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Dinuclear (Arene)ruthenium Complexes Containing a Chiral-at-Phosphorus Phosphanido Bridge

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Dedicated to Professor Hans-Ludwig Krauss on the occasion of his 80th birthday

Keywords: Arene ligands / Ruthenium / Tethered complexes / P ligands / Hydride ligands

The unsaturated diruthenium cation $[(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}p\text{-}i\text{PrMeC}_6H_4)Ru_2(\mu_2\text{-}H)_3]^+$ reacts with $PPh_2(CH_2)_3Ph$ to give the phosphanido complex $[(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}p\text{-}i\text{PrMeC}_6H_4)Ru_2\{\mu_2\text{-}PPh(CH_2)_3Ph\}(\mu_2\text{-}H)_2]^+$ (**1**), which contains a stereogenic phosphorus atom in the bridge, and benzene. Heating of **1** in bromobenzene gives the first chiral-at-phosphorus diruthenium complex $[(\eta^6\text{-}C_6Me_6)Ru_2\{\mu_2\text{-}PPh(CH_2)_3\text{-}\eta^6\text{-}Ph\}(\mu_2\text{-}Br)_2]^+$ (**3**) due to the replacement of the *p*-cymene ligand by the phenyl group at the pendant arm and hydrido bridges by bromido bridges. The single-crystal X-ray structure analysis of [**3**][BF_4] reveals a racemic mixture of both enantiomers (R_P)-**3** and (S_P)-**3** in the crystal. Similarly, the reaction of $[(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}p\text{-}i\text{PrMeC}_6H_4)Ru_2(\mu_2\text{-}H)_3]^+$ and the enantiopure phosphane (*R*)-$PPh_2(CH_2)_2CHMePh$ yields the complex $[(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}p\text{-}i\text{PrMeC}_6H_4)Ru_2\{\mu_2\text{-}(R)\text{-}PPh(CH_2)_2CHMePh\}(\mu_2\text{-}H)_2]^+$ (**4**) as a mixture of diastereomers. An optically active mixture (*de* = 4 %) of phosphanido-bridged complexes $[(\eta^6\text{-}C_6Me_6)Ru_2\{\mu_2\text{-}(R)\text{-}PPh(CH_2)_2CHMe\text{-}\eta^6\text{-}Ph\}(\mu_2\text{-}Br)_2]^+$ (**6**), containing the (R_C,S_P) and (R_C,R_P) diastereomers, is obtained upon heating of **4** in bromobenzene. The molecular structure of [**6**][BF_4] reveals that the two diastereomers (R_C,S_P)-**6** and (R_C,R_P)-**6** exist as two conformers. The non-chiral-at-phosphorus analogues $[(\eta^6\text{-}C_6Me_6)_2Ru_2\{\mu_2\text{-}PPh(CH_2)_3Ph\}(\mu_2\text{-}H)_2]^+$ (**2**) and $[(\eta^6\text{-}C_6Me_6)_2Ru_2\{\mu_2\text{-}(R)\text{-}PPh(CH_2)_2CHMePh\}(\mu_2\text{-}H)_2]^+$ (**5**) have also been synthesized and structurally characterized by single-crystal X-ray structure analyses of [**2**][BF_4] and [**5**][BF_4].

Introduction

(Arene)ruthenium complexes, in spite of their venerable history, have not lost their fascination thanks to their rich and diversified chemistry.[1] An increasing number of catalytic reactions involving (arene)ruthenium complexes, such as transfer hydrogenation reactions,[2] alkene metathesis[3] or Diels–Alder reactions,[4] have contributed to the steadily growing interest in these complexes, which owe their fertility and versatility mainly to the stability of the arene–ruthenium bond. The complete loss of the arene ligand can be an undesired side-reaction during a catalytic process, although the stability of the (arene)ruthenium moiety can be increased by arene ligands containing chelating substituents.[5] The synthesis of such (arene)ruthenium complexes can be achieved by intramolecular arene ligand exchange at the ruthenium atom, which works only if either an electron-poor arene ligand is replaced by an electron-rich one[6] or if the reaction can take advantage of the chelate effect.[5] Thus, examples of tethered (arene)ruthenium complexes containing oxygen,[7] phosphorus,[5,6,8] sulfur[9] and carbon or nitrogen[10] donor atoms have been reported.

Recently, we found that the unsaturated dinuclear cation $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ reacts with tertiary phosphanes such as PPh_3 and $PPhMe_2$ to give the phosphanido-bridged complexes $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PR_2)(\mu_2\text{-}H)_2]^+$ (R = Ph, Me) and benzene.[11] The reaction proceeds by P–C activation intermediates containing a bridging phenyl ligand, $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PR_2)(\mu_2\text{-}Ph)(\mu_2\text{-}H)]^+$ (R = Ph, Me), and the phenyl derivative is isolated as the tetrafluoroborate salt. This P–C bond-cleavage reaction occurs even in the case of trialkylphosphanes such as P*n*Bu_3 and P*n*Oct_3 to give the cations $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PR_2)(\mu_2\text{-}H)_2]^+$ (R = *n*Bu, *n*Oct) and the corresponding olefin and dihydrogen.[11] The diphenylphosphanido derivative $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}H)_2]^+$ turned out to be a highly selective catalyst for hydrogenation of carbon–carbon double bonds.[12]

The mixed dinuclear (arene)trihydridoruthenium complex $[(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}p\text{-}i\text{PrMeC}_6H_4)Ru_2(\mu_2\text{-}H)_3]^+$, which we synthesized recently,[13] reacts with phosphanes in the same way as its symmetrical analogue, $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$, although, because of the asymmetry of the diruthenium backbone, the reaction with mixed phosphanes allows

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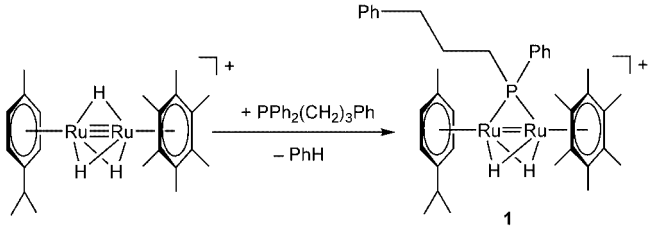
the synthesis of phosphanido-bridged diruthenium complexes that are chiral at the phosphorus atom. Moreover, the use of mixed phosphanes containing a phenyl substituent at the end of a pendant arm should give access to tethered P-chiral diruthenium complexes.

In this paper, we report the synthesis of the first tethered chiral-at-phosphorus diruthenium complex, $[(\eta^6\text{-}C_6Me_6)Ru_2\{\mu_2\text{-}PPh(CH_2)_3\text{-}\eta^6\text{-}Ph\}(\mu_2\text{-}Br)_2]^+$ (**3**), which was obtained as a racemic mixture by heating of $[(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}p\text{-}i\text{PrMeC}_6H_4)Ru_2\{\mu_2\text{-}PPh(CH_2)_3Ph\}(\mu_2\text{-}H)_2]^+$ (**1**) in bromobenzene. The enantiopure phosphane (*R*)-$PPh_2(CH_2)_2$-CHMePh, reported by Zenneck et al.,[8c] gave an optically active mixture of the diastereomeric complexes (R_C,S_P)- and (R_C,R_P)-$[(\eta^6\text{-}C_6Me_6)Ru_2\{\mu_2\text{-}(R)\text{-}PPh(CH_2)_2CHMe\text{-}\eta^6\text{-}Ph\}(\mu_2\text{-}Br)_2]^+$ (**6**).

Results and Discussion

The dinuclear trihydrido complex $[(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}i\text{PrMeC}_6H_4)Ru_2(\mu_2\text{-}H)_3]^+$ reacts with the mixed phosphane $PPh_2(CH_2)_3Ph$, which was recently reported by Wright et al.,[5] to give the phosphanido-bridged complex $[(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}p\text{-}i\text{PrMeC}_6H_4)Ru_2\{\mu_2\text{-}PPh(CH_2)_3Ph\}(\mu_2\text{-}H)_2]^+$ (**1**; Scheme 1). The reaction was carried out at 55 °C in dichloromethane solution, and the yield of [**1**][BF_4] can be increased from 30% to 38% by performing the reaction under hydrogen pressure (3 bar). The reason for the use of hydrogen in this reaction is the conversion of the intermediate $[(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}p\text{-}i\text{PrMeC}_6H_4)Ru_2\{\mu_2\text{-}PPh(CH_2)_3Ph\}(\mu_2\text{-}Ph)(\mu_2\text{-}H)]^+$, which was observed by mass spectrometry in accordance with the fully characterized analogue $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}PPh_2)(\mu_2\text{-}Ph)(\mu_2\text{-}H)]^+$,[11] into **1** by reaction with H_2.



Scheme 1. Synthesis of $[(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}p\text{-}i\text{PrMeC}_6H_4)Ru_2\{\mu_2\text{-}PPh(CH_2)_3Ph\}(\mu_2\text{-}H)_2]^+$ (**1**).

Complex **1** possesses a stereogenic phosphanido bridge and was obtained as a racemic mixture since the nucleophilic attack of the phosphane occurs at one of the two ruthenium atoms and none of the two P–$C_{(aryl)}$ bonds is preferentially cleaved. The two hydrido ligands in **1** are diastereotopic, as seen by the ^{1}H NMR spectrum, which exhibits two doublets of doublets in the hydride region at δ = –14.65 (dd, $^2J_{H,H}$ = 2.8, $^2J_{H,P}$ = 28 Hz, 1 H) and –16.06 (dd, $^2J_{H,H}$ = 2.8, $^2J_{H,P}$ = 31 Hz, 1 H) ppm. The two enantiomers of **1** are shown in Figure 1.

