Chiral Arene Ruthenium Complexes: Synthesis and Molecular Structure of the Enantiopure Cluster Cation (*S*)-$[H_3Ru_3\{C_6H_5[CH(CH_3)CH_2OH]\}(C_6Me_6)_2(O)]^+$

Ludovic Vieille-Petit,[a] Bruno Therrien,[a] and Georg Süss-Fink*[a]

Keywords: Arene ligands / Chirality / Cluster compounds / Ruthenium

The reaction of enantiopure (*R*)-(2-cyclohexa-1,4-dienyl)propan-1-ol with ruthenium chloride hydrate yields, without racemisation of the chiral ligand, the chloro-bridged dinuclear complex (*S*,*S*)-$[RuCl_2\{C_6H_5[CH(CH_3)CH_2OH]\}]_2$ (**1**). The dimer **1** reacts with triphenylphosphane to give the mononuclear complex (*S*)-$[RuCl_2\{C_6H_5[CH(CH_3)CH_2OH]\}(PPh_3)]$ (**2**). A single-crystal X-ray structure analysis of **2** reveals the absolute configuration of the asymmetric carbon atom to have remained, the change from (*R*) to (*S*) being due to the priority change caused by coordination; in the solid state, one-dimensional hydrogen-bonded chains are formed between the hydroxy functions and chloro ligands of neighbouring molecules. The mononuclear cationic complex (*S*)-$[Ru\{C_6H_5[CH(CH_3)CH_2OH]\}(H_2O)_3]^{2+}$, formed in situ from **1** in aqueous solution, reacts with the dinuclear complex $[H_3Ru_2(C_6Me_6)_2]^+$ to give a chiral trinuclear arene-ruthenium cluster, the cation (*S*)-$[H_3Ru_3\{C_6H_5[CH(CH_3)CH_2OH]\}(C_6Me_6)_2(O)]^+$ (**3**). This enantiopure cation has been isolated and characterised as its tetrafluoroborate salt. The single-crystal X-ray structure analysis of (*S*)-[**3**][BF_4] shows a strong intramolecular hydrogen bond between the μ_3-oxo cap and the hydroxy function, which also persists in acetone solvent, as demonstrated by NMR spectroscopy.

Introduction

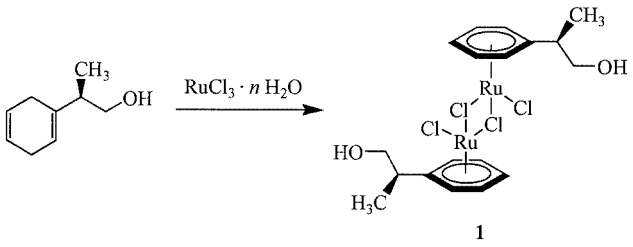
Recently, we found the water-soluble cluster cation $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ to efficiently catalyse the hydrogenation of benzene to give cyclohexane under biphasic conditions.[1,2] On the other hand, much attention has been given to the development of chiral arene-ruthenium complexes for the catalytic transfer hydrogenation of ketones[3−6] and for asymmetric Diels−Alder reactions.[7] Therefore, trinuclear ruthenium cluster cations with functional substituents at the η^6-moiety could give rise to homogeneous catalysts which display special solubility properties or can be immobilised on resins.[8]

Herein we report the synthesis and characterisation of a new chloro-bridged arene-ruthenium dimer, (*S*,*S*)-$[RuCl_2\{C_6H_5[CH(CH_3)CH_2OH]\}]_2$ (**1**), in which the η^6-arene ligand possesses a side-arm substituent incorporating an asymmetric carbon. The dimeric species is used to synthesise an enantiopure mononuclear complex, (*S*)-$[RuCl_2\{C_6H_5[CH(CH_3)CH_2OH]\}(PPh_3)]$ (**2**), as well as an enantiopure trinuclear cluster cation, (*S*)-$[H_3Ru_3\{C_6H_5[CH(CH_3)CH_2OH]\}(C_6Me_6)_2(O)]^+$ (**3**). NMR spectroscopy as well as single-crystal X-ray analyses show that the chiral centre is stable under various reaction conditions.[9]

