

Microwave-Assisted Organometallic Syntheses: Formation of Dinuclear [(Arene)Ru(μ -Cl)₃RuCl(L-L')] Complexes (L-L': Chelate Ligands with *P*-, *N*-, or *S*-Donor Atoms) by Displacement of Arene π Ligands

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Keywords: Dinuclear complexes / Microwave synthesis / Arene ligands / Phosphane ligands / Ruthenium

Microwave heating was employed to promote arene displacement in reactions of [(*p*-cymene)RuCl₂]₂ or [(1,3,5-C₆H₃iPr₃)RuCl₂]₂ with neutral chelate ligands L-L' [L-L': 1,1'-bis(diphenylphosphanyl)methane, 1,1'-bis(diphenylphosphanyl)ferrocene, (*S*)-BINAP, (*S,S*)-DIOP, *N,N'*-bis(2,4,6-trimethylphenyl)-1,2-ethanediyldenediamine], (*R*)-Ph-PHOX, and 3-(phenylsulfanylpropyl)diphenylphosphane. The reactions gave complexes of the general formula [(arene)Ru(μ -Cl)₃-RuCl(L-L')] in good yield. The synthesis of [(*p*-cymene)Ru(μ -

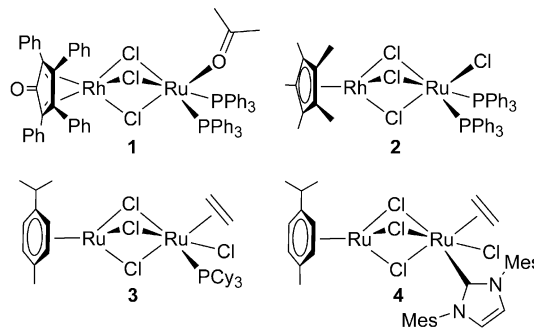
Cl)₃RuCl(PPh₂(CH₂)₃NH₂)] (**22**) was accomplished in two steps via the intermediate [(*p*-cymene)RuCl₂]₂{ μ -PPh₂(CH₂)₃-NH₂]} (**21**). The structures of [(1,3,5-C₆H₃iPr₃)Ru(μ -Cl)₃RuCl(dppf)] (**16**), [(1,3,5-C₆H₃iPr₃)Ru(μ -Cl)₃RuCl((*S*)-BINAP)] (**17**), and [(*p*-cymene)Ru(μ -Cl)₃RuCl(MesNCHCHNMe)] (**18**) were determined by single-crystal X-ray diffraction.

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Introduction

Dinuclear complexes, in which two different metal fragments are connected by either two or three halido bridges, have emerged as a promising class of catalysts. Complexes of this kind were employed for ring-opening and ring-closing metathesis reactions,^[1] for atom-transfer radical reactions,^[2] and for the oxidation of alcohols.^[3] The Rh^I-Ru^{II} complex **1**, for example, can be used as a catalyst for the Oppenauer-type oxidation of secondary alcohols under mild conditions,^[3a,3b] whereas the Rh^{III}-Ru^{II} complex **2**^[2e] and the Ru^{II}-Ru^{II} complex **3**^[2a,2c] are highly active catalysts for the atom-transfer radical addition of polychlorinated compounds to olefins. The *N*-heterocyclic carbene (NHC) complex **4**, on the other hand, is a good catalyst for metathesis reactions.^[1a]

The common feature of the above-mentioned complexes is that (π ligand)M fragments are connected through three chlorido bridges to Ru complexes with monodentate phosphane or NHC ligands. We were interested in developing a versatile synthetic route that would allow the preparation of structurally related complexes of the general formula [(π ligand)M(μ -Cl)₃RuCl(L-L')], L-L' being a neutral chelate



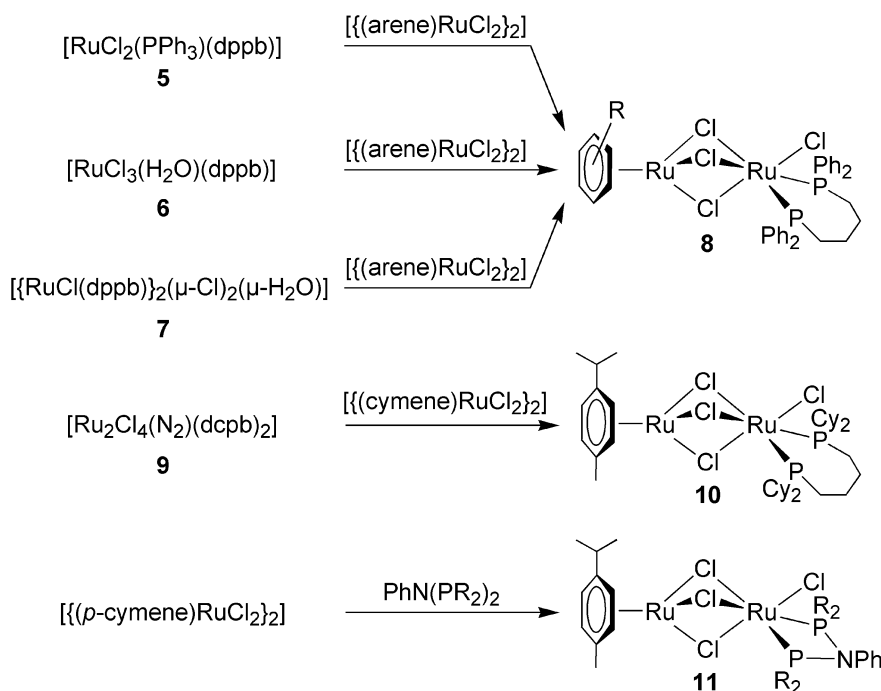
ligand containing *P*-, *N*-, or *S*-donor atoms. The incorporation of chelate ligands should be of interest for potential catalytic applications of such complexes.

A few examples of [(π ligand)M(μ -Cl)₃RuCl(L-L')] complexes have already been described. Complexes containing a RuCl(dppb) fragment [dppb: 1,4-bis(diphenylphosphanyl)butane] opposite to an (arene)Ru fragment were synthesized by starting from the mononuclear complexes **5**^[3c] and **6**^[4] or the dinuclear complex **7**^[5] (Scheme 1). The related 1,4-bis(dicyclohexylphosphanyl)butane (dcphb) complex **10** was obtained by reaction of the dinitrogen complex **9** with [(*p*-cymene)RuCl₂]₂.^[5] All these reactions require the utilization of preformed Ru(dppb) or Ru(dcphb) complexes. The synthesis of complexes with other chelate ligands instead of dppb or dcphb is therefore not straightforward.