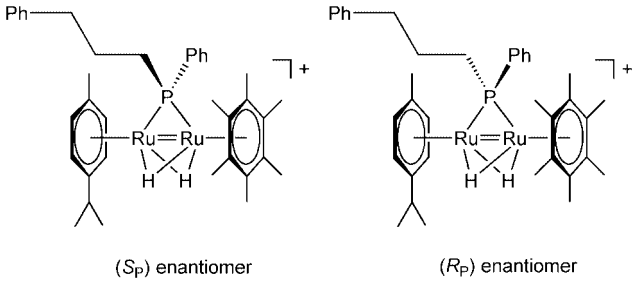


Figure 1. The two enantiomers of $[(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}p\text{-}i\text{PrMeC}_6H_4)Ru_2\{\mu_2\text{-}PPh(CH_2)_3Ph\}(\mu_2\text{-}H)_2]^+$ (**1**).

As we failed to obtain crystals of [**1**][BF_4] suitable for X-ray structure analysis, we synthesized an achiral analogue of **1** containing two hexamethylbenzene ligands. The cation $[(\eta^6\text{-}C_6Me_6)_2Ru_2\{\mu_2\text{-}PPh(CH_2)_3Ph\}(\mu_2\text{-}H)_2]^+$ (**2**) is accessible in the same way as **1** from $PPh_2(CH_2)_3Ph$ and $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ (Scheme 2). The reaction was carried out under the same conditions as for **1** (CH_2Cl_2, 55 °C, 3 bar H_2) and, in this case, the yield of the reaction was much higher (85%). Dark-red crystals of [**2**][BF_4] suitable

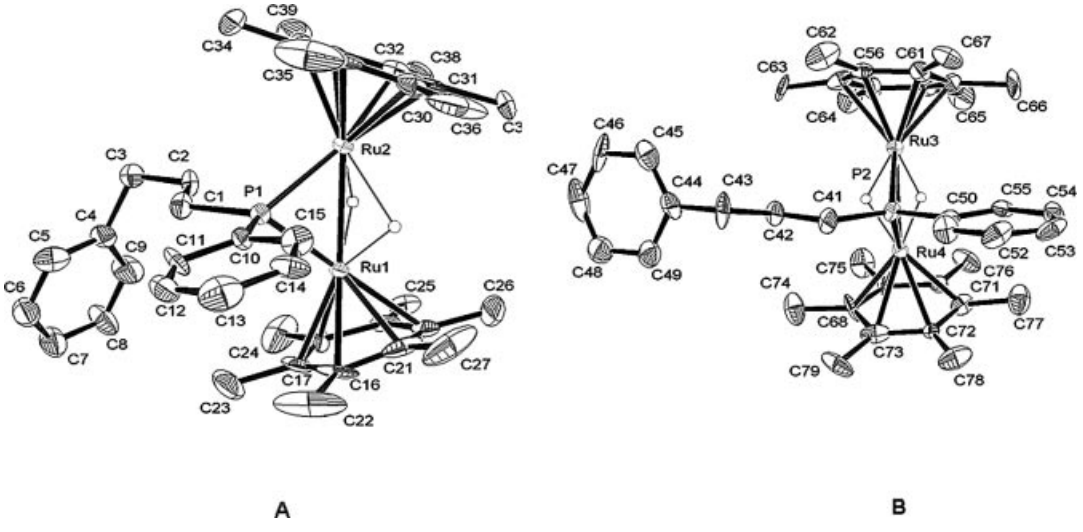
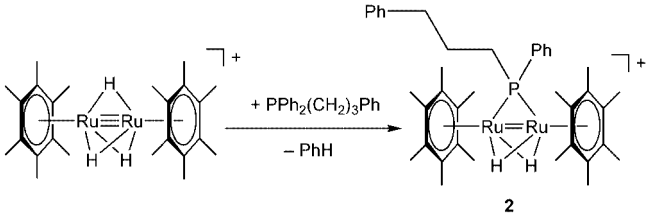


Figure 2. Molecular structure of the two independent molecules of cation **2** (anions, solvent molecules, and hydrogen atoms, except for the hydrido ligands, have been omitted for clarity).

for X-ray structure analysis were obtained by slow diffusion of hexane into a concentrated dichloromethane solution of [**2**][BF_4]. The molecular structure of cation **2** is shown in Figure 2.



2

Scheme 2. Synthesis of [(η^6-C_6Me_6)$_2$$Ru_2${$\mu_2$-PPh$(CH_2)_3$Ph}($\mu_2$-H)$_2$]$^+$ (**2**).

The single-crystal X-ray structure analysis for cation **2** reveals a PPh$(CH_2)_3$Ph moiety and two hydrido ligands bridging the two ruthenium atoms, with each ruthenium atom also being coordinated to an η^6-C_6Me_6 ligand. The Ru–Ru distances [2.670(2) and 2.767(2) Å] are similar to those expected for a ruthenium–ruthenium double bond. Two independent molecules are observed in the crystal structure of [**2**][BF_4], with the major difference between them being the conformation of the P$(CH_2)_3$Ph unit (see Figure 2). Thus, the C1–C2–C3–C4 torsion angle in molecule **A** is 170(3)° (*anti* conformation), while in molecule **B** the C41–C42–C43–C44 torsion angle is –69(2)° (*syn* conformation). These two molecules adopt a pairwise arrangement in the unit cell of [**2**][BF_4], as shown in Figure 3. The presence of a bridging PPh$(CH_2)_3$Ph ligand forces the arene moieties to adopt a tilted geometry. The two C_6Me_6 arene ligands are not parallel to each other, and the angles between the C_6Me_6 planes are 34.9(2)° and 34.4(4)° for molecules **A** and **B**, respectively.

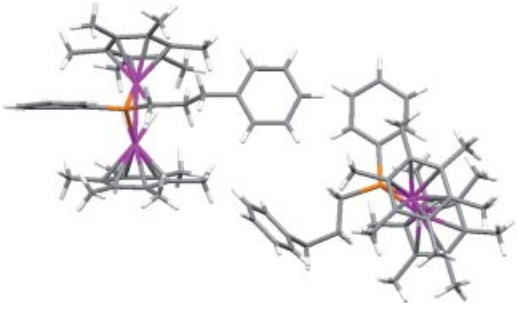
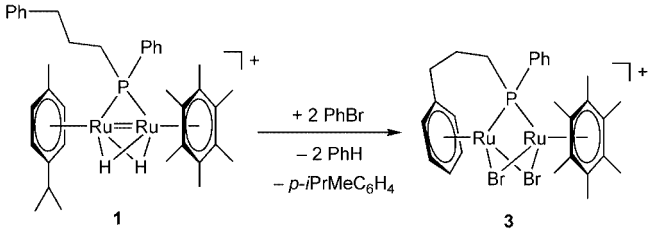


Figure 3. Pairwise arrangement of *anti*-**2** (molecule **A**) and *syn*-**2** (molecule **B**) in the unit cell of [**2**][BF_4].

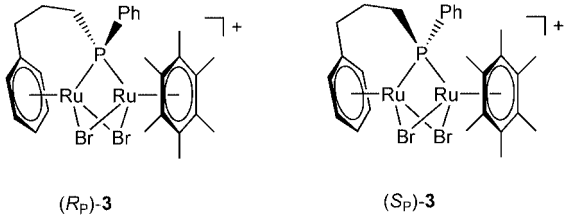
The arene exchange reaction between the *p*-cymene ligand and the phenyl substituent in the pendant arm of the phosphanido ligand in [(η^6-C_6Me_6)(η^6-*p*-*i*PrMeC_6H_4)-Ru_2{μ_2-PPh$(CH_2)_3$Ph}(μ_2-H)$_2$]$^+$ (**1**) is achieved by heating of [**1**][BF_4] at 150 °C in bromobenzene. The reaction leads to the dibromo complex [(η^6-C_6Me_6)Ru_2{μ_2-PPh$(CH_2)_3$-η^6-Ph}(μ_2-Br)$_2$]$^+$ (**3**; Scheme 3), and the reaction requires more forcing conditions than in the case of [(η^6-*p*-*i*PrMeC_6H_4)-Ru{$PPh_2(CH_2)_3$Ph}Cl_2].[5] Replacement of the C_6M_6 ligand is not observed.



1 3

Scheme 3. Synthesis of [(η^6-C_6Me_6)Ru_2{μ_2-PPh$(CH_2)_3$-η^6-Ph}(μ_2-Br)$_2$]$^+$ (**3**).

The surprising substitution of the two hydrido bridges in **1** by two bromido bridges in **3** that occurs during arene ligand exchange was confirmed by NMR monitoring: on comparing the ^{1}H NMR spectra of [**1**][BF_4] and [**3**][BF_4] it becomes clear that both the *p*-cymene signals and the hydride signals have disappeared and that coordination of the η^6-C_6H_5 substituent of the pendant arm gives rise to three new signals at δ = 6.25 (m, 2 H, *H-ortho*), 5.43 (t, $^3J_{H,H}$ = 4.8 Hz, 1 H, *H-para*), and 5.04 (m, 2 H, *H-meta*) ppm. As expected, the three methylene groups in the ligand arm give rise to two signals each because the CH_2 protons are diastereotopic (Figure 4). In contrast to **1** and **2**, the $^4J_{P,H}$ coupling (1 Hz) for **3**, which gives rise to a doublet at δ = 1.94 ppm, is visible for the methyl protons of the η^6-C_6Me_6 ligand, presumably due to the almost parallel arrangement of the two η^6-arene ligands. A similar $^4J_{P,H}$ coupling has been observed in the mononuclear complexes [(η^6-C_6Me_6)-Ru(CO)(PMe_3)Me]$^+$,[14] [(η^6-C_6Me_6)Ru(PR_3)Me_2], and [(η^6-C_6Me_6)Ru(PR_3)(OCOCF_3)Me] (PR_3 = PMe_3, PPh_3, PMe_2Ph).[15] In accordance with the presence of two bromido ligands, the ESI mass spectrum of [**3**][BF_4] shows a parent peak at *m*/*z* = 752. The molecular structure of this complex was finally confirmed by single-crystal X-ray analysis.