[a] Institut de Chimie, Université de Neuchâtel,
Case postale 2, CH-2007 Neuchâtel, Switzerland
E-mail: georg.suess-fink@unine.ch

Results and Discussion

The reaction of (*R*)-(2-cyclohexa-1,4-dienyl)propan-1-ol, accessible from the Birch reduction[10] of commercially available (*R*)-(2-phenyl)propan-1-ol, with ruthenium(III) chloride hydrate, in refluxing ethanol, gives the new chiral chloro-bridged dimer (*S*,*S*)-$[RuCl_2\{C_6H_5[CH(CH_3)CH_2OH]\}]_2$ (**1**), which can be isolated quantitatively as an orange powder (Scheme 1). From enantiopure (2-cyclohexa-1,4-dienyl)propan-1-ol only the (*S*,*S*)-isomer is formed. There is no change in the absolute configuration of the asymmetric carbon atom, the change from (*R*) to (*S*) in the denomination is only due to the change in the priority (Cahn−Ingold−Prelog rules) by the coordination of the phenyl group to a ruthenium atom.



1

Scheme 1

Despite the strong acidic conditions during the dehydrogenation reaction, there is no evidence for racemisation of the (*R*)-(2-phenyl)propanol ligands. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **1** show only one set of signals, the $^{13}C\{^1H\}$

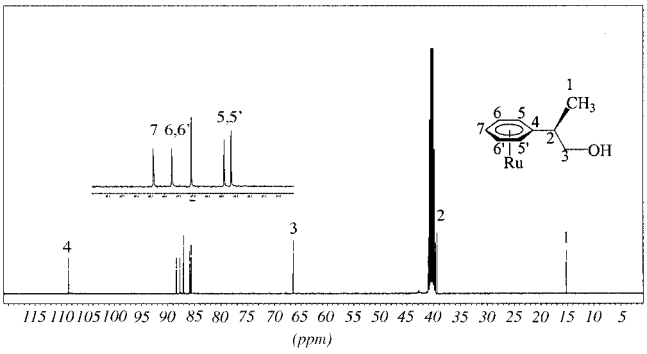
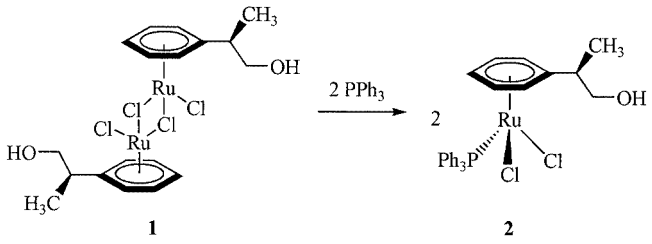


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of **1** in $[D_6]$DMSO (400 MHz)



Scheme 2

NMR spectrum in $[D_6]$DMSO is presented in Figure 1. Except for the distinction between the two carbons at the *ortho* positions as well as the two carbons at the *meta* positions of the η^6-arene moiety, all diastereotopic carbons can be assigned unambiguously.

Cleavage of the chloro bridges of the dinuclear complex **1** with two equivalents of triphenylphosphane in CH_2Cl_2 gives the mononuclear complex (*S*)-$[RuCl_2\{C_6H_5$-$[CH(CH_3)CH_2OH]\}(PPh_3)]$ (**2**) in good yield (Scheme 2). The formation of **2** is conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy, the $^{31}P\{^1H\}$ NMR signal being shifted downfield by 33.2 ppm (as compared to uncoordinated triphenylphosphane).

The orange air-stable compound was crystallised from a slow diffusion of hexane into a chloroform solution containing **2**. A single-crystal X-ray analysis was performed, confirming the molecular structure of **2** (Figure 2).