Recently, Balakrishna et al. have shown that the dinuclear complex **11** can be obtained in an arene displacement reaction of [(*p*-cymene)RuCl₂]₂ with an aminobis(phosphonite) ligand (Scheme 1).^[6] We were wondering whether

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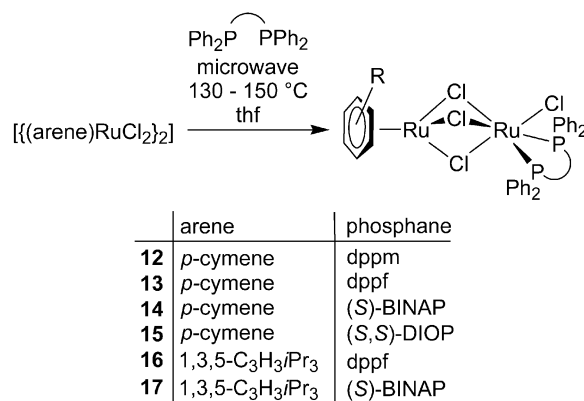


Scheme 1. Strategy for the synthesis of dinuclear ruthenium complexes containing bidentate phosphane ligands.

this type of reaction would be applicable to other chelate ligands. It is known that the exchange of arene ligands in (arene)Ru complexes is strongly dependent on the nature of the arene and the incoming ligand. For example, the displacement of an 1,3,5- $\text{C}_3\text{H}_3\text{iPr}_3$ ligand with the sterically demanding PCy_3 ligand can be achieved under mild conditions,^[2d] whereas the displacement of p -cymene with other arenes requires prolonged heating at $T > 160^\circ\text{C}$.^[7] To facilitate the potentially problematic arene exchange, we decided to employ microwave heating. This decision was inspired by recent findings of the group of Demonceau, who observed that microwave heating can promote atom-transfer radical reactions with $[(p\text{-cymene})\text{RuCl}_2(\text{PAr}_3)]$ complexes,^[8] reactions which are believed to require the release of the arene π ligand.^[2d,9] In this paper, we describe that $[(\text{arene})\text{Ru}(\mu\text{-Cl})_3\text{RuCl}(\text{L-L}')]_2$ complexes with a diverse set of chelate ligands L-L' can indeed be prepared by microwave-assisted arene displacement reactions.

Results and Discussion

In a first set of experiments, we focused on arene displacement reactions of $[(p\text{-cymene})\text{RuCl}_2]_2$ with the bidentate phosphane ligands 1,1'-bis(diphenylphosphanyl)methane (dppm), 1,1'-bis(diphenylphosphanyl)ferrocene (dppf), (S)-BINAP, and (S,S)-DIOP. It was found that the desired dinuclear complexes **12–15** were formed in good yield if the chlorido-bridged Ru complex and the respective ligand were heated in thf in a microwave reactor for 4 h at 150°C (Scheme 2). The products could be isolated by precipitation with n -hexane.



Scheme 2. Microwave-assisted synthesis of dinuclear ruthenium complexes containing P–P-chelate ligands.

The fact that the products contained the p -cymene π ligand and the phosphane ligand in a ratio 1:1 was established by NMR spectroscopy (^1H , ^{13}C , and ^{31}P). As a consequence of the chirality of the (S)-BINAP and the (S,S)-DIOP ligand, the ^{31}P NMR spectra of **14** and **15** showed two doublets instead of the singlets observed for **12** and **13**.

The synthetic procedure described above benefits from the high temperature, which can be achieved in the microwave reactor (a pressure increase of up to 7 bar was observed). For comparison, we have attempted the synthesis of the (S,S)-DIOP complex **15** under standard conditions by heating a thf solution of $[(p\text{-cymene})\text{RuCl}_2]_2$ and (S,S)-DIOP under reflux. But after 12 h, the complex $[\{\text{RuCl}_2(\text{cymene})\}_2\{\mu\text{-(S,S)-DIOP}\}]$ was formed in nearly quantitative yield instead of **15** as estimated by NMR spec-

troscopic investigations (^1H , ^{13}C , ^{31}P) of the crude mixture. By changing the solvent to 2-ethoxyethanol and increasing the reaction temperature to 130 °C, the target complex **15** could be isolated after 12 h of reaction time in lower yield (42%). These results clearly show the practical advantage of the microwave-assisted synthesis.

To test whether microwave heating could be used for the synthesis of dinuclear complexes with other (arene)Ru fragments, we then investigated the reaction $[\{(1,3,5\text{-C}_3\text{H}_3\text{iPr}_3)\text{RuCl}_2\}_2]$ with dppf and (*S*)-BINAP. Tris(isopropyl)benzene was chosen as the π ligand because its Ru complexes generally display a very good solubility in organic solvents.^[2b] Furthermore, it tends to undergo exchange reactions more easily than the standard *p*-cymene ligand.^[2d] In fact, heating an equimolar mixture of $[\{(1,3,5\text{-C}_3\text{H}_3\text{iPr}_3)\text{RuCl}_2\}_2]$ and the phosphane ligand to 130 °C for 4 h was sufficient to generate the dimeric complexes **16** and **17**. Similar to the *p*-cymene complexes, they were characterized by multinuclear NMR spectroscopy and elemental analysis. Furthermore, we were able to obtain single crystals, which were analyzed by X-ray crystallography. Both complexes show the expected structure with a $(1,3,5\text{-C}_3\text{H}_3\text{iPr}_3)\text{Ru}$ fragment connected through three chlorido bridges to a $\text{RuCl}(\text{dppf})$ or a $\text{RuCl}\{(\text{S})\text{-BINAP}\}$ fragment (Figures 1 and 2).^[10] The key bond lengths and angles of the complexes **16** and **17** are summarized in Table 1. Overall, they are similar to what has been observed for the dppb complex **8**.^[3c]

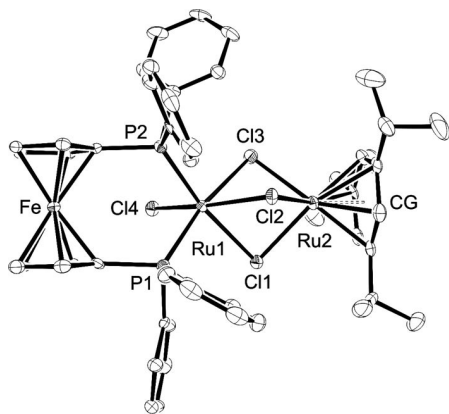


Figure 1. Molecular structure of complex **16** with ellipsoids at the 50% probability level. The co-crystallized solvent molecule (CH_2Cl_2) and the hydrogen atoms are omitted for clarity.

Next, we investigated whether chelate ligands with other donor atoms could be employed. Reactions of $[\{(p\text{-cymene})\text{RuCl}_2\}_2]$ with the *N*-*N'*-chelate *N,N'*-bis(2,4,6-trimethylphenyl)-1,2-ethanediyldenediamine, with the *P*-*S*-chelate 3-(phenylsulfanylpropyl)diphenylphosphane, or with the *N*-*P*-chelate (*R*)-(-)-2-[2-(diphenylphosphanyl)phenyl]-4-phenyl-2-oxazoline [(*R*)-Ph-PHOX] gave the dimeric products **18**, **19**, and **20** in good yields (Scheme 3). Microwave-assisted arene displacement reactions with the *P*-*N*-chelate 3-(diphenylphosphanyl)-1-propylamine, however, gave small amounts of side products, which were difficult to remove. For this ligand, the following two-step procedure was found to be advantageous: First, the dimer $[\{(p\text{-cymene})\text{RuCl}_2\}_2]$

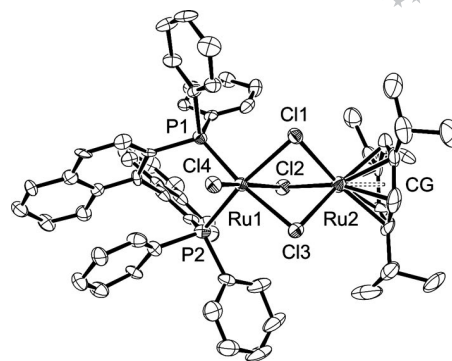


Figure 2. Molecular structure of complex **17** with ellipsoids at the 50% probability level. The co-crystallized solvent molecule (CH_2Cl_2) and the hydrogen atoms are omitted for clarity.

Table 1. Selected distances [\AA] and angles [$^\circ$] of the dinuclear complexes **16** and **17**.