(R_P)-**3** (S_P)-**3**

Figure 4. The two enantiomers (R_P)-**3** and (S_P)-**3**.

Dark-orange crystals of [**3**][BF_4] suitable for an X-ray structure analysis were obtained by slow diffusion of diethyl ether into a concentrated acetone solution of [**3**][BF_4]. Two enantiomers are observed independently in the asymmetric unit of [**3**][BF_4] (see Figure 5).

The ruthenium atoms in [**3**][BF_4] are in a distorted octahedral geometry in which the two metal centers are bridged by a tethered phosphanido and two bromido ligands. The Ru–Br bond lengths [ranging from 2.552(1) to 2.586(1) Å] and Ru–Br–Ru angles [ranging from 82.16(4) to 82.90(4)°] are similar to those found in other dinuclear (η^6-arene)-ruthenium complexes bridged by bromine atoms, for example [Ru_2(η^6-1,3,5-$C_6H_3Et_3$)$_2$(μ_2-Br)$_3$][$Re_2(CO)_6$(μ_2-Br)$_3$] and [Ru_2(η^6-*p*-*i*PrMeC_6H_4)$_2$(μ_2-Br)$_3$][$Re_2(CO)_6$(μ_2-Br)$_3$].[16] The

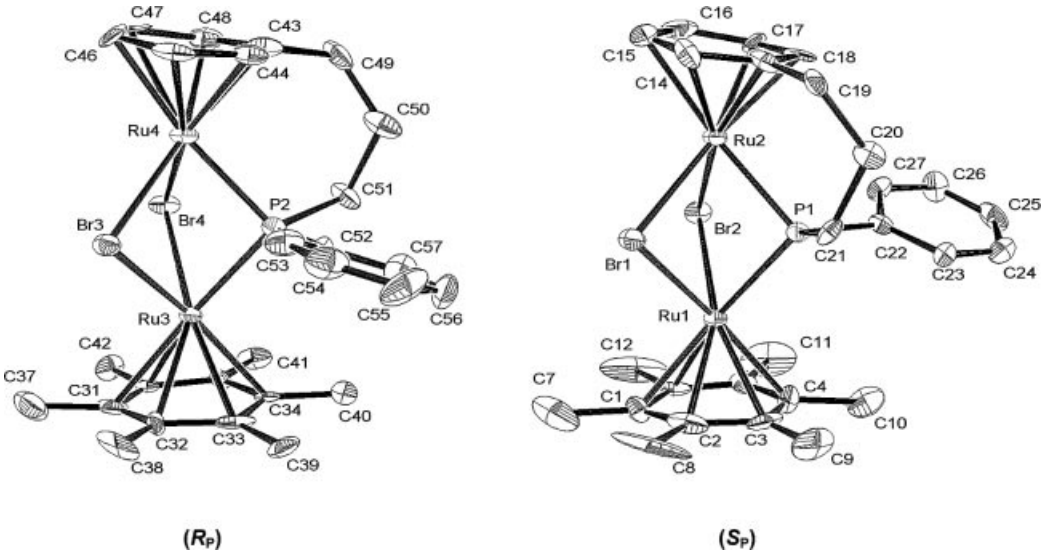


Figure 5. Molecular structure of the two independent enantiomers of cation **3** (anions and hydrogen atoms have been omitted for clarity).

Ru–Ru distances [3.3973(3) and 3.3764(3) Å] are well outside the range (2.28–2.95 Å) for a metal–metal single bond.[17] The phenyl rings of the η⁶-arene ligands are almost parallel, with an angle between the two planes of 8.8(7)° in (R_P)-**3** and 9.8(7)° in (S_P)-**3**. The *p*-cymene ligand in [**1**][BF_4] is replaced by the phenyl ring of the pendant arm of the phosphanido ligand upon formation of [**3**][BF_4], which gives rise to a six-membered metallacycle. Both enantiomers of **3** show a chair-like conformation for the six-membered metallacycles (see Figure 6).

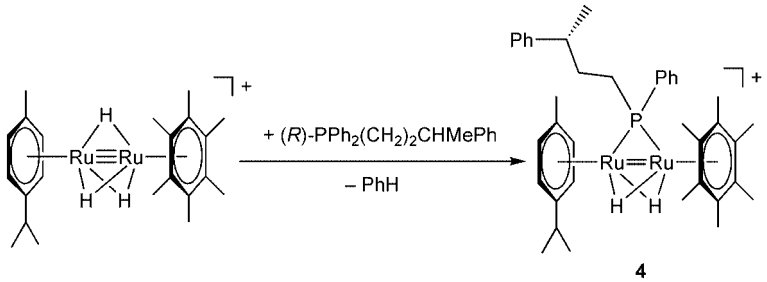
Figure 6. Capped-stick representation of the chair-like conformation observed in cations (R_P)-**3** and (S_P)-**3**.

In order to obtain a mixture of diastereomers instead of a racemic mixture of enantiomers we decided to treat [(η⁶-C_6Me_6)(η⁶-*p*-*i*PrMeC_6H_4)Ru_2(μ₂-H)₃]⁺ with the enantiopure phosphane (*R*)-$PPh_2(CH_2)_2$CHMePh, which contains a stereogenic carbon center and is similar to the achiral analogue $PPh_2(CH_2)_3$Ph. Given the fact that racemization of the stereogenic carbon atom in this ligand was not observed during the synthesis of [$RuCl_2${η¹-(*R*)-$PPh_2(CH_2)_2$-CHMe-η⁶-Ph}],[8c] we can assume that the (R_C) configuration of (*R*)-$PPh_2(CH_2)_2$CHMePh also does not change in the reaction with the dinuclear trihydrido complex.

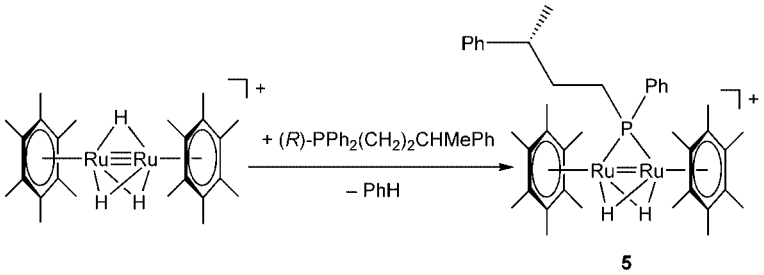
The trihydrido complex [(η⁶-C_6Me_6)(η⁶-*p*-*i*PrMeC_6H_4)-Ru_2(μ₂-H)₃]⁺ reacts with the enantiopure phosphane (*R*)-$PPh_2(CH_2)_2$CHMePh to give the cation [(η⁶-C_6Me_6)(η⁶-*p*-*i*PrMeC_6H_4)Ru_2{μ₂-(*R*)-PPh$(CH_2)_2$CHMePh}(μ₂-H)₂]⁺ (**4**), which was obtained as a mixture of the two diastereomers (R_C,R_P)-**4** and (R_C,S_P)-**4** (Scheme 4). The reaction was carried out in dichloromethane at 55 °C under hydrogen (3 bar). The yield of 38% is similar to that for the synthesis of **1**. Unfortunately, we were not able to separate the two diastereomers either by crystallization or by chromatography on silica gel.

As no X-ray quality crystals of [**4**][BF_4] could be obtained, we treated the enantiopure phosphane (*R*)-$PPh_2(CH_2)_2$CHMePh with the bis(hexamethylbenzene) analogue [(η⁶-C_6Me_6)$_2Ru_2$(μ₂-H)₃]⁺ to obtain [(η⁶-C_6Me_6)$_2$-Ru_2{μ₂-(*R*)-PPh$(CH_2)_2$CHMePh}(μ₂-H)₂]⁺ (**5**; Scheme 5).

The dark-red crystals of [**5**][BF_4] obtained by slow diffusion of diethyl ether into a concentrated solution of



Scheme 4. Synthesis of [(η⁶-C_6Me_6)(η⁶-*p*-*i*PrMeC_6H_4)Ru_2{μ₂-(*R*)-PPh$(CH_2)_2$CH-MePh}(μ₂-H)₂]⁺ (**4**).



Scheme 5. Synthesis of $[(\eta^6\text{-}C_6Me_6)_2Ru_2\{\mu_2\text{-}(R)\text{-}PPh(CH_2)_2CHMePh\}(\mu_2\text{-}H)_2]^+$ (**5**).

[**5**][BF_4] in dichloromethane were found to be suitable for X-ray analysis. The molecular structure of cation **5** was confirmed by X-ray crystal structure analysis of its tetrafluoroborate salt (Figure 7).

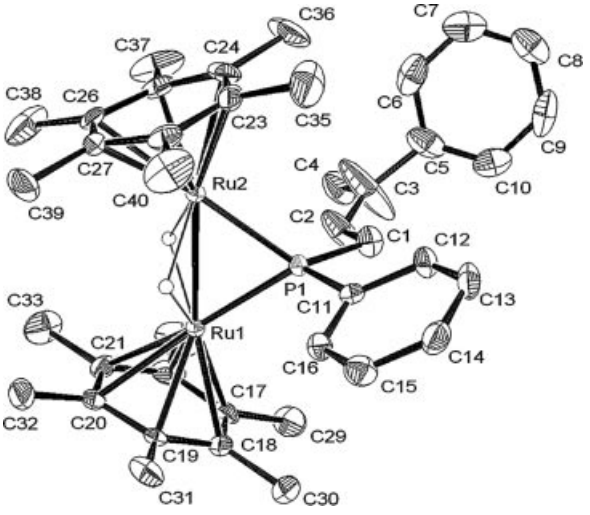


Figure 7. Molecular structure of cation **5** (anion and hydrogen atoms other than the hydrido ligands have been omitted for clarity).

