Structural Studies of an Array of Mixed Diamine Phosphine Ruthenium(II) Complexes[1]

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Treatment of $RuCl_2(\eta^2\text{-}Ph_2PCH_2CH_2OCH_3)_2$ with various chelating diamines permitted the isolation of the corresponding $RuCl_2(\eta^1\text{-}Ph_2PCH_2CH_2OCH_3)_2$(diamine) complexes in high yield (diamine = 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane, 1,2-phenylenediamine, 1,8-diaminonaphthalene, 2,2′-bipyridine, 1,10-phenanthroline). In solution, all complexes prefer the *trans*-chloro *cis*-phosphine arrangement, as deduced by NMR spectroscopy. X-ray studies showed that in the solid state all three possible isomers of the octahedral $RuCl_2P_2$(diamine) complexes are present. The reaction of the $RuCl_2(\eta^1\text{-}Ph_2PCH_2CH_2OCH_3)_2$(diamine) complexes with 1 equiv of $AgSbF_6$, $AgBF_4$, or $TlPF_6$ leads to the abstraction of one chloride by simultaneously coordinating one ether oxygen to ruthenium and forming monocationic $[RuCl(\eta^1\text{-}Ph_2PCH_2CH_2OCH_3)(\eta^2\text{-}Ph_2PCH_2CH_2OCH_3)(\text{diamine})]^+$ compounds. If a large excess of silver or thallium salt is used, the dichloro complexes are converted to the $[Ru(\eta^2\text{-}Ph_2PCH_2CH_2OCH_3)_2(\text{diamine})]^{2+}$ dications. In the case of 1,2-phenylendiamine as coligand, the corresponding dication is only observed in traces. NMR spectroscopic investigations and X-ray structural analyses confirm the η^1 and η^2 coordination of the ether−phosphine ligands in the corresponding mono- and dicationic ruthenium(II) complexes.

Introduction

The combinatorial approach as well as miniaturization, automated parallel synthesis, and screening methods have become increasingly important in many areas of chemistry.[2−5] Besides the enormous gain in time in the development of new drugs and catalysts, a further driving force is the saving of expensive and environmentally encumbering chemicals. While in drug design there have already been a number of successful applications of these new techniques,[6] in catalysis research these new methods have been introduced only gradually.[4,5,7] Many approaches to parallelization in catalysis focus on screening methods.[8−12] Highly selective catalysts require transition-metal complexes with well-designed structural, electronic, and stereochemical features. Small differences in the coordination sphere of the transition metal commonly lead to dramatic changes in the selectivity and activity of the catalytic conversion.[13] Thus, the relation between the structure of the ligands and the physicochemical properties of the corresponding metal complexes has been the subject of many investigations in order to understand the selectivity in catalysis.

A prospective objective of our group is the combination of parallel synthesis and interphase chemistry. As an example, neutral and cationic diamine(ether−phosphine)ruthenium(II) complexes were selected. We have successfully supported (ether−phosphine)ruthenium(II) complexes on polysiloxane phases by the sol−gel route[14−18] and demonstrated their use as catalysts in interphases.[19,20] For the development of parallel and screening methods for this chemistry, the (ether−phosphine)ruthenium(II) complexes have to be modified in order to create a large array of structurally different

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compounds. Thus, diamines which are easily accessible in various forms were introduced as coligands. Diaminediphosphineruthenium(II) complexes with various combinations of phosphine and diamine ligands have been successfully developed[21−30] to catalyze the hydrogenation of ketones in the presence of carbon−carbon multiple bonds with high diastereo- and enantioselectivity.[31−36]

Here we wish to report on the validation of a synthetic route to novel highly reactive bis(chelated) diamine(ether−phosphine)ruthenium(II) complexes and their complete characterization by NMR and MS spectroscopy and X-ray diffractometry. These complexes will serve as benchmarks for parallel synthesized libraries of these types of complexes.