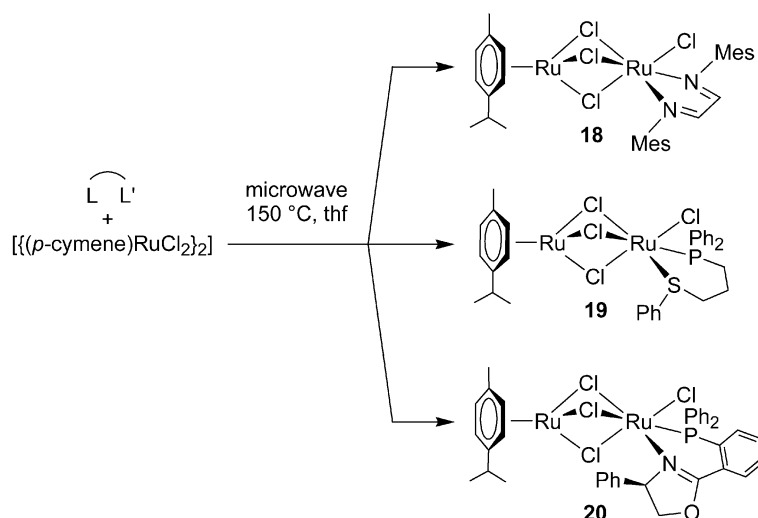
	16	17
Ru1–Cl1	2.541(1)	2.505(2)
Ru1–Cl2	2.444(1)	2.417(2)
Ru1–Cl3	2.541(1)	2.509(2)
Ru1–Cl4	2.388(1)	2.370(2)
Ru1–P1	2.270(1)	2.263(2)
Ru1–P2	2.272(1)	2.252(2)
CG ^[a] ...Ru2	1.639(2)	1.644(4)
Ru1...Ru2	3.332(1)	3.325(1)
Ru1–Cl1–Ru2	84.17(3)	84.99(7)
P1–Ru1–P2	95.28(4)	91.20(8)
Cl2–Ru1–Cl4	163.52(4)	164.94(7)

[a] CG: center of gravity.

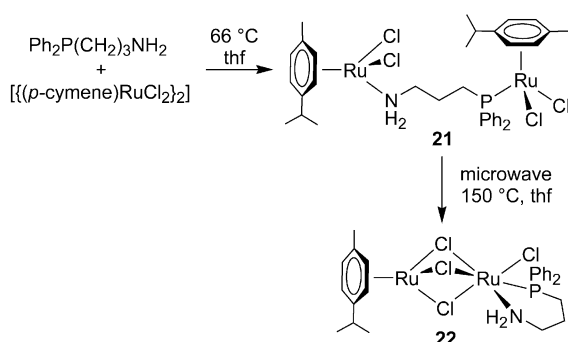
was heated with the ligand in thf for 5 min without microwave heating to give the dinuclear complex $[\{(p\text{-cymene})\text{RuCl}_2\}_2\{\mu\text{-PPH}_2(\text{CH}_2)_3\text{NH}_2\}]$ (**21**). Complex **21** was isolated by precipitation and then subjected to microwave heating at 150 °C in thf for 4 h to give the desired complex **22** in 70% isolated yield (Scheme 4).

Complexes **19**, **20**, and **22**, with *P*-*S*- and *P*-*N*-chelate ligands, are chiral (stereogenic metal center). As a consequence, four doublets are observed for the aromatic CH protons of the cymene π ligand and two doublets for the CH_3 groups of the *i*Pr side chain. Interestingly, only one set of signals was observed for complex **20** containing the chiral (*R*)-Ph-PHOX ligand. This indicates that compound **20** is formed in a highly diastereoselective fashion. A noteworthy feature of the NMR spectra of complex **18** is the apparent lack of symmetry for the two mesityl groups (e.g. three signals are observed for the CH_3 groups). This points to a hindered rotation around the C–N single bond. A related phenomenon has been observed for mononuclear Ru complexes with this bulky chelate ligand.^[11]

The structure of complex **18** was determined by single-crystal X-ray crystallography (Figure 3). The bond lengths between the ruthenium atoms and the chlorido ligands are similar to those of the phosphane complexes **16** and **17**: The average Ru–Cl distance to the bridging chlorido ligands is 2.45 \AA , and the Ru–Cl bond to the terminal chlorido ligand has a length of 2.3666(6) \AA . The bulky mesityl groups are



Scheme 3. Microwave-assisted direct synthesis of dinuclear ruthenium complexes containing *N*-*N'*-, *N*-*S*-, and *N*-*P*-chelate ligands.



Scheme 4. Two-step synthesis of complex **22**.

arranged nearly perpendicular to the plane defined by $\text{N}=\text{CH}-\text{CH}=\text{N}$ unit (80.4° and 87.9°). The $\text{Ru}-\text{N}$ bond

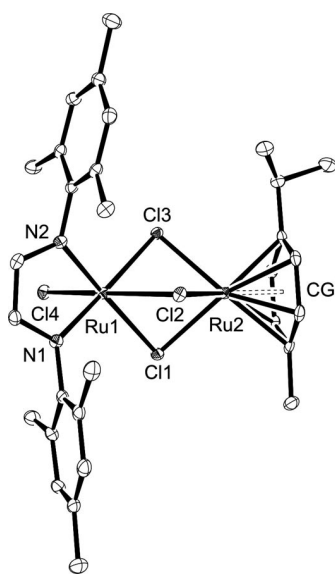


Figure 3. Molecular structure of complex **18** with ellipsoids at the 50% probability level. The two co-crystallized solvent molecules (CHCl_3) and the hydrogen atoms are omitted for clarity.

lengths of $1.9907(18)$ Å and $2.0047(18)$ Å are comparable to what has been observed for the α -diimine complexes $\text{cis}[\text{RuCl}_2(\text{CyNCHCHNCy})_2]$ ($2.01\text{--}2.06$ Å)^[12] and $[\text{CpRu}(\text{ToINCHCHNTol})(\text{C}_2\text{H}_4)](\text{OTf})$ [$2.052(4)$ and $2.055(4)$ Å].^[13] With $1.324(3)$ and $1.318(3)$ Å, the $\text{C}=\text{N}$ bonds are slightly enlarged as compared to what is found for free α -diimine ligands [$d(\text{C}=\text{N}) \approx 1.29$ Å]. This can be explained by π back-bonding into the π^* orbitals of the ligand, which have antibonding character with respect to the $\text{C}=\text{N}$ bond.^[14,15]

Conclusions

Over the last years, the utilization of microwave irradiation has become a standard tool in organic synthesis.^[16] Although this technique has been widely used for transition-metal-catalyzed reactions, there are relatively few reports about its application in preparative organometallic chemistry.^[17] We have found that microwave heating can facilitate arene exchange in reactions of $[(\text{arene})\text{RuCl}_2]_2$ complexes with neutral chelate ligands. The method was used for a variety of different ligands such as diphosphanes, a bulky α -diimine, a chiral *P*-*N*-, and nonchiral *P*-*N*- and *P*-*S*-chelates, and it is likely that many other chelate ligands can be employed as well. The fact that $[(\text{arene})\text{Ru}(\mu\text{-Cl})_3\text{RuCl}(\text{L}-\text{L}')]_2$ complexes with a diverse set of chelate ligands $\text{L}-\text{L}'$ are easily accessible should be of interest for potential applications in Ru-catalyzed reactions.