The centrosymmetric space group $P2_1/c$ of [**5**][BF_4] suggests a racemic mixture of (R_C) and (S_C) enantiomers of **5** in the crystal. However, the stereogenic carbon atom (C3 in Figure 7) in **5** is highly disordered, as demonstrated by the exceptionally stretched ellipsoid along the C–H axis in the ORTEP plot (Figure 7), which may give rise to a centrosymmetric space group despite retention of the (R_C) configuration. The Ru–Ru distance [2.6346(8) Å] is similar to those observed in [**2**][BF_4] and remains within the range of a ruthenium–ruthenium double bond. As in [**2**][BF_4], the presence of a bridging phosphanido ligand forces the arene moieties to adopt a tilted geometry. The angle between the two C_6Me_6 planes is 38.8(2)°.

As the question of the enantiomeric purity of **5** could not be solved by X-ray crystallography because of the centrosymmetric space group ($P2_1/c$) and disorder problems, we used circular dichroism to find out whether or not the stereogenic carbon center in the side-chain has racemized during the synthesis of **5**, despite the known enantiostability of (*R*)-$PPh_2(CH_2)_2CHMePh$.[8c] Although the concentration-dependent CD signal at 350 nm (Figure 8) shows **5** to be optically active, which suggests that the stereogenic carbon center has (*R*) configuration, we cannot exclude partial racemization during the synthesis of this compound.

As in the case of **1**, the ligand exchange reaction between *p*-cymene and the phenyl substituent on the pendant arm

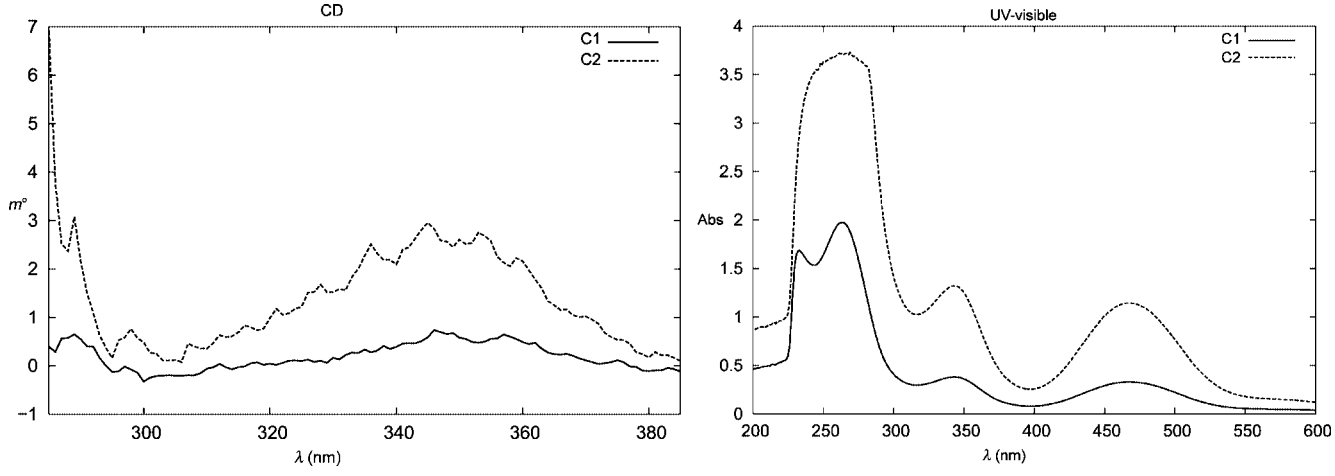
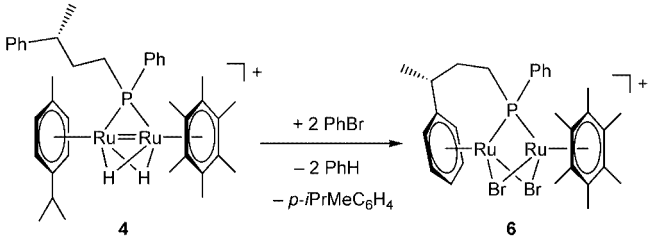


Figure 8. CD (left) and UV/Vis (right) spectra of [**5**][BF_4] recorded in CH_2Cl_2 at two different concentrations ($c_1 = 5.05 \times 10^{-4}$ M, $c_2 = 1.67 \times 10^{-3}$ M), $m° = 10^{-3}°$.

was achieved by heating of $[(\eta^6\text{-}C_6Me_6)(\eta^6\text{-}p\text{-}i\text{PrMeC}_6H_4)\text{-}Ru_2\{\mu_2\text{-}(R)\text{-}PPh(CH_2)_2CHMePh\}(\mu_2\text{-}H)_2]^+$ (**4**) at 150 °C in bromobenzene. This reaction also leads to the dibromido derivative $[(\eta^6\text{-}C_6Me_6)Ru_2\{\mu_2\text{-}(R)\text{-}PPh(CH_2)_2CHMe\text{-}\eta^6\text{-}Ph\}(\mu_2\text{-}Br)_2]^+$ (**6**; Scheme 6), which was obtained as a mixture of (R_C,S_P) and (R_C,R_P) diastereomers (Figure 9).



Scheme 6. Synthesis of $[(\eta^6\text{-}C_6Me_6)Ru_2\{\mu_2\text{-}(R)\text{-}PPh(CH_2)_2CHMe\text{-}\eta^6\text{-}Ph\}(\mu_2\text{-}Br)_2]^+$ (**6**).

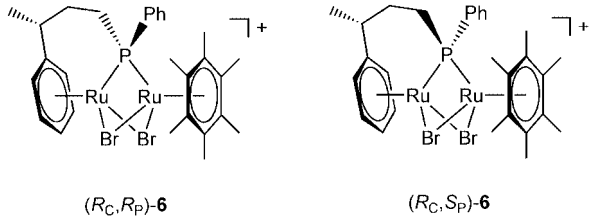


Figure 9. The two diastereomers (R_C,R_P)-**6** and (R_C,S_P)-**6**.

Single crystals suitable for an X-ray structure analysis were obtained by slow diffusion of diethyl ether into a concentrated acetone solution of [**6**][BF_4]. Examination of the structure with PLATON[18] revealed an ambiguity over the choice of the space group ($P1$ or $P\bar{1}$). Expecting a chiral molecule, resolution was performed in the noncentrosymmetric group $P1$. The structure was refined to convergence with a Flack parameter of 0.23(2). Both diastereomers, (R_C,R_P)-**6** and (R_C,S_P)-**6**, show the two ruthenium atoms to be in a distorted octahedral geometry in which the metal

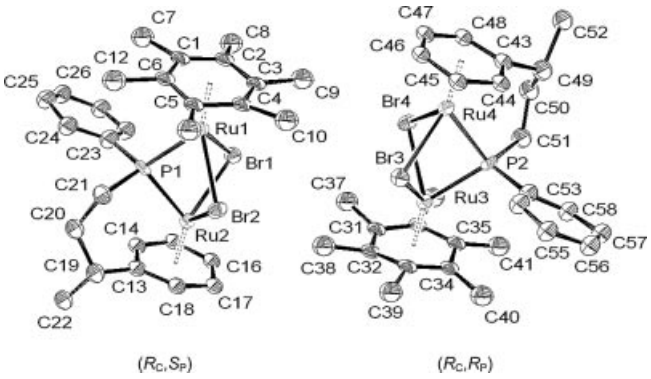


Figure 10. The molecular structure of the diastereomers of cation **6** (anions, solvent molecules, and hydrogen atoms have been omitted for clarity).

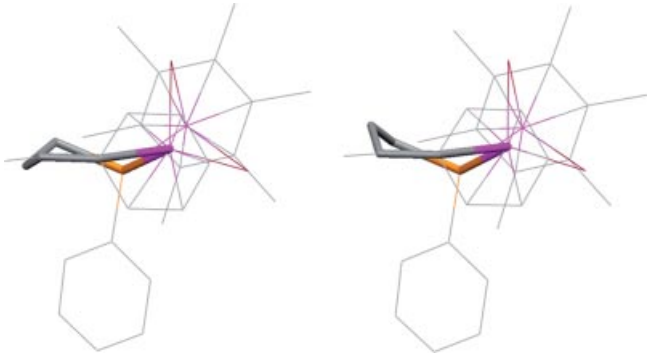


Figure 11. The chair-like (left) and half-twist-like (right) conformations in cation **6**.

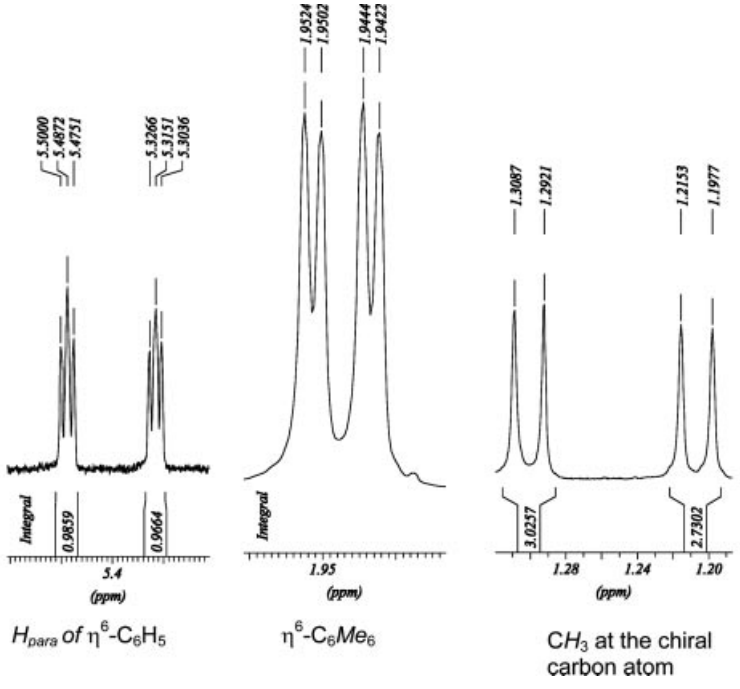


Figure 12. Selected ^{1}H NMR signals ([D_6] acetone) of the diastereomeric mixture of [**6**][BF_4].