The ruthenium atom possesses a pseudo-octahedral geometry, and the metrical parameters around the metallic core compare well with those of similar three-legged pianostool $[RuCl_2(\eta^6$-arene$)(PPh_3)]$ complexes.[11−14] A distortion at the arene ligand is present, the Ru−C bond length *trans* to the phosphorous atom, Ru(1)−C(1) 2.274(4) Å, is elongated as compared to the other Ru−C bonds [ranging between 2.187(4) and 2.244(3) Å]. In the solid state, a series of hydrogen bonds between hydroxy functions and chloride

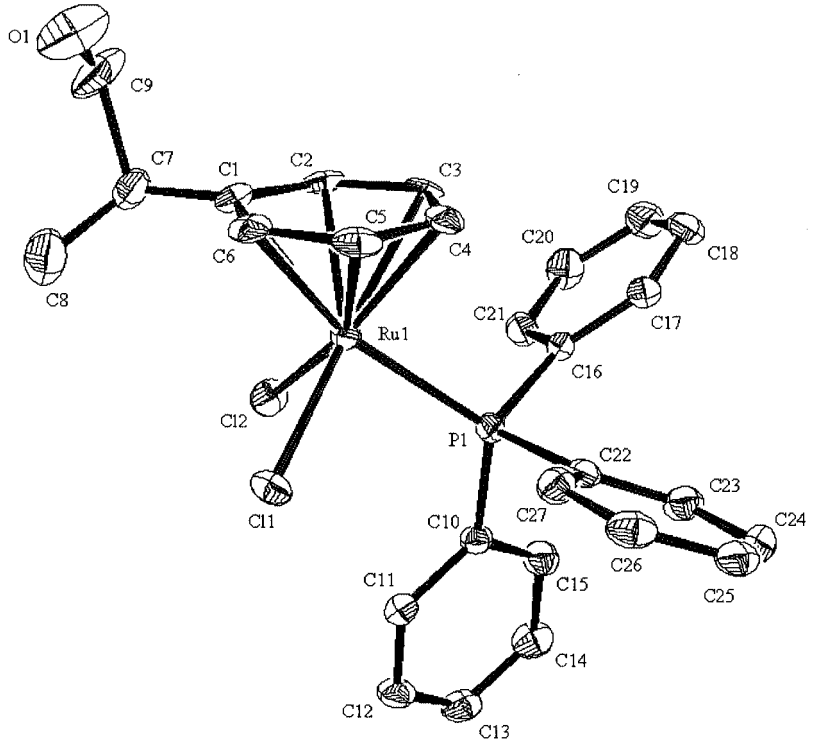


Figure 2. ORTEP view of **2**; displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms and chloroform molecule are omitted for clarity; selected bond lengths (Å) and angles (°): Ru(1)−P(1) 2.3530(10), Ru(1)−Cl(1) 2.4134(9), Ru(1)−Cl(2) 2.3995(10), Ru(1)−C(1) 2.274(4), Ru(1)−C(2) 2.187(4), Ru(1)−C(3) 2.205(4), Ru(1)−C(4) 2.195(4), Ru(1)−C(5) 2.187(4), Ru(1)−C(6) 2.244(3); P(1)−Ru(1)−Cl(1) 91.81(3), P(1)−Ru(1)−Cl(2) 86.34(4), Cl(1)−Ru(1)−Cl(2) 86.62(4)