Experimental Section

General: The microwave syntheses were performed with a Biotage Initiator 2.0 instrument using 5-mL reaction vials (Biotage). All other reactions and manipulations were performed under an atmosphere of dry N_2 by using standard Schlenk techniques. The solvents were either dried by using a solvent purification system from Innovative Technologies, Inc. or distilled from appropriate drying agents. The NMR spectra (^1H , ^{13}C , ^{31}P) were recorded at room

temperature with a Bruker ADVANCE DPX 400 spectrometer or a Bruker ADVANCE-200 spectrometer. Chemical shifts are relative to solvent signals (CDCl_3 , $\delta_{\text{H}} = 7.24$ ppm, $\delta_{\text{C}} = 77.0$ ppm, CD_2Cl_2 , $\delta_{\text{H}} = 5.32$ ppm, $\delta_{\text{C}} = 53.8$ ppm) as internal references; $\delta(^{31}\text{P})$ are relative to external H_3PO_4 (85% in D_2O). In order to characterize higher-order spectra, the parameter N , the shift difference (given in Hz) between the outer lines, is introduced.^[18] Microanalyses (C, H, N) were performed with a EA 1110 CHN Carlo Erba instrument. The complexes $[(p\text{-cymene})\text{RuCl}_2]_2$ ^[19] and $[(1,3,5\text{-C}_6\text{H}_3\text{iPr}_3)\text{-RuCl}_2]_2$ ^[20] as well as the ligands 3-(diphenylphosphanyl)-1-propylamine,^[21] 3-(phenylsulfanylpentyl)diphenylphosphane,^[22] and N,N' -bis(2,4,6-trimethylphenyl)-1,2-ethanediylidenediamine,^[23] were prepared according to literature procedures. The compounds 1,1'-bis(diphenylphosphanyl)ferrocene, 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl [(S)-BINAP], *O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphanyl)butane [(S,S)-DIOP], (*R*)-(-)-2-[2-(diphenylphosphanyl)phenyl]-4-phenyl-2-oxazoline [(*R*)-Ph-PHOX], and 1,1'-bis(diphenylphosphanyl)methane (dppm) were commercially available (Aldrich, Fluka).

General Procedure for the Synthesis of Complexes 12–15: A vial containing a suspension of $[(p\text{-cymene})\text{RuCl}_2]_2$ (100 mg, 163 μmol) and the appropriate bidentate ligand [dppm, dppf, (S)-BINAP, (S,S)-DIOP; 0.163 mmol] in thf (2 mL) was sealed with a septum and subsequently heated with stirring for 4 h at 150 °C (pressure gains up to 7 bar). After allowing the solution to cool down to room temperature, the vial was opened, and *n*-hexane (3 mL) was added with stirring. The resulting orange precipitate was filtered off, washed with *n*-hexane (3 mL), and dried under vacuum.

[(*p*-Cymene)Ru($\mu\text{-Cl}$)₃RuCl(dppm)] (12): Yield: 122 mg (87%). ¹H NMR (200 MHz, CDCl_3): $\delta = 1.35$ [d, ³*J*(H,H) = 7.03 Hz, 6 H, CH(CH₃)₂], 2.34 (s, 3 H, CH₃), 2.95 [sept, ³*J*(H,H) = 7.03 Hz, 1 H, CH(CH₃)₂], 4.39 [dt, ²*J*(P,H) = 11.98, ²*J*(H,H) = 14.43 Hz, 1 H, CH₂], 5.38 ['d', *N* = 5.38 Hz, 2 H, CH(cymene)], 5.56 ['d', *N* = 5.38 Hz, 2 H, CH(cymene)], 7.12–7.76 (m, 20 H, *o*-, *m*-, *p*-CH) ppm. ¹³C NMR (50 MHz, CDCl_3): $\delta = 19.0$ (s, CH₃), 22.4 [s, CH(CH₃)₂], 31.3 [s, CH(CH₃)₂], 44.9 [s (br) CH₂], 78.2 [s, CH(cymene)], 79.1 [s, CH(cymene)], 95.9 [s, C(cymene)], 100.5 [s, C(cymene)], 123.8 ('dt', *N* = 19.6 Hz, *m*-CH), 125.4 [d, ⁴*J*(P,C) = 14.7 Hz, *p*-CH], 127.8 ('dt', *N* = 31.9 Hz, *o*-CH), 130.8 ('dt', *N* = 99.3 Hz, *i*-C) ppm. ³¹P NMR (81 MHz, CDCl_3): $\delta = 18.4$ (s) ppm. IR: $\tilde{\nu} = 3049$ (w), 2960 (w), 1435 (m), 1096 (m), 883 (w), 738 (m), 723 (s), 699 (s) cm⁻¹. C₃₅H₃₆Cl₄P₂Ru₂ (862.56): calcd. C 48.74, H 4.21; found C 48.34, H 4.13.

[(*p*-Cymene)Ru($\mu\text{-Cl}$)₃RuCl(dppf)] (13): Yield: 153 mg (91%). ¹H NMR (200 MHz, CDCl_3): $\delta = 1.26$ [d, ³*J*(H,H) = 6.85 Hz, 6 H, CH(CH₃)₂], 2.20 (s, 3 H, CH₃), 2.86 [sept, ³*J*(H,H) = 6.85 Hz, 1 H, CH(CH₃)₂], 4.00 [s (br), 2 H, CH(Cp)], 4.08 [s (br), 2 H, CH(Cp)], 4.17 [s (br), 2 H, CH(Cp)], 4.97 [s (br), 2 H, CH(Cp)], 5.21 ['d', *N* = 4.65 Hz, 2 H, CH(cymene)], 5.31 ['d', *N* = 4.65 Hz, 2 H, CH(cymene)], 7.12–7.86 (m, 20 H, *o*-, *m*-, *p*-CH) ppm. ¹³C NMR (50 MHz, CDCl_3): $\delta = 14.6$ (s, CH₃), 18.2 [s, CH(CH₃)₂], 26.8 [s, CH(CH₃)₂], 65.2 [m, *N* = 5.3 Hz, CH(Cp)], 67.9 [m, *N* = 6.2 Hz, CH(Cp)], 70.6 [m, *N* = 4.1 Hz, CH(Cp)], 73.8 [s, CH(cymene)], 74.2 ['t', *N* = 10.6 Hz, CH(Cp)], 75.0 [s, CH(cymene)], 80.2 ['t', *N* = 53.6 Hz, CH(Cp)], 90.7 [s, C(cymene)], 97.8 [s, C(cymene)], 122.6 [s (br), *p*-CH], 124.8 ('d', *N* = 39.2 Hz, *o*-CH), 131.0 ('dt', *N* = 19.6 Hz, *m*-CH), 133.8 ('dt', *N* = 99.3 Hz, *i*-C) ppm. ³¹P NMR (81 MHz, CDCl_3): $\delta = 59.6$ (s) ppm. IR: $\tilde{\nu} = 3062$ (w), 3045 (w), 2958 (w), 1481 (w), 1432 (m), 1160 (m), 1094 (m), 1029 (m), 812 (m), 748 (sh), 740 (m), 692 (s), 685 (s) cm⁻¹. C₄₄H₄₄Cl₄FeP₂Ru₂ (1034.56): calcd. C 51.08, H 4.29; found C 51.62, H 4.04.