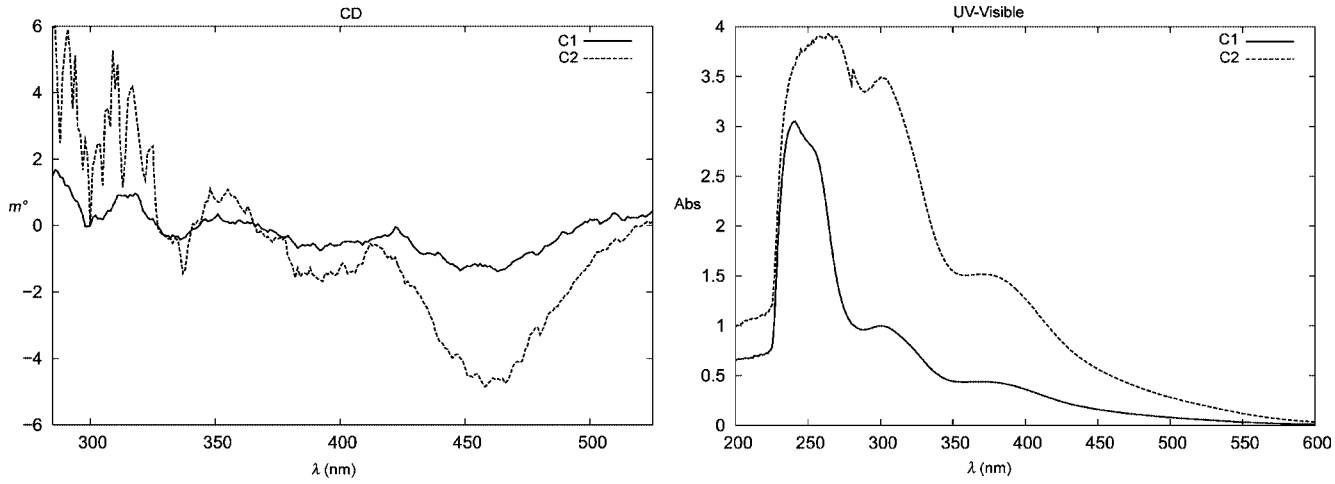


Figure 13. CD and UV/Vis spectra of [**6**][BF_4] at two different concentrations ($c_1 = 5.86 \times 10^{-4}$ M, $c_2 = 2.05 \times 10^{-3}$ M).

centers are bridged by a tethered phosphanido and two bromido ligands (Figure 10). The Ru–Br bond lengths (average 2.572 Å) and the Ru–Br–Ru angles (average 82.15°) are similar to those found in [**3**][BF_4]. Similarly, the Ru–Ru distances [identical at 3.380(2) Å] are similar to those observed in [**3**][BF_4]. The two η^6-arene ligands are almost parallel to each other in both molecules, with an angle between the two aromatic planes of 10.2(4)° for the (R_C,S_P) and 12.1(4)° for the (R_C,R_P) isomer. Replacement of the *p*-cymene ligand by a phenyl ring at the pendant arm of the phosphanido ligand in [**6**][BF_4] generates a six-membered metallacycle upon coordination. Surprisingly, two conformations are observed for the six-membered metallacycle, a chair-like (R_C,S_P) and a half-twist-like (R_C,R_P) conformation for the diastereomers of **6** (Figure 11).[19]

The two diastereomers (R_C,S_P)-**6** and (R_C,R_P)-**6** are distinguishable in the ^{1}H NMR spectrum, which shows two doublets of almost equal intensity for the η^6-C_6Me_6 protons at δ = 1.95 and 1.94 ppm. As in **3**, the $^4J_{P,H}$ coupling (0.9 Hz) is also observable for the methyl protons of the η^6-C_6Me_6 ligand in **6** since the two arene ligands in this complex are almost parallel to each other. Accordingly, two signals are observed for the *para* protons of the η^6-C_6H_5 ligand [δ = 5.48 (t) and 5.31 ppm (t)] and for the methyl substituent at the stereogenic carbon atom [δ = 1.29 (d) and 1.20 (d) ppm]. The integration of the ^{1}H NMR signals suggests that both diastereomers are present in almost equal quantities, with a slight excess of one (52:48; Figure 12). This diastereoselectivity (*de* = 4%) was confirmed by circular dichroism: The CD spectrum of [**6**][BF_4] in dichloromethane, recorded at two different concentrations, indeed shows a small concentration-dependent CD signal centered at 460 nm (Figure 13).

Conclusions

We have synthesized several chiral-at-phosphorus phosphanidodiruthenium complexes and shown that an intramolecular ligand exchange between one arene ligand at the ruthenium atom and a phenyl substituent in the side-arm of the phosphanido bridge leads to chiral tethered derivatives. Introduction of a stereogenic carbon atom in the pendant arm of the phosphanido bridging ligand gives rise to the formation of diastereomeric complexes.

Experimental Section

General Remarks: All manipulations were carried out under nitrogen using standard Schlenk techniques. All solvents were degassed with nitrogen prior to use. The silica gel (type G) used for preparative thin-layer chromatography was purchased from Macherey–Nagel GmbH. The phosphanes were synthesized according to previously described methods.[5,8c] The starting compounds [(η^6-C_6Me_6)(η^6-*p*-*i*PrMeC_6H_4)Ru_2(μ_2-H)$_3$][BF_4][13] and [(C_6Me_6)$_2Ru_2$(μ_2-H)$_3$][BF_4][20] were synthesized according to previously described methods. Bromobenzene (puriss.) was purchased from Fluka, stored under nitrogen, and dried with molecular sieves (4 Å). Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. NMR spectra were recorded with a Bruker 400 MHz spectrometer. Mass spectra were recorded by Prof. Titus Jenny at the University of Fribourg. Microanalyses were carried out in the Laboratory of Pharmaceutical Chemistry at the University of Geneva.

Synthesis of [(η^6-C_6Me_6)(η^6-*p*-*i*PrMeC_6H_4)Ru_2{μ_2-PPh(CH_2)$_3$Ph}-(μ_2-H)$_2$][BF_4] [1][BF_4]: [(η^6-C_6Me_6)(η^6-*p*-*i*PrMeC_6H_4)Ru_2(μ_2-H)$_3$]-[BF_4] (230 mg, 0.39 mmol) was dissolved in dichloromethane (250 mL) in a pressure Schlenk tube and the phosphane PPh_2-(CH_2)$_3$Ph (178 mg, 0.58 mmol) was added. The solution was then flushed and pressurized with hydrogen (3 bar) and stirred at 55 °C under hydrogen pressure for 18 h. After cooling to room temperature, the solvent was evaporated to dryness and the brown product obtained was purified by preparative thin-layer chromatography on silica gel (acetone/dichloromethane, 1:10). The product was extracted from the silica with acetone from the brown band, and evaporation of the solvent gave the pure product (yield: 38%, 120 mg, 0.15 mmol). ^{1}H NMR (400 MHz, [D_6]acetone, 25 °C): δ = 7.32–7.20 (m, 8 H, *H*-Ph), 7.04 (m, 2 H, *H*-Ph), 6.03 (t, $^3J_{H,H}$ = 5 Hz, 2 H, *H*-Ar *p*-cymene), 5.72 (d, $^3J_{H,H}$ = 5.9 Hz, 1 H, *H*-Ar *p*-cymene), 5.65 (d, $^3J_{H,H}$ = 6.2 Hz, 1 H, *H*-Ar *p*-cymene), 2.73 (m, 2 H, PPhCH_2CH_2CH_2Ph), 2.57 (m, 3 H, *H*-*i*Pr, PPhCH_2CH_2CH_2Ph), 2.11 [s, 18 H, C_6(Me)$_6$], 2.02 (s, 3 H,

$CH_3C_6H_4iPr$), 1.27 [t, $^3J_{H,H}$ = 7 Hz, 6 H, $CH(CH_3)_2$] 0.89 (m, 2 H, $PPhCH_2CH_2CH_2Ph$), –14.65 (dd, $^2J_{H,H}$ = 2.8, $^2J_{H,P}$ = 28 Hz, 1 H, hydride), –16.06 (dd, $^2J_{H,H}$ = 2.8, $^2J_{H,P}$ = 31 Hz, 1 H, hydride) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]acetone, 25 °C): δ = 142.7 (*C*-Ar), 142.1 (*C*-Ar), 132.67 (*C*-Ar), 132.5 (*C*-Ar), 129.6 (*C*-Ar), 129.6 (*C*-Ar), 129.4 (*C*-Ar), 129.3 (*C*-Ar), 129.2 (*C*-Ar), 128.37 (*C*-Ar), 128.2 (*C*-Ar), 126.7 (*C*-Ar), 99.2 (Me*i*PrC_6H_4), 97.4 [C_6(Me)$_6$], 97.2 (Me*i*PrC_6H_4), 85.3 (Me*i*PrC_6H_4), 84.6 (Me*i*PrC_6H_4), 82.8 (Me-*i*PrC_6H_4), 81.5 (Me*i*PrC_6H_4), 37.1 (d, $J_{C,P}$ = 18 Hz, CH_2), 32.7 (CH_2), 31.7 (d, $J_{C,P}$ = 6.4 Hz, CH_2), 23.7 [$CH(CH_3)_2$], 23.7 [$CH(CH_3)_2$], 20.3 ($C_6H_4CH_3$), 17.5 [$C_6(CH_3)_6$] ppm. $^{31}P\{^1H\}$ NMR (160 MHz, [D$_6$]acetone, 25 °C): δ = 114.62 (s) ppm. MS (ESI): *m*/*z* = 728 $[M + H]^+$. $C_{37}H_{50}BF_4PRu_2$ (814.71): calcd. C 54.54, H 6.18; found C 54.51, H 6.20.