Results and Discussion

For the synthesis of the mixed diaminediphosphineruthenium(II) complexes **3**−**5** according to Scheme 1, advantage was taken of the hemilabile character of the ether−phosphine ligand $Ph_2PCH_2CH_2OCH_3$.[37−39] This route was found to be the most straightforward and efficient way to generate the highly reactive products **5a**−**g**. Moreover, this method is generally applicable to numerous comparable examples and thus is promising for later use in parallel synthesis. The hemilabile ether−phosphines serve several purposes: (i) the coordinated phosphines stabilize the complexes and increase the electron density at the metal site (η^1(P)-coordinated, P∼O), (ii) the ether functions act as synthetic tools during preparation of the diamine complexes **3a**−**g**, and (iii) the ether complexes act as protecting groups of the reactive sites in the catalyst precursors **5a**−**g** (η^2(P,O)-coordinated, P⌒O).[40]

Scheme 1

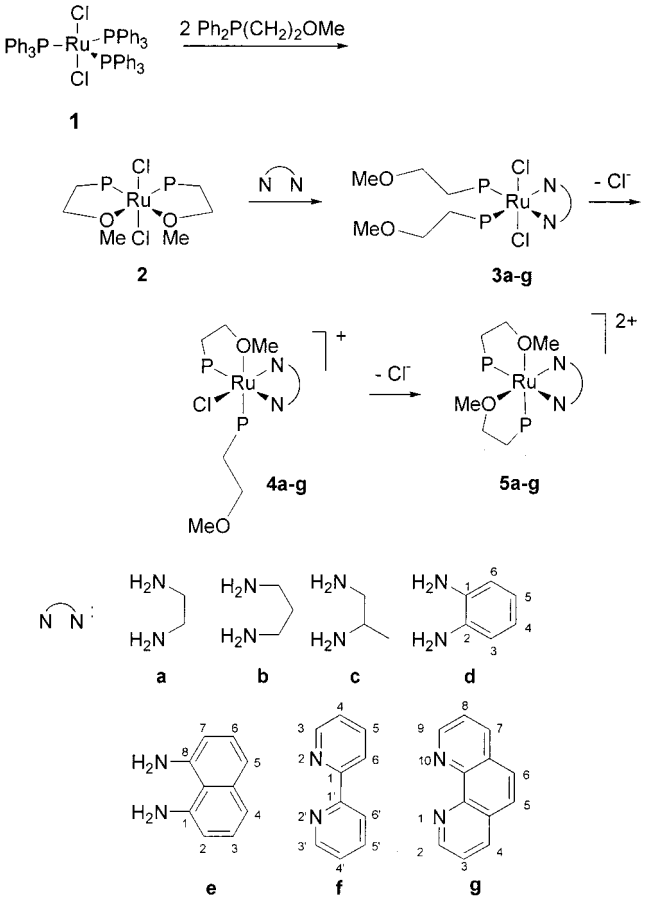
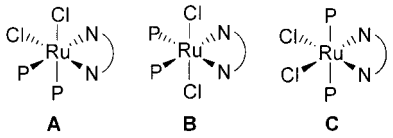


Chart 1



Synthesis and Characterization of the $RuCl_2P_2$(diamine) Complexes 3a−g. The bis(ether−phosphine)ruthenium(II)[37,39] complex **2** has two weak ruthenium−oxygen interactions which are easily cleaved by the stronger nitrogen donors of bidentate diamine ligands. Thus, mixing the bis-chelate **2** with a slight excess of the diamines **a**−**g** in dichloromethane gives the ruthenium(II) species $RuCl_2P_2$(diamine) (**3a**−**g**) in good to very good yield (Scheme 1). The yellow (**3a**−**d**), brown (**3e**,**f**), and red (**3g**) solids are soluble in organic solvents. For octahedral structures of the general formula $RuCl_2P_2$(diamine) there are three possible coordination geometries. NMR spectroscopy allows us to distinguish between the isomers which are displayed in Chart 1. In the ^{1}H NMR spectra of $RuCl_2P_2$(diamine) (**3a**−**g**), characteristic sets of signals are observed which can be assigned to the phosphine as well as to the diamine ligands. In all cases the broad and featureless peaks prevent a detailed analysis; however, the integration of the proton resonances indicates that the phos-