[(*p*-Cymene)Ru($\mu\text{-Cl}$)₃RuCl{(S)-BINAP}] (14): Yield: 131 mg (73%). ¹H NMR (200 MHz, CDCl_3): $\delta = 1.30$ [d, ³*J*(H,H) = 7.09 Hz, 6 H, CH(CH₃)₂], 2.24 (s, 3 H, CH₃), 2.95 [sept, ³*J*(H,H) = 7.09 Hz, 1 H, CH(CH₃)₂], 5.31 ('d', *N* = 6.36 Hz, 2 H, CH), 5.48 ('d', *N* = 6.36 Hz, 2 H, CH), 6.26–8.14 [m, 32 H, *o*-, *m*-, *p*-CH, CH(naphthyl)] ppm. ¹³C NMR (50 MHz, CDCl_3): $\delta = 14.4$ (s, CH₃), 17.9 [s, CH(CH₃)₂], 18.2 [s, CH(CH₃)₂], 26.9 [s, CH(CH₃)₂], 27.0 [s, CH(CH₃)₂], 74.0 [s, CH(cymene)], 74.3 [s, CH(cymene)], 74.5 [s, CH(cymene)], 74.7 [s, CH(cymene)], 91.3 (s, 1 C), 97.6 (s, 1 C), 120.9–135.4 [C, CH(Ph, naphthyl)] ppm. ³¹P NMR (81 MHz, CDCl_3): $\delta = 54.7$ [d, ²*J*(P,P) = 41.6 Hz], 60.2 [d, ²*J*(P,P) = 41.6 Hz] ppm. IR: $\tilde{\nu} = 3054$ (w), 2961 (w), 1434 (w), 1089 (m), 813 (m), 742 (s), 696 (s) cm⁻¹. C₅₄H₄₆Cl₄P₂Ru₂ (1100.84): calcd. C 58.92, H 4.21; found C 58.67, H 4.20.

[(*p*-Cymene)Ru($\mu\text{-Cl}$)₃RuCl{(S,S)-DIOP}] (15): Yield: 108 mg (68%). ¹H NMR (200 MHz, CD_2Cl_2): $\delta = 1.19$ [m, 12 H, CH(CH₃)₂, C(CH₃)₂], 2.16 (s, 3 H, CH₃), 2.35 [m, 1 H, CH₂(DIOP)], 2.70 [m, 3 H, CH(CH₃)₂], CH(DIOP), 3.30 [m, 1 H, CH₂(DIOP)], 3.86 [m, 1 H, CH(DIOP)], 4.23 [m, 1 H, CH(DIOP)], 5.15 (m, 2 H, CH), 5.26 (m, 2 H, CH), 7.11–8.14 (m, 20 H, *o*-, *m*-, *p*-CH) ppm. ¹³C NMR (50 MHz, CDCl_3): $\delta = 14.3$ (s, CH₃), 17.8 [s, CH(CH₃)₂], 18.0 [s, CH(CH₃)₂], 22.5 [s, CH₃(DIOP)], 22.7 [s, CH₃(DIOP)], 23.7 [d, ¹*J*(P,C) = 30.1 Hz, CH₂(DIOP)], 26.8 [s (br), CH(CH₃)₂], 30.9 [d, ¹*J*(P,C) = 30.6 Hz, CH₂(DIOP)], 68.7 [d, ²*J*(P,C) = 12.3 Hz, CH(DIOP)], 74.0 [s, CH(cymene)], 74.3 [s, CH(cymene)], 74.5 [s, CH(cymene)], 74.6 [s, CH(cymene)], 75.7 [d, ²*J*(P,C) = 8.0 Hz, CH(DIOP)], 91.1 [s, C(cymene)], 97.1 [s, C(cymene)], 103.6 [s, C(DIOP)], 123.2–138.1 (*i*-C, *o*-, *m*-, *p*-CH) ppm. ³¹P NMR (81 MHz, CDCl_3): $\delta = 44.7$ [d, ²*J*(P,P) = 44.6 Hz], 51.5 [d, ²*J*(P,P) = 44.6 Hz] ppm. IR: $\tilde{\nu} = 3056$ (w), 2982 (w), 2919 (w), 2870 (w), 1433 (w), 1374 (w), 1242 (w), 1220 (sh), 1160 (w), 1093 (m), 1046 (s), 884 (m), 817 (m), 741 (s), 693 (s) cm⁻¹. C₄₁H₄₆Cl₄O₂-P₂Ru₂ (976.70): calcd. C 50.42, H 4.75; found C 50.35, H 4.77.

General Procedure for the Synthesis of Complexes 16 and 17: A vial containing a solution of $[(1,3,5\text{-C}_6\text{H}_3\text{iPr}_3)\text{RuCl}_2]_2$ (100 mg, 133 μmol) and the appropriate bidentate ligand [dppf or (S)-BINAP; 133 μmol] in thf (2 mL) was closed with a septum and subsequently heated with stirring for 4 h at 130 °C (pressure gains up to 6 bar). After allowing the solution to cool down to room temperature, the vial was opened, and *n*-hexane (3 mL) was added with stirring. The resulting orange precipitate was filtered off, washed with cold *n*-hexane (1 mL), and dried under vacuum.

[(1,3,5-C₆H₃iPr₃)Ru($\mu\text{-Cl}$)₃RuCl(dppf)] (16): Yield: 98 mg (67%). ¹H NMR (200 MHz, CDCl_3): $\delta = 1.27$ [d, ³*J*(H,H) = 6.85 Hz, 18 H, CH(CH₃)₂], 2.85 [sept, ³*J*(H,H) = 6.85 Hz, 3 H, CH(CH₃)₂], 3.98 [s (br), 2 H, CH(Cp)], 4.07 [s (br), 2 H, CH(Cp)], 4.14 [s (br), 2 H, CH(Cp)], 4.94 [s (br), 2 H, CH(Cp)], 5.21 (s, 3 H, CH), 7.21 (m, 12 H, *o*-, *p*-CH), 7.78 (m, 8 H, *m*-CH) ppm. ¹³C NMR (50 MHz, CDCl_3): $\delta = 18.5$ [s, CH(CH₃)₂], 27.0 [s, CH(CH₃)₂], 65.5 [m, CH(Cp)], 67.9 [m, CH(Cp)], 70.5 [m, CH(Cp)], 73.3 (s, CH), 74.3 [m, CH(Cp)], 83.6 [m, CH(Cp)], 122.5 [s (br), *p*-CH], 124.6 ('d', *N* = 36.8 Hz, *o*-CH), 130.9 ('dt', *N* = 22.7 Hz, *m*-CH), 133.2 (m, *i*-C) ppm. ³¹P NMR (81 MHz, CDCl_3): $\delta = 58.9$ (s) ppm. IR: $\tilde{\nu} = 3050$ (w), 2971 (w), 2918 (w), 2870 (w), 1434 (m), 1187 (w), 1099 (m), 1064 (m), 919 (w), 723 (s), 712 (sh), 695 (s) cm⁻¹. C₄₉H₅₂Cl₄FeP₂Ru₂ (1102.68): calcd. C 53.37, H 4.75; found C 53.54, H 4.79.

[(1,3,5-C₆H₃iPr₃)Ru($\mu\text{-Cl}$)₃RuCl{(S)-BINAP}] (17): Yield: 86 mg (55%). ¹H NMR (400 MHz, CDCl_3): $\delta = 1.29$ [d, ³*J*(H,H) = 7.09 Hz, 9 H, CH(CH₃)₂], 1.31 [d, ³*J*(H,H) = 7.07 Hz, 9 H, CH(CH₃)₂], 2.94 [sept, ³*J*(H,H) = 7.09 Hz, 3 H, CH(CH₃)₂], 5.26 (s, 3 H, CH), 6.27–7.55 [m, 32 H, *o*-, *m*-, *p*-CH, CH(naphthyl)]

ppm. ^{13}C NMR (101 MHz, CDCl_3): δ = 21.2 [s, $\text{CH}(\text{CH}_3)_2$], 22.7 [s, $\text{CH}(\text{CH}_3)_2$], 31.1 [s (br), $\text{CH}(\text{CH}_3)_2$], 73.5 (s, CH), 103.3 (s, 1 C), 124.7–136.7 [C, $\text{CH}(\text{Ph}$, naphthyl)] ppm. ^{31}P NMR (162 MHz, CDCl_3): δ = 53.7 [d, $^2J(\text{P},\text{P})$ = 41.6 Hz], 58.9 [d, $^2J(\text{P},\text{P})$ = 41.6 Hz] ppm. IR: $\tilde{\nu}$ = 3060 (w), 2958 (w), 2869 (w), 1433 (w), 1310 (w), 1089 (m), 815 (m), 739 (s), 696 (s) cm^{-1} . $\text{C}_{59}\text{H}_{56}\text{Cl}_4\text{P}_2\text{Ru}_2$ (1170.97): calcd. C 60.52, H 4.82; found C 60.22, H 4.79.