Synthesis of [(η^6-C_6Me_6)$_2$Ru$_2${μ_2-PPh(CH$_2$)$_3$Ph}(μ_2-H)$_2$][BF$_4$] [2][BF$_4$]: [(η^6-C_6Me_6)$_2$Ru$_2$(μ_2-H)$_3$][BF$_4$] (150 mg, 0.24 mmol) was dissolved in dichloromethane (200 mL) in a pressure Schlenk tube and the phosphane $PPh_2(CH_2)_3Ph$ (93 mg, 0.30 mmol) was added. The solution was then flushed and pressurized with hydrogen (3 bar) and stirred at 55 °C under hydrogen pressure for 18 h. After cooling to room temperature, the solvent was evaporated to dryness and the brown product obtained was purified by preparative thin-layer chromatography on silica gel (acetone/dichloromethane, 1:10). The product was extracted with acetone from the brown band, and evaporation of the solvent gave the pure product (yield: 85%, 172 mg, 0.20 mmol). Crystals suitable for X-ray structure analysis were obtained by diffusion of diethyl ether into a concentrated dichloromethane solution of [**2**][BF$_4$]. ^1H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 7.38–7.20 (m, 8 H, *H*-Ph), 6.95 (m, 2 H, *H*-Ph), 2.78 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, $PPhCH_2CH_2CH_2Ph$), 2.55 (m, 2 H, $PPhCH_2CH_2CH_2Ph$), 2.17 [s, 18 H, $C_6(CH_3)_6$], 0.86 (m, 2 H, $PPhCH_2CH_2CH_2Ph$), –15.18 (dd, $^2J_{H,H}$ = 3, $^2J_{H,P}$ = 28 Hz, 1 H, hydride), –16.50 (dd, $^2J_{H,H}$ = 3, $^2J_{H,P}$ = 30 Hz, 1 H, hydride) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]acetone, 25 °C): δ = 142.4 (*C*-Ar), 132.1 (*C*-Ar), 132.0 (*C*-Ar), 128.9 (*C*-Ar), 128.8 (*C*-Ar), 128.0 (*C*-Ar), 127.9 (*C*-Ar), 126.3 (*C*-Ar), 96.9 [C_6(Me)$_6$], 36.7 (d, $J_{C,P}$ = 20 Hz, CH_2), 31.8 (CH_2), 31.52 (d, $J_{C,P}$ = 12 Hz, CH_2), 17.4 [$C_6(CH_3)_6$] ppm. $^{31}P\{^1H\}$ NMR (160 MHz, [D$_6$]acetone, 25 °C): δ = 101.73 (s) ppm. MS (ESI): *m*/*z* 756 $[M + H]^+$. $C_{39}H_{56}BF_4PRu_2$ (844.78): calcd. C 55.45, H 6.68; found C 55.39, H 6.61.

Synthesis of [(η^6-C_6Me_6)Ru$_2${μ_2-PPh(CH$_2$)$_3$-η^6-Ph}(μ_2-Br)$_2$][BF$_4$] [3][BF$_4$]: [(η^6-C_6Me_6)(η^6-*p*-*i*PrMeC_6H_4)Ru$_2${μ_2-PPh(CH$_2$)$_3$Ph}(μ_2-H)$_2$][BF$_4$] (120 mg, 0.15 mmol) was dissolved in bromobenzene (25 mL) that had been dried with molecular sieves (4 Å) and saturated with nitrogen prior to use. The solution was heated at 150 °C for 20 h. After cooling to room temperature, the solvent was evaporated to dryness in a trap-to-trap apparatus. The brown-red product obtained was purified by preparative thin-layer chromatography on silica gel (acetone/dichloromethane, 1:10). The product was extracted with acetone from the lowest major orange band (R_f = 0.4). Evaporation of the solvent gave the pure product (yield: 30%, 38 mg, 0.045 mmol). Crystals suitable for X-ray structure analysis were obtained by slow diffusion of diethyl ether into a concentrated acetone solution of [**3**][BF$_4$]. ^1H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 7.96 (br., 2 H, P-*Ph*), 7.53 (m, 3 H, P-*Ph*), 6.25 (m, 2 H, *H-ortho* η^6-*Ph*), 5.43 (t, $^3J_{H,H}$ = 4.8 Hz, 1 H, *H-para* η^6-*Ph*), 5.04 (m, 2 H, *H-meta* η^6-*Ph*), 3.44 (m, 1 H, CH_2), 3.05 (td, $^3J_{H,H}$ = 3.7, $^2J_{H,H}$ = 15.3 Hz, 1 H, CH_2), 2.58 (m, 1 H, CH_2), 2.38 (m, 1 H, CH_2), 1.98 (m, 1 H, CH_2), 1.94 [d, $^4J_{P,H}$ = 1 Hz, 18 H, $C_6(CH_3)_6$], 1.40 (m, 1 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]acetone, 25 °C): δ = 136.6 (P-*Ph*), 136.4 (P-*Ph*), 130.6 (P-*Ph*), 130.6 (P-*Ph*), 129.2 (P-*Ph*), 129.1 (P-*Ph*), 99.2 (η^6-*Ph*), 94.9 (η^6-*Ph*), 93.8 [$C_6(CH_3)_6$], 84.9 (η^6-*Ph*), 82.0 (η^6-*Ph*), 81.7 (η^6-*Ph*), 72.5 (η^6-*Ph*), 30.2 (d, $J_{C,P}$ = 33 Hz, CH_2), 24.5 (d, $J_{C,P}$ = 7 Hz, CH_2), 20.2 (d, $J_{C,P}$ = 16 Hz, CH_2), 15.3 [$C_6(CH_3)_6$] ppm. $^{31}P\{^1H\}$ NMR (160 MHz, [D$_6$]acetone, 25 °C): δ = –14.53 (s) ppm. MS (ESI): *m*/*z* = 752 $[M + H]^+$. $C_{27}H_{34}BBr_2F_4PRu_2$ (838.29): calcd. C 38.68, H 4.08; found C 38.75, H 4.16.

Synthesis of [(η^6-C_6Me_6)(η^6-*p*-*i*PrMeC_6H_4)Ru$_2${μ_2-(*R*)-PPh(CH$_2$)$_2$-CHMePh}(μ_2-H)$_2$][BF$_4$] [4][BF$_4$]: Synthesis of this complex followed the procedure described for [**1**][BF$_4$] but with [(η^6-C_6Me_6)(η^6-*p*-*i*PrMeC_6H_4)Ru$_2$(μ_2-H)$_3$][BF$_4$] (260 mg, 0.44 mmol) and (*R*)-$PPh_2(CH_2)_2CHMePh$ (210 mg, 0.66 mmol) as starting materials. The product was extracted from the brown band with acetone, and evaporation of the solvent gave the pure product (yield: 38%, 138 mg, 0.17 mmol). ^1H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 7.32 (m, 16 H, *H*-Ph), 6.98 (m, 4 H, *H*-Ph β of P), 6.09 (d, $^3J_{H,H}$ = 6 Hz, 1 H, *p*-*i*PrMeC_6H_4), 6.04 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H, *p*-*i*PrMeC_6H_4), 5.98 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H, *p*-*i*PrMeC_6H_4), 5.95 (d, $^3J_{H,H}$ = 6 Hz, 1 H, *p*-*i*PrMeC_6H_4), 5.75 (d, $^3J_{H,H}$ = 6 Hz, 1 H, *p*-*i*PrMeC_6H_4), 5.70 (t, $^3J_{H,H}$ = 6.6 Hz, 1 H, *p*-*i*PrMeC_6H_4), 5.64 (d, $^3J_{H,H}$ = 5.8 Hz, 1 H, *p*-*i*PrMeC_6H_4), 2.88 [m, 2 H, $MeC_6H_4CH(CH_3)_2$], 2.7–2.2 [m, 6 H, $PhCH(CH_3)CH_2CH_2PPh_2$], 2.13 [s, 18 H, $C_6(CH_3)_6$], 2.06 [s, 18 H, $C_6(CH_3)_6$], 2.02 [s, 3 H, $MeC_6H_4CH(CH_3)_2$], 1.98 [s, 3 H, $MeC_6H_4CH(CH_3)_2$], 1.28 [m, 18 H, $MeC_6H_4CH(CH_3)_2$, $PhCH(CH_3)CH_2CH_2PPh_2$], 1.25–0.7 [m, 4 H, $PhCH(CH_3)CH_2CH_2PPh_2$], –14.68 (td, $^2J_{H,H}$ = 2.8, $^2J_{H,P}$ = 27.6 Hz, 2 H, hydride), –16.04 (dd, $^2J_{H,H}$ = 2.8, $^2J_{H,P}$ = 30.7 Hz, 1 H, hydride), –16.10 (dd, $^2J_{H,H}$ = 2.8, $^2J_{H,P}$ = 30.9 Hz, 1 H, hydride) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]acetone, 25 °C): δ = 147.2 (*C*-Ar), 147.2 (*C*-Ar), 141.7 (*C*-Ar), 141.5 (*C*-Ar), 132.2 (*C*-Ar), 132.1 (*C*-Ar), 129.2 (*C*-Ar), 129.2 (*C*-Ar), 128.8 (*C*-Ar), 128.8 (*C*-Ar), 127.9 (*C*-Ar), 127.8 (*C*-Ar), 127.5 (*C*-Ar), 127.3 (*C*-Ar), 126.6 (*C*-Ar), 113.3 (*C*-Ar), 98.8 (Me*i*PrC_6H_4), 98.3 (Me*i*PrC_6H_4), 97.1 [$C_6(CH_3)_6$], 97.0 [$C_6(CH_3)_6$], 96.8 (Me*i*PrC_6H_4), 85.2 (Me*i*PrC_6H_4), 84.8 (Me*i*PrC_6H_4), 84.2 (Me*i*PrC_6H_4), 83.9 (Me*i*PrC_6H_4), 82.9 (Me*i*PrC_6H_4), 81.2 (Me*i*PrC_6H_4), 81.1 (Me*i*PrC_6H_4), 41.1 (*C*HMe), 40.9 (d, $J_{C,P}$ = 4.3 Hz, CH_2), 38.2 (d, $J_{C,P}$ = 21 Hz, CH_2), 32.3 [$CH(CH_3)_2$], 23.3 [$CH(CH_3)$], 23.3 [$CH(CH_3)_2$], 21.5 [$CH(CH_3)_2$], 21.2 ($C_6H_4CH_3$), 20.0 [$CH(CH_3)$],17.2 [$C_6(CH_3)_6$], 17.2 [$C_6(CH_3)_6$] ppm. $^{31}P\{^1H\}$ NMR (160 MHz, [D$_6$]acetone, 25 °C): δ = 114.82 (s), 114.73 (s) ppm. MS (ESI): *m*/*z* = 742 $[M + H]^+$. $C_{38}H_{54}BF_4PRu_2$ (830.75): calcd. C 54.93, H 6.55; found C 55.09, H 6.72.