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phine-to-diamine ratio is in agreement with the composition of **3a**−**g**. Furthermore, the chemical shifts of the singlets due to the protons of the methoxy functions agree well with the η^1-P∼O unit. The singlets in the $^{31}P\{^1H\}$ NMR spectra of **3a**,**b** and **3d**−**g** indicate that the phosphine groups are chemically equivalent, which is only the case if the structure of the $RuCl_2P_2$(diamine) isomers has C_{2v} symmetry, as in **B** or **C** (Chart 1). The nonsymmetrical diamine in **3c** causes the loss of the C_2 axis, which results in the splitting of the phosphorus resonances into an AB pattern. For compounds **3d**,**f**, additional AX multiplets are observed in the $^{31}P\{^1H\}$ NMR spectra. These signals are generated from minor amounts of the C_1-symmetrical *cis*,*cis*,*cis*-$RuCl_2P_2$-(diamine) isomers (structure **A**), which are also formed during the reaction. The phosphorus chemical shifts of **3a**−**g** and the phosphorus−phosphorus coupling constants of **3c** suggest that the ether−phosphines are η^1-(P)-coordinated[37,39] and are positioned cis to one another. Given also the presence of the diamine chelate, the chlorines have to be in a mutually trans arrangement. This supports structure **B** as the most favored geometry in solution. The $^{13}C\{^1H\}$ NMR spectra are consistent with these findings. Characteristic signals are found due to the η^1(P)-ether−phosphines as well as due to the aliphatic (**3a**−**c**) and aromatic diamines (**3d**−**g**). In the $^{13}C\{^1H\}$ NMR spectra of complexes **3a**,**b**,**d**−**g** the AXX′ splitting patterns which are observed for the carbon atoms attached to phosphorus are caused by the interaction of the magnetically inequivalent phosphorus atoms with the ^{13}C nuclei. They are also compatible with structure **B** (Chart 1).

While geometry **B** is preferred in solution, all three structures **A**−**C** (Chart 1) are found in the solid state. This was confirmed by single-crystal X-ray diffraction studies of the complexes **3a**−**c**,**e**,**g**. Examples for structure **A** (**3a**) and **B** (**3e**) are shown in Figure 1, and selected bond distances and angles are summarized in Table 1. The 1,3-diaminopropane (**3b**),[41] 1,2-diaminopropane (**3c**),[41] and 1,8-diaminonaphthaline (**3e**) (Figure 1) derivatives crystallize in the coordination geometry **B**, which represents the most commonly found structure for mixed-ligand ruthenium complexes of this type.[21] Rarely observed is the cis,cis,cis form **A**, which is favored by the 1,2-diaminoethane complex **3a** (Figure 1), and the geometry **C**, where the phosphines are located mutually trans to each other as in the 1,10-phenanthroline complex **3g**. Unfortunately, the quality of the crystal of **3g** was so poor that, besides the arrangements of the ligands around ruthenium, no further information can be given with respect to bond lengths and angles.

Crystal Structures of 3a and 3e. In **3a**, the all-cis isomer **A** (Chart 1), the octahedral coordination of ruthenium is slightly distorted, the equatorial plane consisting of the atoms Cl(2), P(1), N(1), and N(2) being displaced toward the sterically less demanding Cl(1) such that Ru(1) is shifted out of this plane toward P(2) by almost 0.2 Å. This is also reflected in the fact that most of the angles formed by Cl(1) with ligands in cis positions are significantly smaller than 90°, with the Cl(1)−Ru(1)−Cl(2) angle of 92.86(6)° being the exception. In contrast, the Cl(1)−Ru(1)−P(2) angle between the axial ligands, 174.49(6)°, deviates moderately from a linear arrangement. The different trans influences of the ligands at ruthenium affects the Ru−P distances only marginally, with Ru(1)−P(1) (2.296(2) Å, trans to nitrogen) slightly longer than Ru(1)−P(2) (2.244(2) Å, trans to chlorine). The methoxyethyl chains of both phosphine ligands implement all-trans conformations, with torsional angles being in the range of 171−176°. The 1,2-diaminoethane chelate adopts a twist conformation, with C(10) and C(11) twisted out of the plane formed by Ru(1), N(1), and N(2) by 0.4 and −0.2 Å.