[(*p*-Cymene) $\text{Ru}(\mu\text{-Cl})_3\text{RuCl}(\text{MesNCHCHNMe})$] (18): A vial containing a suspension of [$\{(\textit{p}\text{-cymene})\text{RuCl}_2\}_2$] (306 mg, 500 μmol) and *N,N'*-bis(2,4,6-trimethylphenyl)-1,2-ethanediyldenediamine (146 mg, 500 μmol) in thf (20 mL) was sealed with a septum and subsequently heated with stirring for 5 h at 150 °C (pressure gains up to 9–10 bar). After allowing the solution to cool down to room temperature the vial was opened, and *n*-pentane (75 mL) was added with stirring. The resulting orange precipitate was filtered off, washed with ethyl ether (2 \times 15 mL), and dried under vacuum. Yield: 340 mg (88%). ^1H NMR (400 MHz, CDCl_3): δ = 1.18 [d, $^3J(\text{H},\text{H})$ = 6.90 Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.79 [s, 6 H, *o*- $\text{CH}_3(\text{Mes})$], 2.21 (s, 3 H, CH_3), 2.28 [s, 6 H, *o*- $\text{CH}_3(\text{Mes})$], 2.47 [s, 6 H, *p*- $\text{CH}_3(\text{Mes})$], 2.76 [sept, $^3J(\text{H},\text{H})$ = 6.90 Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 5.26 [‘d’, *N* = 5.90 Hz, 2 H, $\text{CH}(\text{cymene})$], 5.46 [‘d’, *N* = 5.90 Hz, 2 H, $\text{CH}(\text{cymene})$], 6.78 [s, 2 H, $\text{CH}(\text{Mes})$], 6.93 [s, 2 H, $\text{CH}(\text{Mes})$], 8.50 (s, 2 H, $\text{CH}=\text{N}$) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 18.9 (s, CH_3), 20.0 [s, $\text{CH}(\text{CH}_3)_2$], 21.1 [s, *o*- $\text{CH}_3(\text{Mes})$], 21.4 [s, *o*- $\text{CH}_3(\text{Mes})$], 22.3 [s, *p*- $\text{CH}_3(\text{Mes})$], 31.4 [s, $\text{CH}(\text{CH}_3)_2$], 77.8 [s, $\text{CH}(\text{cymene})$], 79.4 [s, $\text{CH}(\text{cymene})$], 96.2 [s, C(cymene)], 100.1 [s, C(cymene)], 128.5 (s, *m*-CH), 129.7 (s, *m*-CH), 130.8 (s, *i*-C), 133.2 (s, *o*-C), 136.6 (s, *o*-C), 150.7 (s, *p*-C), 165.6 (s, $\text{CH}=\text{N}$) ppm. $\text{C}_{30}\text{H}_{38}\text{Cl}_4\text{N}_2\text{Ru}_2 \cdot 1.5\text{CHCl}_3$ (949.65): calcd. C 39.84, H 4.19, N 2.95; found C 39.58, H 4.35, N 2.73.

[(*p*-Cymene) $\text{Ru}(\mu\text{-Cl})_3\text{RuCl}\{\text{PPh}_2(\text{CH}_2)_3\text{SPh}\}$] (19): A vial containing a suspension of [$\{(\textit{p}\text{-cymene})\text{RuCl}_2\}_2$] (100 mg, 163 μmol) and 3-(phenylsulfanylpropyl)-diphenylphosphane (55 mg, 0.163 mmol) in thf (2 mL) was sealed with a septum and subsequently heated with stirring for 4 h at 150 °C (pressure gains up to 7 bar). After allowing the solution to cool down to room temperature, the vial was opened, and *n*-hexane (3 mL) was added with stirring. The resulting orange precipitate was filtered off, washed with *n*-hexane (3 mL), and dried under vacuum. Yield: 104 mg (78%). ^1H NMR (200 MHz, CD_2Cl_2): δ = 1.29 [d, $^3J(\text{H},\text{H})$ = 7.09 Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.73 (m, 2 H, CH_2), 2.19 (s, 3 H, CH_3), 2.29 (m, 2 H, PPh_2CH_2), 2.83 [sept, $^3J(\text{H},\text{H})$ = 7.09 Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 2.85 (m, 1 H, SPhCH_2), 3.52 (m, 1 H, SPhCH_2), 5.29 (m, 2 H, CH), 5.47 (m, 2 H, CH), 7.33–7.89 (m, 25 H, *o*-, *m*-, *p*-CH, Ph) ppm. ^{13}C NMR (50 MHz, CD_2Cl_2): δ = 14.4 (s, CH_3), 17.9 [s, $\text{CH}(\text{CH}_3)_2$], 18.0 [s, $\text{CH}(\text{CH}_3)_2$], 18.7 [s (br), CH_2], 22.3 [d, $^1J(\text{P},\text{C})$ = 32.5 Hz, PPh_2CH_2], 27.0 [s, $\text{CH}(\text{CH}_3)_2$], 27.1 [s, $\text{CH}(\text{CH}_3)_2$], 32.0 (s, SPhCH_2), 32.1 (s, SPhCH_2), 73.7 [s, CH, (cymene)], 73.8 CH, (cymene), 74.8 [s (br), CH, (cymene)], 91.7 (s, 1 C), 96.1 (s, 1 C), 123.2 [d, $^2J(\text{P},\text{C})$ = 9.7 Hz, *o*-CH, (PPh_2)], 123.5 [d, $^2J(\text{P},\text{C})$ = 9.3 Hz, *o*-CH, (PPh_2)], 124.4 [s, *o*-CH, (SPh)], 125.0 [d, $^4J(\text{P},\text{C})$ = 2.5 Hz, *p*-CH, (PPh_2)], 125.1 [s, *p*-CH, (SPh)], 125.5 [d, $^4J(\text{P},\text{C})$ = 2.5 Hz, *p*-CH, (PPh_2)], 128.6 [s, *m*-CH, (SPh)], 129.3 [d, $^3J(\text{P},\text{C})$ = 9.2 Hz, *m*-CH, (PPh_2)], 129.7 [d, $^1J(\text{P},\text{C})$ = 44.7 Hz, *i*-C, (PPh_2)], 129.9 [s, *i*-C, (SPh)], 130.1 [d, $^3J(\text{P},\text{C})$ = 8.6 Hz, *m*-CH, (PPh_2)], 132.7 [d, $^1J(\text{P},\text{C})$ = 46.6 Hz, *i*-C, (PPh_2)] ppm. ^{31}P NMR (81 MHz, CD_2Cl_2): δ = 50.8 (s) ppm. IR: $\tilde{\nu}$ = 3053 (w), 2963 (w), 2922 (w), 2870 (w), 1471 (w), 1433 (m), 1089 (m), 757 (m), 750 (m), 740 (m), 699 (s), 694 (s) cm^{-1} . $\text{C}_{31}\text{H}_{35}\text{Cl}_4\text{PRu}_2\text{S}$ (814.60): calcd. C 45.71, H 4.33; found C 45.53, H 4.26.