Synthesis of [(η^6-C_6Me_6)$_2$Ru$_2${μ_2-(*R*)-PPh(CH$_2$)$_2$CHMePh}(μ_2-H)$_2$][BF$_4$] [5][BF$_4$]: Synthesis of this complex followed the procedure described for [**2**][BF$_4$] but with [(η^6-C_6Me_6)$_2$Ru$_2$(μ_2-H)$_3$][BF$_4$] (100 mg, 0.16 mmol) and (*R*)-$PPh_2(CH_2)_2CHMePh$ (57 mg, 0.18 mmol) as starting materials. The product was extracted from the brown band with acetone, and evaporation of the solvent gave the pure product (yield: 86%, 117 mg, 0.14 mmol). Crystals suitable for X-ray structure analysis were obtained by slow diffusion of diethyl ether into a concentrated acetone solution of [**5**][BF$_4$]. ^1H NMR (400 MHz, [D$_2$]dichloromethane, 25 °C): δ = 7.36–7.17 (m, 8 H, *H*-Ph), 6.75 (m, 2 H, *H*-Ph), 2.76 [q, $^3J_{H,H}$ = 7 Hz, 1 H, $PhCH(CH_3)(CH_2)_2PPh_2$], 2.40–2.10 [m, 2 H, $PhCH(CH_3)CH_2CH_2PPh_2$], 2.13 [s, 18 H, $C_6(CH_3)_6$], 2.05 [s, 18 H, $C_6(CH_3)_6$], 1.29 [d, $^3J_{H,H}$ = 7 Hz, 3 H, $PPhCH(CH_3)CH_2CH_2Ph$] 0.65 [m, 2 H, $PPhCH(CH_3)CH_2CH_2Ph$], –15.28 (dd, $^2J_{H,H}$ = 3, $^2J_{H,P}$ = 28.1 Hz, 1 H, hydride), –16.67 (dd, $^2J_{H,H}$ = 3, $^2J_{H,P}$ = 31.3 Hz, 1 H, hydride) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]acetone, 25 °C): δ = 147.3 (*Ph*), 140.8 (*Ph*), 132.1 (*Ph*), 132.0 (*Ph*), 128.9 (*Ph*), 128.8 (*Ph*), 128.0 (*Ph*), 127.9 (*Ph*), 127.3 (*Ph*), 126.6 (*Ph*), 96.9 [C_6-$(CH_3)_6$], 41.1 (d, $J_{C,P}$ = 18 Hz, CH_2), 41.0 (*C*H), 38.2 (d, $J_{C,P}$ = 8 Hz, CH_2), 21.2 [$CH(CH_3)$] 17.4 [$C_6(CH_3)_6$], 17.3 [$C_6(CH_3)_6$] ppm. $^{31}P\{^1H\}$ NMR (160 MHz, [D$_6$]acetone, 25 °C): δ = 102.33 (s) ppm.

Table 1. Crystallographic and selected experimental data for [**2**][BF_4]·0.5CH_2Cl_2, [**3**][BF_4], [**5**][BF_4], and [**6**][BF_4]·$(CH_3)_2CO$.

	[**2**][BF_4]·0.5CH_2Cl_2	[**3**][BF_4]	[**5**][BF_4]	[**6**][BF_4]·$(CH_3)_2CO$
Empirical formula	$C_{39.5}H_{55}BClF_4PRu_2$	$C_{27}H_{34}BBr_2F_4PRu_2$	$C_{40}H_{56}BF_4PRu_2$	$C_{31}H_{42}BBr_2F_4OPRu_2$
Formula mass	885.21	838.28	856.77	910.39
Crystal system	orthorhombic	triclinic	monoclinic	triclinic
Space group	$Pca2_1$	$P\bar{1}$	$P2_1/c$	$P1$
Crystal color and shape	red block	orange plate	red plate	red block
Crystal size	0.85 × 0.28 × 0.12	0.48 × 0.20 × 0.07	0.40 × 0.28 × 0.10	0.46 × 0.28 × 0.12
a [Å]	18.7393(15)	10.4799(11)	10.756(2)	10.4690(9)
b [Å]	20.0175(10)	16.6813(17)	20.776(4)	11.3906(9)
c [Å]	20.8971(18)	18.038(2)	17.745(4)	15.5091(13)
α [°]		99.150(15)		95.506(10)
β [°]		105.969(14)	104.29(3)	101.751(10)
γ [°]		102.461(12)		110.354(9)
V [Å^3]	7838.8(10)	2879.1(5)	3842.7(13)	1669.4(2)
Z	8	4	4	2
T [K]	173(2)	173(2)	173(2)	173(2)
D_c [g cm^{-3}]	1.500	1.934	1.481	1.811
μ [mm^{-1}]	0.926	3.923	0.874	3.393
Scan range [°]	$4.62 < 2\theta < 54.18$	$3.92 < 2\theta < 51.96$	$4.74 < 2\theta < 51.64$	$4.32 < 2\theta < 51.98$
Unique reflections	11455	9529	5612	10511
Reflections used [$I > 2\sigma(I)$]	2657	3436	3860	8765
R_{int}	0.0766	0.0739	0.0484	0.0495
Final R indices [$I > 2\sigma(I)$][a]	0.0464, wR_2 0.0713	0.0467, wR_2 0.0748	0.0511, wR_2 0.1468	0.0635, wR_2 0.1659
R indices (all data)	0.2138, wR_2 0.1234	0.1615, wR_2 0.0899	0.0789, wR_2 0.1620	0.0760, wR_2 0.2010
Goodness-of-fit	0.469	0.672	1.033	1.096
Max/min $\Delta\rho$/e [Å^{-3}]	0.441, –0.499	1.225, –1.183	0.763, –0.845	1.640, –3.755

[a] Structures were refined on F_o^2: $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$, where $w^{-1} = [\Sigma(F_o^2) + (aP)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$.

MS (ESI): m/z = 770 [M + H]$^+$. $C_{40}H_{56}BF_4PRu_2$ (856.79): calcd. C 56.07, H 6.58; found C 56.03, H 6.51.

Synthesis of [(η^6-C_6Me_6)Ru_2{μ$_2$-(*R*)-PPh(CH_2)$_2$CHMe-η^6-Ph}(μ$_2$-Br)$_2$][BF_4] [6][BF_4]: Synthesis of this complex followed the procedure described for [**3**][BF_4] but with [(η^6-C_6Me_6)(η^6-*p*-*i*PrMe-C_6H_4)Ru_2{μ$_2$-(*R*)-PPh(CH_2)$_2$CHMePh}(μ$_2$-H)$_2$][BF_4] (110 mg, 0.13 mmol) as starting material. The product was extracted from the lowest main orange band (R_f = 0.4) with acetone and evaporation of the solvent gave the pure product (yield: 40%, 45 mg, 0.053 mmol). Crystals suitable for X-ray structure analysis were obtained by slow diffusion of diethyl ether into a concentrated acetone solution of [**6**][BF_4]. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 7.97 (br., 4 H, P-*Ph*), 7.54 (m, 6 H, P-*Ph*), 6.25 (m, 4 H, η^6-*Ph*), 5.47 (t, $^3J_{H,H}$ = 4.9 Hz, 1 H, η^6-*Ph*), 5.30 (t, $^3J_{H,H}$ = 4.5 Hz, 1 H, η^6-*Ph*), 5.05 (m, 4 H, η^6-*Ph*), 3.52 (m, 1 H, C*H*$_2$), 3.27 (m, 1 H, C*H*$_2$), 2.98 (m, 1 H, C*H*), 2.70–2.0 (m, 5 H, C*H*, C*H*$_2$), 1.95 [d, $^4J_{P,H}$ = 0.9 Hz, 18 H, $C_6(CH_3)_6$], 1.94 [d, $^4J_{P,H}$ = 0.9 Hz, 18 H, $C_6(CH_3)_6$], 1.64 (m, 1 H, C*H*$_2$), 1.52 (m, 1 H, C*H*$_2$), 1.29 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, C*H*$_3$), 1.20 (d, $^3J_{H,H}$ = 7 Hz, 3 H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]acetone, 25 °C): δ = 137.6 (P-*Ph*), 137.6 (P-*Ph*), 134.0 (br., P-*Ph*), 132.6 (P-*Ph*), 132.0 (P-*Ph*), 131.7 (P-*Ph*), 130.2, 130.2 (br., P-*Ph*), 130.0 (P-*Ph*), 129.9 (P-*Ph*), 129.3 (P-*Ph*), 128.5 (P-*Ph*), 99.0 (η^6-*Ph*), 96.1 (η^6-*Ph*), 94.9 [*C*$_6$(CH$_3$)$_6$], 90.7 (η^6-*Ph*), 90.3 (η^6-*Ph*), 83.8 (η^6-*Ph*), 82.2 (η^6-*Ph*), 81.9 (η^6-*Ph*), 78.1 (η^6-*Ph*), 75.0 (η^6-*Ph*), 73.5 (η^6-*Ph*), 72.7 (η^6-*Ph*), 39.1 (*C*H$_2$), 34.2 (d, $J_{C,P}$ = 15 Hz, *C*H$_2$), 31.8 (*C*H), 29.1, 24.5 [CH(*C*H$_3$)], 23.5, 20.0, 16.4 [$C_6(CH_3)_6$] ppm. ^{31}P{^{1}H} NMR (160 MHz, [D$_6$]acetone, 25 °C): δ = –8.71 (s), –9.82 (s) ppm. MS (ESI): m/z = 766 [M + H]$^+$. $C_{28}H_{36}BBr_2F_4PRu_2$ (852.31): calcd. C 39.45, H 4.26; found C 39.65, H 4.45.