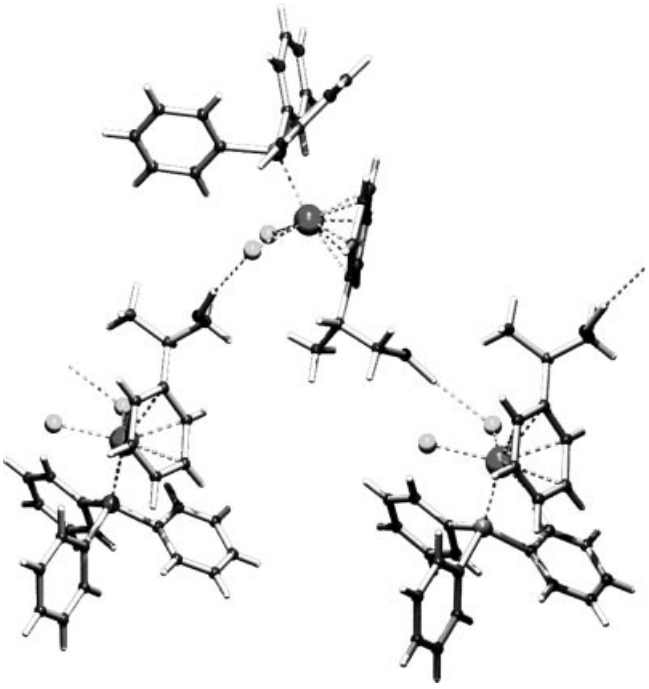
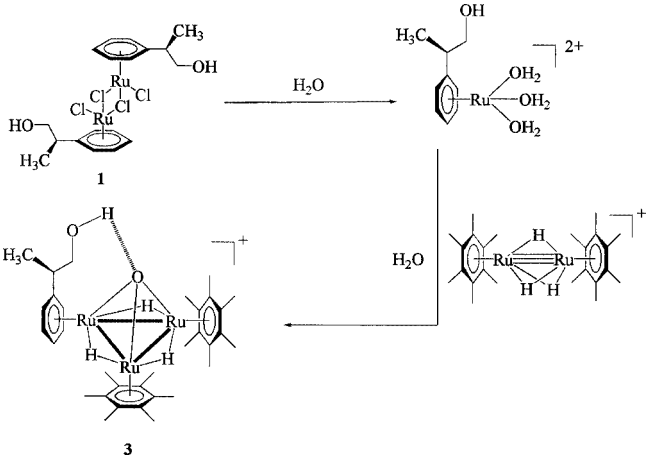


Figure 3. One-dimensional hydrogen bonded chains in the crystalline form of **2**

ligands of neighbouring molecules forms one dimensional chains through the crystal (Figure 3).

In aqueous solution, the dinuclear complex **1** forms the mononuclear complex $[Ru\{C_6H_5[CH(CH_3)CH_2OH]\}(H_2O)_3]^{2+}$, an analogue of the known cation $[(C_6H_6)Ru(H_2O)_3]^{2+}$,[15] which reacts in situ with the dinuclear complex $[H_3Ru_2(C_6Me_6)_2]^+$ [16,17] to give the chiral cluster cation (*S*)-$[H_3Ru_3\{C_6H_5[CH(CH_3)CH_2OH]\}(C_6Me_6)_2(O)]^+$ (**3**; Scheme 3).



Scheme 3

The enantiopure cation (*S*)-[**3**] has been isolated and characterised as its tetrafluoroborate salt. Whereas the known trinuclear ruthenium cluster cation analogues $[H_3Ru_3(\eta^6\text{-arene})(\eta^6\text{-arene'})_2(O)]^+$ [1,14,18,19] give rise to two hydride signals, a triplet and a doublet integrating for one and two protons, respectively, in the ^1H NMR spectra. The three hydrido ligands in **3** are all inequivalent and give rise to three independent signals. The ^1H NMR spectrum of **3** in [D_6]acetone shows three multiplets at high field centered at $\delta = -19.86$, -19.43 and -19.23 ppm, due to the presence of the asymmetric α-carbon on the side arm. In order to ascertain the retention of the chirality during the synthesis of **3**, a single crystal structure analysis of [**3**][BF_4] was performed.