[(*p*-Cymene) $\text{Ru}(\mu\text{-Cl})_3\text{RuCl}\{(\textit{R})\text{-Ph-PHOX}\}$] (20): A vial containing a suspension of [$\{(\textit{p}\text{-cymene})\text{RuCl}_2\}_2$] (100 mg, 163 μmol) and (*R*)-

(–)-2-[2-(diphenylphosphanyl)phenyl]-4-phenyl-2-oxazoline [(*R*)-Ph-PHOX] (66 mg, 163 μmol) in thf (2 mL) was sealed with a septum and subsequently heated with stirring for 4 h at 150 °C (pressure gains up to 7 bar). After allowing the solution to cool down to room temperature, the vial was opened, and the resulting violet precipitate was filtered off, washed with *n*-hexane (3 mL), and dried under vacuum. Yield: 120 mg (83%). ^1H NMR (400 MHz, CDCl_3): δ = 1.22 [d, $^3J(\text{H},\text{H})$ = 6.90 Hz, $\text{CH}(\text{CH}_3)_2$], 1.26 [d, $^3J(\text{H},\text{H})$ = 6.90 Hz, $\text{CH}(\text{CH}_3)_2$], 2.19 (s, 3 H, CH_3), 2.78 [sept, $^3J(\text{H},\text{H})$ = 6.90 Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 4.22 [dd, $^2J(\text{H},\text{H})$ = 8.30, $^3J(\text{H},\text{H})$ = 3.10 Hz, 1 H, OCH_2], 4.81 [dd, $^2J(\text{H},\text{H})$ = 8.60, $^3J(\text{H},\text{H})$ = 9.0 Hz, 1 H, OCH_2], 5.17 (m, 1 H, CH), 5.21 (m, 1 H, CH), 5.33 (m, 1 H, CH), 5.44 (m, 1 H, CH), 6.11 [dd, $^3J(\text{H},\text{H})$ = 9.40, $^3J(\text{H},\text{H})$ = 3.00 Hz, 1 H, NCH], 6.80–8.01 (m, 19 H, Ph) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 18.9 (s, CH_3), 22.4 [s, $\text{CH}(\text{CH}_3)_2$], 22.7 [s, $\text{CH}(\text{CH}_3)_2$], 30.9 [s, $\text{CH}(\text{CH}_3)_2$], 74.2 (s, NCH), 74.9 (s, OCH_2), 77.6 [s, CH, (cymene)], 77.8 CH, (cymene), 78.4 [s, CH, (cymene)], 78.8 [s, CH, (cymene)], 95.5 (s, C), 100.0 (s, C), 126.6 (s, *o*-CH, Ph), 127.0 (s, *p*-CH, Ph), 127.6 [d, $^3J(\text{P},\text{C})$ = 9.8 Hz, *m*-CH, PPh_2], 127.7 (s, *m*-CH, Ph), 128.0 [d, $^3J(\text{P},\text{C})$ = 10.3 Hz, *m*-CH, PPh_2], 129.2 [d, $^4J(\text{P},\text{C})$ = 2.2 Hz, CH, Ar], 129.6 [d, $^2J(\text{P},\text{C})$ = 11.9 Hz, C, P–Ph–Oxa], 130.0 [d, $^4J(\text{P},\text{C})$ = 1.5 Hz, CH, Ar], 130.2 (s, *p*-CH, Ar), 130.2 [d, $^2J(\text{P},\text{C})$ = 10.0 Hz, CH, P–Ph–Oxa], 131.9 [d, $^1J(\text{P},\text{C})$ = 43.9 Hz, *i*-C, P–Ph–Oxa], 132.0 [d, $^3J(\text{P},\text{C})$ = 6.6 Hz, CH, P–Ph–Oxa], 132.4 (br. s, *p*-CH, PPh_2), 133.5 [d, $^2J(\text{P},\text{C})$ = 9.6 Hz, *o*-CH, PPh_2], 135.5 [d, $^2J(\text{P},\text{C})$ = 10.4 Hz, *o*-CH, PPh_2], 136.4 [d, $^1J(\text{P},\text{C})$ = 47.7 Hz, *i*-C, PPh_2], 140.7 (s, *i*-C, Ph), 166.9 [d, $^3J(\text{P},\text{C})$ = 5.2 Hz, C=N] ppm. ^{31}P NMR (81 MHz, CD_2Cl_2): δ = 75.0 (s) ppm. IR: $\tilde{\nu}$ = 3088 (w), 3053 (w), 2955 (w), 2878 (w), 1432 (m), 1358 (m), 1220 (m), 1103 (m), 1094 (m), 922 (m), 762 (m), 721 (m), 687 (s), 667 (s) cm^{-1} . $\text{C}_{37}\text{H}_{36}\text{Cl}_4\text{NOPRu}_2$ (885.61): calcd. C 50.18, H 4.10, N 1.58; found C 50.11, H 3.90, N 1.72.

[(*p*-Cymene) $\text{RuCl}_2\}_2\{\mu\text{-PPh}_2(\text{CH}_2)_3\text{NH}_2\}$] (21): To a solution of [$\{(\textit{p}\text{-cymene})\text{RuCl}_2\}_2$] (100 mg, 163 μmol) in thf (2 mL) was added 3-(diphenylphosphanyl)-1-propylamine (40.0 mg, 163 μmol). The reaction mixture was heated under reflux for 5 min while an orange solid of [$\{\text{Ru}(\textit{p}\text{-cymene})\text{Cl}_2\}_2\{\mu\text{-PPh}_2(\text{CH}_2)_3\text{NH}_2\}$] precipitated. After cooling to room temperature, *n*-hexane (2 mL) was added with stirring. The latter complex was filtered off, washed with *n*-hexane (5 mL), and dried in vacuo. Yield: 131 mg (94%). ^1H NMR (200 MHz, CD_2Cl_2): δ = 0.88 [d, $^3J(\text{H},\text{H})$ = 6.85 Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.24 [d, $^3J(\text{H},\text{H})$ = 6.85 Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.35 (m, 2 H, CH_2), 1.70 [s (br) 2 H, NH_2], 1.88 (s, 3 H, CH_3), 2.12 (s, 3 H, CH_3), 2.48 [sept, $^3J(\text{H},\text{H})$ = 6.85 Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 2.56 (m, 2 H, PPh_2CH_2), 2.84 (m, 1 H, NH_2CH_2), 2.86 [sept, $^3J(\text{H},\text{H})$ = 6.85 Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.69 (m, 1 H, NH_2CH_2), 5.22 (m, 8 H, CH), 7.54 (m, 6 H, *o*-, *p*-CH), 7.83 (m, 4 H, *m*-CH) ppm. ^{31}P NMR (81 MHz, CDCl_3): δ = 23.9 (s) ppm. IR: $\tilde{\nu}$ = 3272 (w), 3056 (w), 2956 (w), 2867 (w), 1575 (m), 1466 (m), 1433 (m), 1099 (m), 1057 (m), 1017 (m), 878 (m), 798 (s), 750 (s), 697 (s) cm^{-1} .