X-ray Crystallographic Study: Crystals of [**2**][BF_4]·0.5CH_2Cl_2, [**3**][BF_4], [**5**][BF_4], and [**6**][BF_4]·$(CH_3)_2CO$ were mounted individually on a Stoe Image Plate Diffraction system equipped with a φ circle goniometer, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data were collected in the φ range 0–200°, with increments of 1.2°, 1.5°, 1.0° and 1.0°, respectively, in the 2θ range from 2.0–26° (D_{max}–D_{min} = 12.45–0.81 Å). The structures were solved by direct methods using the program SHELXS-97.[21] Refinement and all further calculations were carried out using SHELXL-97.[22] The H atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters in all cases. The non-H atoms were refined anisotropically, using weighted full-matrix least squares on F^2. Crystallographic details are summarized in Table 1. Figures 2, 5, 7, and 10 were drawn with ORTEP,[23] while Figures 3, 6, and 11 were produced with the program MERCURY.[24] CCDC-629980 ([**2**][BF_4]·0.5CH_2Cl_2), -629981 ([**3**][BF_4]), -629982 ([**5**][BF_4]), and -629983 {[**6**][BF_4]·$(CH_3)_2CO$} 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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[1] a) M. A. Bennett, *Comprehensive Organometallic Chemistry II*, Pergamon Press, Oxford, **1995**, vol. 7, p. 549; b) H. Le Bozec, D. Touchard, P. H. Dixneuf, *Adv. Organomet. Chem.* **1989**, *29*, 163–247.

[2] a) K. J. Haack, S. Hashigushi, A. Fujii, T. Ikariya, R. Noyori, *Angew. Chem.* **1997**, *109*, 297–300; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 285–288; b) R. Noyori, M. Yamakawa, S. Hashigushi, *J. Org. Chem.* **2001**, *66*, 7931–7944; c) D. G. I. Petra, J. N. H.

Reek, J. W. Handgraaf, E. J. Meijer, P. Dierkes, P. C. J. Kramer, J. Brussee, H. E. Schoemaker, P. W. N. M. van Leeuwen, *Chem. Eur. J.* **2000**, *6*, 2818–2829; d) S. Ogo, T. Abura, Y. Watanabe, *Organometallics* **2002**, *21*, 2964–2969; e) S. Ogo, K. Uehara, T. Abura, Y. Watanabe, S. Fukuzumi, *Organometallics* **2004**, *23*, 3047–3052; f) J. Canivet, L. Karmazin-Brelot, G. Süss-Fink, *J. Organomet. Chem.* **2005**, *690*, 3202–3211; g) J. Canivet, G. Labat, H. Stoeckli-Evans, G. Süss-Fink, *Eur. J. Inorg. Chem.* **2005**, 4493–4500; h) J. Hannedouche, G. J. Clarkson, M. Wills, *J. Am. Chem. Soc.* **2004**, *126*, 986–987; i) D. J. Cross, I. Houson, A. M. Kawamoto, M. Wills, *Tetrahedron Lett.* **2004**, *45*, 843–846; j) D. Sterk, M. S. Stephan, B. Mohar, *Tetrahedron Lett.* **2004**, *45*, 535–537; k) K. Everaere, A. Mortreux, M. Bulliard, J. Brussee, A. van der Gen, G. Nowogrocki, J.-F. Carpentier, *Eur. J. Org. Chem.* **2001**, 275–291; l) A. M. Maj, K. M. Pietrusiewicz, I. Suisse, F. Agbossou, A. Mortreux, *J. Organomet. Chem.* **2001**, *626*, 157–160; m) K. Everaere, A. Mortreux, J.-F. Carpentier, *Adv. Synth. Catal.* **2003**, *345*, 67–77.

[3] a) D. Jan, L. Delaude, F. Simal, A. Demonceau, *J. Organomet. Chem.* **2000**, *606*, 55–64; b) R. Castarlenas, M. Eckert, P. H. Dixneuf, *Angew. Chem.* **2005**, *117*, 2632–2635; *Angew. Chem. Int. Ed.* **2005**, *44*, 2576–2579.

[4] J. W. Faller, A. Lavoie, *J. Organomet. Chem.* **2001**, *630*, 17–22.

[5] P. D. Smith, A. H. Wright, *J. Organomet. Chem.* **1998**, *559*, 141–147.

[6] B. Therrien, T. R. Ward, M. Pilkington, C. Hoffman, F. Gilardoni, J. Weber, *Organometallics* **1998**, *17*, 330–337.

[7] a) Y. Miyaki, T. Onishi, I. Kurosawa, *Inorg. Chim. Acta* **2000**, *300–302*, 369–377; b) G. Marconi, H. Baier, F. W. Heinemann, P. Pinto, H. Pritzkow, U. Zenneck, *Inorg. Chim. Acta* **2003**, *352*, 188–200; c) T. Ohnishi, Y. Miyaki, H. Asano, H. Kurosawa, *Chem. Lett.* **1999**, *28*, 809–810.

[8] a) B. Therrien, T. R. Ward, *Angew. Chem.* **1999**, *111*, 418–421; *Angew. Chem. Int. Ed.* **1999**, *38*, 405–408; b) B. Therrien, A. König, T. R. Ward, *Organometallics* **1999**, *18*, 1565–1568; c) P. Pinto, G. Marconi, F. W. Heinemann, U. Zenneck, *Organometallics* **2004**, *23*, 374–380; d) K. Umezawa-Vizzini, I. Y. Guzman-Jimenez, K. H. Whitmire, T. R. Lee, *Organometallics* **2003**, *22*, 3059–3065; e) J. W. Faller, P. P. Fontaine, *Organometallics* **2005**, *24*, 4132–4138; f) V. Cadierno, J. Diez, J. Garcia-Alvarez, J. Gimeno, *Chem. Commun.* **2004**, 1820–1821; g) J. W. Faller, D. G. D′Alliessi, *Organometallics* **2003**, *22*, 2749–2757; h) P. D. Smith, T. Geldrich, M. B. Hursthouse, *J. Organomet. Chem.* **2002**, *659*, 1–9; i) K. Umezawa-Vizzini, T. R. Lee, *Organometallics* **2003**, *22*, 3066–3076; j) P. Pinto, A. W. Götz, G. Marconi, B. A. Hess, A. Marinetti, F. W. Heinemann, U. Zenneck, *Organometallics* **2006**, *25*, 2607–2616.

[9] R. Y. C. Shin, G. K. Tan, L. L. Koh, L. Y. Goh, *Organometallics* **2004**, *23*, 6293–6298.

[10] a) T. J. Geldbach, G. Laurenczy, R. Scopelliti, P. J. Dyson, *Organometallics* **2006**, *25*, 733–742; b) A. M. Hayes, D. J. Morris, G. J. Clarkson, M. Wills, *J. Am. Chem. Soc.* **2005**, *127*, 7318–7319; c) H. Brunner, C. Valerio, M. Zabel, *New J. Chem.* **2000**, *24*, 275–279.

[11] M. J.-L. Tschan, F. Chérioux, L. Karmazin-Brelot, G. Süss-Fink, *Organometallics* **2005**, *24*, 1974–1981.

[12] M. J.-L. Tschan, G. Süss-Fink, F. Chérioux, B. Therrien, *Chem. Eur. J.* **2007**, *13*, 292–299.

[13] L. Vieille-Petit, G. Süss-Fink, B. Therrien, T. R. Ward, H. Stoeckli-Evans, G. Labat, L. Karmazin-Brelot, A. Neels, T. Bürgi, R. G. Finke, C. M. Hagen, *Organometallics* **2005**, *24*, 6104–6119.

[14] H. Werner, R. Werner, *J. Organomet. Chem.* **1979**, *174*, C67–C69.

[15] H. Werner, H. Kletzin, *J. Organomet. Chem.* **1982**, *228*, 289–300.

[16] A. C. da Silva, H. Piotrowski, P. Mayer, K. Polborn, K. Severin, *J. Chem. Soc. Dalton Trans.* **2000**, 2960–2963.

[17] K. Mashima, A. Mikami, A. Nakamura, *Chem. Lett.* **1992**, 1795–1798.

[18] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

[19] F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry Part A: Structure and Mechanisms*, 2nd ed., Plenum Press, New York **1984**, p. 113.

[20] M. Jahncke, G. Meister, G. Rheinwald, H. Stoeckli-Evans, G. Süss-Fink, *Organometallics* **1997**, *16*, 1137–1143.

[21] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.

[22] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany **1999**.

[23] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

[24] I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson, R. Taylor, *Acta Crystallogr., Sect. B* **2002**, *58*, 389–397.

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