.9 (d, $^3J(\text{PC}) = 7.7$ Hz, CH_3 of $\text{P}(\text{OEt})_3$), 10.5 (s, C_5Me_5).

3.5. Carbonyl[dicyclohexyl(2-methoxyethyl)phosphine-P](η^2 -ethene)(pentamethylcyclopentadienyl)ruthenium(II) tetraphenylborate (**5a**)

A solution of **3a** (300 mg, 0.36 mmol) in 20 ml of CH_2Cl_2 was stirred for 30 min under an ethene atmosphere (1 bar) at room temperature. The solvent was removed completely under vacuum and the residue was washed with 10 ml of *n*-pentane. The pale beige precipitate was collected by filtration (G3) and dried in vacuo to yield 312 mg (100%) of **5a**; MS (FD, 60°C) m/e = 549.0 [$\text{M}^+ - \text{BPh}_4$]. Anal. Calcd. for $\text{C}_{52}\text{H}_{68}\text{BO}_2\text{PRu}$: C, 71.96%; H, 7.90%; Ru, 11.64%. Found: C, 71.64%; H, 7.56%; Ru, 12.06%. IR (KBr): $\nu(\text{CO}) = 1970$ (vs) cm^{-1} . $^{31}\text{P}(\text{H})$ NMR (32.39 MHz, CH_2Cl_2 , -30°C): $\delta = 43.4$ (s). $^{13}\text{C}(\text{H})$ NMR (20.15 MHz, CD_2Cl_2 , 22°C): $\delta = 208.0$ (d, $^2J(\text{PC}) = 18.1$ Hz, CO), 164.5 (q, $^1J(\text{CB}) = 49.3$ Hz, *ipso*-C of BPh_4), 136.4–122.0 (m, C–Ph), 101.3 (s, C_5Me_5), 68.2 (s, CH_2O), 58.2 (s, OCH_3), 47.9 (s, C=C), 39.7 (d, $^1J(\text{PC}) = 23.0$ Hz, PCH), 30.3–26.2 (m, CH_2 of C_6H_{11}), 24.7 (d, $^1J(\text{PC}) = 24.4$ Hz, PCH $_2$), 9.9 (s, C_5Me_5).

3.6. Benzylidenecarbene(carbonyl)[dicyclohexyl(2-methoxyethyl)phosphine-P](pentamethylcyclopentadienyl)ruthenium(II) tetraphenylborate (**6a**)

A solution of **3a** (430 mg, 0.51 mmol) in 20 ml of CH_2Cl_2 was treated with phenylacetylene (52 mg, 0.51 mmol) and was stirred for 5 min at room temperature. The solvent was removed completely in vacuo and the residue was washed with 10 ml of *n*-pentane. The brownish orange precipitate was collected by filtration (G3), washed several times with 10 ml of *n*-pentane and dried in vacuo yielding 441 mg (92%) of **6a**; mp. 57°C (dec); MS (FD, 60°C) m/e = 622.8 [$\text{M}^+ - \text{BPh}_4$]. Anal. Calcd. for $\text{C}_{58}\text{H}_{70}\text{BO}_2\text{PRu}$: C, 73.95%; H, 7.49%; Ru, 10.72%. Found: C, 73.54%; H, 7.82%; Ru, 10.37%. IR (KBr): $\nu(\text{CO}) = 1980$ (vs) cm^{-1} , $\nu(\text{C}=\text{C}) = 1625$ (s) cm^{-1} . $^{31}\text{P}(\text{H})$ NMR (32.39 MHz, CH_2Cl_2 , -30°C): $\delta = 53.0$ (s). $^{13}\text{C}(\text{H})$ NMR (20.15 MHz, CD_2Cl_2 , -30°C): $\delta = 368.2$ (d, $^2J(\text{PC}) = 12.7$ Hz, Ru=C), 200.1 (d, $^2J(\text{PC}) = 15.7$ Hz, CO), 163.8 (q, $^1J(\text{CB}) = 49.2$ Hz, *ipso*-C of BPh_4), 135.7–121.8 (m, C–Ph), 117.3 (s, CHC_6H_5), 106.4 (s, C_5Me_5), 67.8 (s, CH_2O), 58.6 (s, OCH_3), 37.3, 36.7 (d, $^1J(\text{PC}) = 25.8$ and 23.4 Hz, PCH), 29.6–24.1 (m, CH_2 of C_6H_{11} and PCH $_2$), 10.5

(s, C_5Me_5). ^1H NMR (80.13 MHz, CD_2Cl_2 , -30°C): $\delta = 7.4$ – 6.9 (m, 25H, Ph), 6.1 (d, $^4J(\text{PH}) = 2.2$ Hz, 1H, CHPh), 3.90–0.90 (m, 44H, alkanes), 1.98 (s, 15 H, Cp^*).

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