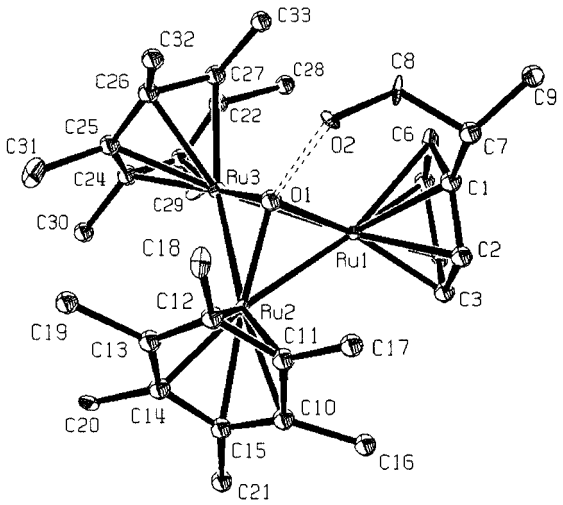


Figure 4. ORTEP view of [**3**]$^+$; displacement ellipsoids are drawn at the 35% probability level, hydrogen atoms, solvent, and the anion are omitted for clarity; selected bond lengths (A) and angles (°): Ru(1)−Ru(2) 2.751(3), Ru(1)−Ru(3) 2.749(3), Ru(2)−Ru(3) 2.785(2), Ru(1)−O(1) 2.058(16), Ru(2)−O(1) 1.935(18), Ru(3)−O(1) 1.971(16); Ru(1)−Ru(2)−Ru(3) 59.54(7), Ru(2)−Ru(3)−Ru(1) 59.62(7), Ru(3)−Ru(1)−Ru(2) 60.84(6), Ru(1)−O(1)−Ru(2) 87.0(6), Ru(1)−O(1)−Ru(3) 86.0(6), Ru(2)−O(1)−Ru(3) 90.9(5)

Poor quality crystals of [**3**][BF_4] were obtained by slow diffusion of benzene into an acetone solution of the salt. The asymmetric unit comprises two independent molecules of **3**, two BF_4 anions, and half a molecule of a disordered benzene. Only one molecule of **3** is shown in Figure 4. The two independent molecules show identical symmetrical data.

The metal core consists of three ruthenium atoms, the three Ru−Ru distances being in accordance with a metal-metal single bond. The three ruthenium atoms are capped by a μ_3-oxo ligand which is almost symmetrically coordinated. As shown by its molecular structure, the presence of the $CH(CH_3)CH_2OH$ side-arm allows **3** to form a strong intramolecular hydrogen bond with the μ_3-oxo cap. The distances between the two oxygen atoms involved in the intramolecular hydrogen bonds are 2.69(3) Å for molecule 1 and 2.66(2) Å for molecule 2.

The strong intramolecular hydrogen bond in **3**, found in the solid state, seems to persist also in acetone solution. The ^1H NMR spectrum of **3** in [D_6]acetone shows a well defined doublet of doublets centered at $\delta = 6.67$ ppm attributed to the proton of the OH group coupled to the two diastereotopic protons of the neighbouring CH_2 group.

Conclusion

The chiral chloro-bridged η^6-(*S*)-(2-phenyl)propan-1-ol ruthenium complex (*S*,*S*)-**1** can be synthesised by dehydrogenation of (*R*)-(2-cyclohexa-1,4-dienyl)propan-1-ol without racemisation. Cleavage of the chloro bridges with triphenylphosphane gives the enantiopure mononuclear complex (*S*)-**2** in good yield. The first water-soluble trinuclear arene-ruthenium cluster cation containing an asymmetric carbon atom tethered to an arene ligand was isolated as the tetrafluoroborate salt (*S*)-[**3**][BF_4]. NMR spectroscopy and X-ray analyses show that no racemisation is observed during the different steps of synthesis. The absolute configuration at the asymmetric α-carbon remains unchanged under the different reaction conditions: acidic conditions during the dehydrogenation to form **1**, basic conditions during the cleavage of the chloro bridges of **2** with triphenylphosphane, and aqueous conditions during the formation of **3**.

Experimental Section

General Remarks: All manipulations were carried out by routine methods under a nitrogen atmosphere. De-ionised water and organic solvents were degassed and saturated with nitrogen prior to use. NMR spectra were recorded using a Varian Gemini 200 BB spectrometer and a Bruker 400 MHz spectrometer. Microanalyses were carried out by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland). Electro-spray mass spectra were obtained in positive-ion mode with an LCQ Finnigan mass spectrometer. The starting dinuclear dichloro complex [$RuCl_2(C_6Me_6)]_2$ was prepared according to known literature methods.[20] (*R*)-(2-Cyclohexa-1,4-dienyl)propan-1-ol was synthesised by sodium reduction of (*R*)-(2-phenyl)propan-1-ol in liquid ammonia.[21]