[(*p*-Cymene) $\text{Ru}(\mu\text{-Cl})_3\text{RuCl}\{\text{PPh}_2(\text{CH}_2)_3\text{NH}_2\}$] (22): A vial containing a suspension of complex **21** (131 mg, 153 μmol) in thf (2 mL) was sealed with a septum and subsequently heated with stirring for 4 h at 150 °C. After allowing the solution to cool down to room temperature, the vial was opened, and *n*-hexane (3 mL) was added with stirring. The resulting orange precipitate was filtered off, washed with *n*-hexane (3 mL), and dried under vacuum. Yield: 70 mg (60%). ^1H NMR (200 MHz, CD_2Cl_2): δ = 1.27 [d, $^3J(\text{H},\text{H})$ = 6.85 Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.73 (m, 2 H, CH_2), 2.15 (s, 3 H, CH_3), 2.25 (m, 2 H, PPh_2CH_2), 2.31 [s (br), 2 H, NH_2], 2.78 (m, 1 H, NH_2CH_2), 2.88 [sept, $^3J(\text{H},\text{H})$ = 6.85 Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.27 (m, 1 H, NH_2CH_2), 5.33 (‘d’, *N* = 5.39 Hz, 2 H, CH), 5.47 (‘d’, *N* = 5.39 Hz, 2 H, CH), 7.32 (m, 4 H, CH), 7.50 (m, 4 H, CH), 7.31

Table 2. Crystallographic data for complexes **16** and **17**.

	16 ·CH ₂ Cl ₂	17 ·CH ₂ Cl ₂
Empirical formula	C ₅₀ H ₅₄ Cl ₆ FeP ₂ Ru ₂	C ₆₀ H ₅₈ Cl ₆ P ₂ Ru ₂
<i>M_r</i> [g mol ^{−1}]	1187.56	1255.84
Crystal size [mm]	0.33 × 0.30 × 0.21	0.29 × 0.15 × 0.12
Crystal system	orthorhombic	orthorhombic
Space group	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> [Å]	23.2709(13)	12.2164(13)
<i>b</i> [Å]	21.1710(11)	14.9287(15)
<i>c</i> [Å]	9.8172(6)	29.150(3)
<i>V</i> [Å ³]	4836.6(5)	5316.3(9)
<i>Z</i>	4	4
$\rho_{\text{calcd.}}$ [g cm ^{−3}]	1.631	1.569
Absorption coeff. [mm ^{−1}]	1.345	0.970
<i>F</i> (000)	2400	2552
θ range [°]	3.26 to 25.03	2.80 to 25.03
Index ranges <i>h</i> , <i>k</i> , <i>l</i>	−27−27, −25−25, −10−10	−14−14, −17−15, −34−34
Refln. collected	29237	32700
Refln. independent	7982	9369
Data/parameters/restraints	7982/550/1	9369/ 631/0
Goodness-of-fit on <i>F</i> ²	0.825	0.766
<i>R</i> 1 (Σ)/ <i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0358/ 0.0260	0.0933/0.0483
<i>wR</i> 2 (Σ)/ <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0380/ 0.0363	0.0824/0.0711
<i>T</i> _{min} / <i>T</i> _{max}	0.7993/0.8639	0.7739/0.9617
Largest diff. peak/hole [e Å ^{−3}]	0.363/−0.426	0.776/−0.732

(m, 6 H, CH), 7.50 (m, 2 H, CH), 7.70 (m, 6 H, CH) ppm. ¹³C NMR (50 MHz, CD₂Cl₂): δ = 14.6 (s, CH₃), 17.8 [s (br), CH₂], 18.0 [s, CH(CH₃)₂], 21.5 [s, CH(CH₃)₂], 22.2 [d, ¹*J*(P,C) = 30.6 Hz, PPh₂CH₂], 26.7 [s, CH(CH₃)₂], 27.1 [s, CH(CH₃)₂], 38.2 (s, NH₂CH₂), 38.3 (s, NH₂CH₂), 73.4 [s, CH, (cymene)], 73.7 CH, (cymene), 73.9 [s, CH, (cymene)], 74.2 [s, CH, (cymene)], 91.5 (s, 1 C), 96.3 (s, 1 C), 123.2 [d, ²*J*(P,C) = 9.2 Hz, *o*-CH], 123.4 [d, ²*J*(P,C) = 9.2 Hz, *o*-CH], 124.3 [d, ⁴*J*(P,C) = 2.5 Hz, *p*-CH], 125.0 [d, ⁴*J*(P,C) = 1.8 Hz, *p*-CH], 128.4 [d, ³*J*(P,C) = 8.6 Hz, *m*-CH], 130.1 [d, ³*J*(P,C) = 9.8 Hz, *m*-CH], 132.6 [d, ¹*J*(P,C) = 44.7 Hz, *i*-C], 134.3 [d, ¹*J*(P,C) = 42.9 Hz, *i*-C] ppm. ³¹P NMR (81 MHz, CD₂Cl₂): δ = 60.8 (s) ppm. IR: $\tilde{\nu}$ = 3053 (w), 2957 (w), 2917 (w), 2867 (w), 1432 (m), 1091 (m), 985 (m), 923 (w), 811 (w), 742 (s), 692 (s) cm^{−1}.

C₂₅H₃₂Cl₄NPRu₂·0.5CH₂Cl₂ (763.92): calcd. C 40.09, H 4.35; found C 40.25, H 4.45.

X-ray Crystallography: Intensity data for **16** and **17** were collected by using an Oxford Diffraction KM-4 CCD diffractometer, whereas in the case of **18** a Bruker APEX II CCD was employed, both having kappa geometry and using graphite monochromatized Mo-*K*_α radiation (λ = 0.71073 Å) at low temperature. A summary of the crystallographic data, the data collection parameters, and the refinement parameters are given in Tables 2 and 3. Data reduction was carried out with CrysAlis PRO^[24](**16**, **17**) and EvalCCD^[25](**18**) and then corrected for absorption.^[26] Structure solution and refinement were performed with the SHELXTL software package.^[27] The structures were refined by using the full-matrix least-squares routines on *F*². All non-hydrogen atoms were refined with anisotropic displacement parameters. H atoms were included to the models in calculated positions using the riding model. CCDC-705720 (**16**), CCDC-705721 (**17**), and CCDC-705722 (**18**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 3. Crystallographic data for complex **18**.

	18 ·2CHCl ₃
Empirical formula	C ₃₂ H ₄₀ Cl ₁₀ N ₂ Ru ₂
<i>M_r</i> [g mol ^{−1}]	1009.30
Crystal size [mm]	0.51 × 0.24 × 0.11
Crystal system	triclinic
Space group	<i>P</i> 1
<i>a</i> [Å], α [°]	11.1113(11), 98.573(8)
<i>b</i> [Å], β [°]	13.2579(14), 95.775(9)
<i>c</i> [Å], γ [°]	14.2479(17), 106.109(11)
<i>V</i> [Å ³]	1971.6(4)
<i>Z</i>	2
$\rho_{\text{calcd.}}$ [g cm ^{−3}]	1.700
Absorption coeff. [mm ^{−1}]	1.470
<i>F</i> (000)	1008
θ range [°]	3.31 to 27.50
Index ranges <i>h</i> , <i>k</i> , <i>l</i>	−14−14, −17−17, −18−18
Refln. collected	43358
Refln. independent	8968
Data/parameters/restraints	8968/0/415
Goodness-of-fit on <i>F</i> ²	1.119
<i>R</i> 1 (Σ)/ <i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0381/ 0.0234
<i>wR</i> 2 (Σ)/ <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0495/ 0.0446
<i>T</i> _{min} / <i>T</i> _{max}	1.0000/0.6305
Largest diff. peak/hole [e Å ^{−3}]	0.523/−0.572

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