Complex 1: (*R*)-(2-Cyclohexa-1,4-dienyl)propan-1-ol (2.5 g, 18.1 mmol) was added to a solution of ruthenium trichloride hydrate (1.0 g, 3.8 mmol) in ethanol (70 mL), and the mixture was refluxed overnight. After cooling to room temperature, half of the solvent was evaporated. The orange precipitate was filtered, washed with diethyl ether, and dried under vacuum to give pure [$RuCl_2${C_6H_5[$CH(CH_3)CH_2OH$]}]$_2$. Yield: 1.90 g (81%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.17 (d, ^3J = 6.92 Hz, 6 H, CH_3), 2.73 [m, 2 H, C*H*(CH_3)CH_2OH], 3.44 [dd, ^2J = 10.63, ^3J = 6.01 Hz, 2 H, $CH(CH_3)CH_2$OH], 3.55 [dd, ^2J = 10.63 Hz, ^3J = 5.38 Hz, 2 H, $CH(CH_3)CH_2$OH], 4.06 [br., 2 H, $CH(CH_3)CH_2O$*H*], 5.75 (m, 6 H, H_{arom}), 5.87 (m, 4 H, H_{arom}) ppm. ^{13}C{^{1}H} (100 MHz, [D$_6$]DMSO): δ = 15.24 (CH_3), 39.37 [*C*H(CH_3)CH_2OH], 66.43 [$CH(CH_3)$*C*H_2OH], 85.67, 85.90, 87.06, 87.75, 88.40, 108.63 (C_{arom}) ppm. MS (ESI, positive mode, dmso): *m*/*z* = 580.5 [M − Cl]$^+$ $C_{18}H_{24}Cl_4O_2Ru_2$ (616.3): calcd. C 35.08, H 3.92; found C 34.96, H 4.01.

Complex 2: Two equivalents of triphenylphosphane (170 mg, 0.6 mmol) was added to a suspension of **1** (200 mg, 0.3 mmol) in 30 mL of CH_2Cl_2. The mixture was stirred at room temperature during 2 hours and then filtered through celite to eliminate insoluble degradation materials. The product was purified on a silica gel column, eluting CH_2Cl_2/acetone (10:2) to give **2** as an orange-brown powder. Yield: 295 mg (80%). Orange crystals suitable for X-ray analysis were obtained by recrystallisation from $CHCl_3$/*n*-hexane. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (d, ^3J = 5.98 Hz, 3 H, CH_3), 2.36 [m, 1 H, C*H*(CH_3)CH_2OH], 3.19 [br., 1 H, $CH(CH_3)CH_2O$*H*], 3.99 [m, 1 H, $CH(CH_3)$C*H*$_2$OH], 4.14 [m, 1 H, $CH(CH_3)$C*H*$_2$OH], 4.74 to 4.89 (m, 3 H, Ru-C_6H_5), 5.70 to 5.86 (m, 2 H, Ru-C_6H_5), 7.42 (m, 9 H, P-C_6H_5), 7.76 (m, 6 H, P-C_6H_5) ppm. ^{13}C{^{1}H} (50 MHz, $CDCl_3$): δ = 17.49 (CH_3), 39.06 [*C*H(CH_3)CH_2OH], 66.51 [$CH(CH_3)$*C*H_2OH], 84.10, 84.19, 84.37, 91.78, 92.99, 113.51 (Ru-C_6H_5), 128.48, 130.79, 133.54, 134.45 (P-C_6H_5) ppm. ^{31}P{^{1}H} (80 MHz, $CDCl_3$): δ = 28.93 ppm. MS (ESI, positive mode, CH_3OH): *m*/*z* = 535 [M − Cl]$^+$. $C_{27}H_{27}Cl_2OPRu$ (570.5): calcd. C 56.85, H 4.77; found C 57.02, H 4.71.

Complex 3: A mixture of [$RuCl_2(C_6Me_6)]_2$ (400 mg, 0.6 mmol) and Ag_2SO_4 (376 mg, 1.2 mmol) in water (40 mL) was stirred in the dark for 1 h. During this period the mixture was treated several times with ultrasound, until the orange solid was completely dissolved. The white precipitate (AgCl) was removed by filtration from the yellow solution containing [$Ru(C_6Me_6)(H_2O)_3]^{2+}$. An aqueous solution containing $NaBH_4$ (100 mg, 2.6 mmol, 10 mL H_2O) was then added dropwise to this yellow solution. The solution turned dark-red due to the formation of [$Ru_2(C_6Me_6)_2(\mu_2$-H)$_3]^+$. After filtration, solid [$RuCl_2${C_6H_5[$CH(CH_3)CH_2OH$]}]$_2$ (345 mg, 0.56 mmol) was added. The mixture was heated to 60 °C for 50 hours in a closed pressure Schlenk tube. The resulting red solution was filtered, and a large excess of $NaBF_4$ was added to precipitate [**2**][BF_4]. The precipitate was centrifuged, dissolved in CH_2Cl_2, filtered through celite to eliminate excess $NaBF_4$ and purified on silica-gel plates (eluent: CH_2Cl_2/acetone 2:1). Yield: 210 mg (40%). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = −19.86 (m, 1 H, hydride), −19.43 (m, 1 H, hydride), −19.23 (m, 1 H, hydride), 1.21 [d, ^3J = 7.03 Hz, 3 H, $CH(CH_3)CH_2OH$], 2.49 [m, 1 H, C*H*(CH_3)CH_2OH], 2.77 [s, 18 H, $C_6(CH_3)_6$], 2.78 [s, 18 H, $C_6(CH_3)_6$], 3.63 [m, 1 H, $CH(CH_3)CH_2OH$], 3.90 [m, 1 H, $CH(CH_3)CH_2OH$], 5.39 (m, 2 H, H_{arom}), 5.56 (m, 1 H, H_{arom}), 6.01 (m, 1 H, H_{arom}), 6.10 (m, 1 H, H_{arom}), 6.67 [dd, ^3J = 3.63, ^3J = 11.09 Hz, 1 H, $CH(CH_3)CH_2O$*H*] ppm. ^{13}C{^{1}H} (100 MHz, [D$_6$]acetone): δ = 17.46 [$CH(CH_3)CH_2OH$], 17.51 [$C_6(CH_3)_6$], 42.07 [*C*H(CH_3)CH_2OH], 66.77 [$CH(CH_3)$*C*H_2OH], 74.42, 76.72, 81.57, 84.59, 87.67, 95.29, 113.66 (C_{arom}) ppm. MS (ESI positive mode, acetone): *m*/*z* = 783 [M + H]$^+$. $C_{33}H_{51}BF_4O_2Ru_3$ (869.8): calcd. C 45.57, H 5.91; found C 45.41, H 6.07.

X-ray Crystallographic Study

X-ray Data for (*S*)-[2]·$CHCl_3$: $C_{28}H_{28}Cl_5OPRu$, *M* = 689.79 gmol^{-1}, monoclinic, *P*2$_1$ (no. 4), *a* = 9.6386(9), *b* = 13.5325(11), *c* = 11.4019(12) Å, β = 105.096(11)°, *U* = 1435.9(2) Å^3, *T* = 153 K, *Z* = 2, μ(Mo-K_α) = 1.088 mm^{-1}, 10215 reflections measured, 4654 unique (R_{int} = 0.0317) which were used in all calculations. The final wR_2 (F^2) was 0.0620 (all data).

X-ray Data for (*S*)-[3][BF_4]·C_6H_6: $C_{72}H_{108}B_2F_8O_4Ru_6$, *M* = 1817.62 gmol^{-1}, monoclinic, *P*2$_1$ (no. 4), *a* = 8.8158(9), *b* = 20.2561(14), *c* = 23.352(2) Å, β = 91.870(12)°, *U* = 4167.6(7) Å^3, *T* = 153 K, *Z* = 2, μ(Mo-K_α) = 1.118 mm^{-1}, 15789 reflections measured, 13603 unique (R_{int} = 0.0920) which were used in all calculations. The final wR_2 (F^2) was 0.3828 (all data).

The data were measured using a Stoe Image Plate Diffraction system equipped with a φ circle, using Mo-K_α graphite monochromated radiation (λ = 0.71073 Å) with φ range 0−200°, increment of respectively 1.6 and 1.0°, 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.[22] The refinement and all further calculations were carried out using SHELXL-97.[23] The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined

anisotropically, using weighted full-matrix least-square on F^2. Figure 2 and 4 were drawn with ORTEP [24] and Figure 3 with POV-Ray.[25]

CCDC-213712 (**2**) and -213713 (*S*)-**3**[BF_4] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors are grateful to the Fonds National Suisse de la Recherche Scientifique for financial support. A generous loan of ruthenium chloride hydrate from the Johnson Matthey Technology Centre is gratefully acknowledged.

[1] M. Faure, M. Jahncke, A. Neels, H. Stoeckli-Evans, G. Süss-Fink, *Polyhedron* **1999**, *18*, 2679−2685.
[2] G. Süss-Fink, M. Faure, T. R. Ward, *Angew. Chem.* **2002**, *114*, 105−107; *Angew. Chem. Int. Ed.* **2002**, *41*, 99−101.
[3] Á. Kathó, D. Carmona, F. Viguri, C. D. Remacha, J. Kovács, F. Joó, L. A. Oro, *J. Organomet. Chem.* **2000**, *593−594*, 299−306.
[4] M. Yamakawa, H. Ito, R. Noyori, *J. Am. Chem. Soc.* **2000**, *122*, 1466−1478.
[5] K. Polborn, K. Severin, *Chem. Commun.* **1999**, *24*, 2481−2482.
[6] D. A. Alonso, P. Brandt, S. J. M. Nordin, P. G. Andersson, *J. Am. Chem. Soc.* **1999**, *121*, 9580−9588.
[7] D. L. Davies, J. Fawcett, S. A. Garratt, D. R. Russell, *Chem. Commun.* **1997**, *15*, 1351−1352.
[8] S. B. Wendicke, E. Burri, R. Scopelliti, K. Severin, *Organometallics* **2003**, *22*, 1894−1897.
[9] H. Dialer, P. Mayer, K. Polborn, W. Beck, *Eur. J. Inorg. Chem.* **2001**, 1051−1055.
[10] A. J. Birch, *J. Chem. Soc.* **1950**, 1951.
[11] M. R. J. Elsegood, D. A. Tocher, *Polyhedron* **1995**, *14*, 3147−3156.
[12] A. Hafner, A. Mühlebach, P. A. van der Schaaf, *Angew. Chem.* **1997**, *109*, 2213−2216; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2121.
[13] H. D. Hansen, J. H. Nelson, *Organometallics* **2000**, *19*, 4740−4755.
[14] L. Vieille-Petit, S. Unternährer, B. Therrien, G. Süss-Fink, *Inorg. Chim. Acta*, in press.
[15] M. Stebler-Röthlisberger, W. Hummel, P. A. Pittet, H.-B. Bürgi, A. Ludi, A. E. Merbach, *Inorg. Chem.* **1988**, *27*, 1358−1363.
[16] M. A. Bennett, J. P. Ennett, K. I. Gell, *J. Organomet. Chem.* **1982**, *233*, C17; M. A. Bennett, J. P. Ennett, *Inorg. Chim. Acta* **1992**, *198−200*, 583−592.
[17] M. Jahncke, G. Meister, G. Rheinwald, H. Stoeckli-Evans, G. Süss-Fink, *Organometallics* **1997**, *16*, 1137−1143.
[18] L. Vieille-Petit, B. Therrien, G. Süss-Fink, *Inorg. Chim. Acta*, in press.
[19] L. Vieille-Petit, B. Therrien, G. Süss-Fink, T. R. Ward, *J. Organomet. Chem.*, in press.
[20] M. A. Bennett, T.-N. Huang, T. W. Matheson, A. K. Smith, *Inorg. Synth.* **1982**, *21*, 74−78.
[21] M. E. Kuehne, B. F. Lambert, *Org. Synth.* **1973**, *5*, 400−403.
[22] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
[23] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1999**.
[24] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.
[25] S. Anger, D. Bayer, C. Cason, C. Dayley, S. Demlow, A. Enzmann, D. Farmer, T. Wegner, C. Young, POV-Ray software version 3.1, Indianapolis, USA, **1991**.

Received June 27, 2003