In **3e**, the more common isomer **B** (Chart 1), the atoms Ru(1), P(1), P(2), N(1), and N(2) deviate by less than 0.08 Å from the equatorial least-squares plane. However, the chlorine atoms are pushed from their axial positions toward the diamine by the phosphine ligands,

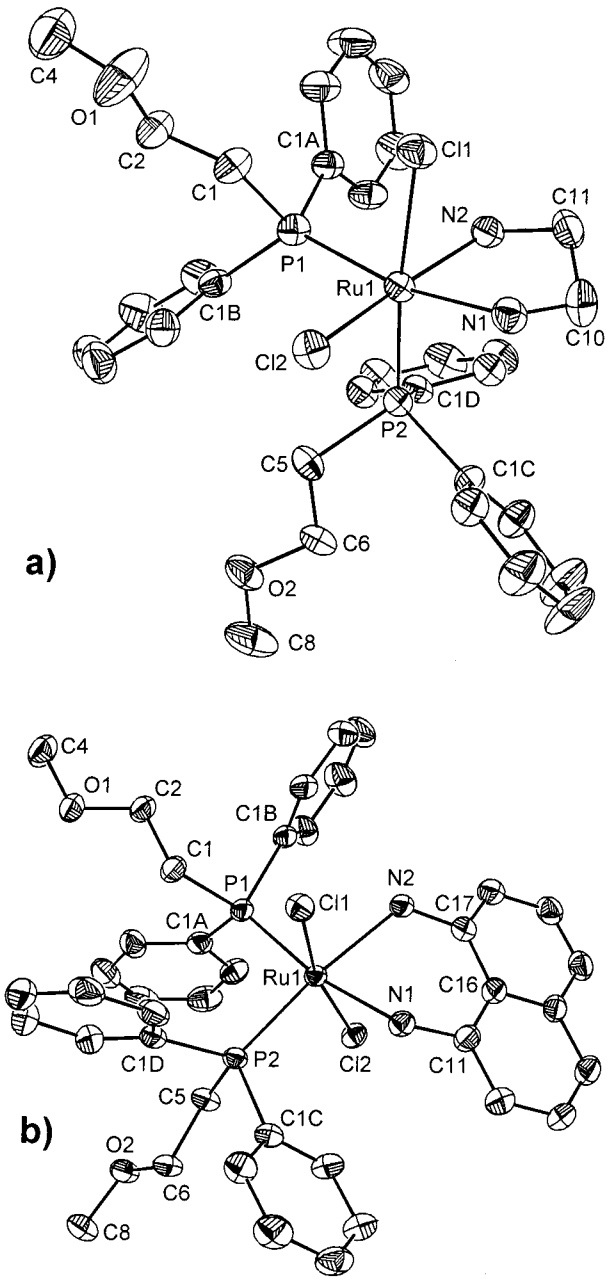

Figure 1. ORTEP plots of (a) **3a** and (b) **3e** shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

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Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 3a,e, 4b, and 5a

	3a	3e	4b	5a
Ru(1)−Cl(1)	2.488(2)	2.420(1)	2.412(1)	
Ru(1)−Cl(2)	2.436(2)	2.416(1)		
Ru(1)−P(1)	2.296(2)	2.275(1)	2.307(1)	2.304(2)
Ru(1)−P(2)	2.244(2)	2.272(1)	2.248(1)	2.234(2)
Ru(1)−N(1)	2.147(5)	2.211(2)	2.178(3)	2.184(7)
Ru(1)−N(2)	2.134(5)	2.208(2)	2.148(3)	2.122(7)
Ru(1)−O(1)			2.309(2)	2.283(7)
Ru(1)−O(2)				2.182(6)
Cl(1)−Ru(1)−Cl(2)	92.86(6)	167.56(2)		
Cl(1)−Ru(1)−N(1)	80.02(15)	81.81(6)	79.97(8)	
Cl(1)−Ru(1)−N(2)	80.05(15)	82.44(6)	165.67(8)	
Cl(1)−Ru(1)−P(1)	86.73(6)	90.80(3)	98.86(3)	
Cl(1)−Ru(1)−P(2)	174.49(6)	97.39(3)	93.45(3)	
P(1)−Ru(1)−P(2)	97.61(6)	92.50(3)	98.63(4)	95.45(8)
N(1)−Ru(1)−N(2)	80.2(2)	75.4(1)	90.1(1)	80.3(3)
O(1)−Ru(1)−N(1)			88.5(1)	90.7(3)
O(1)−Ru(1)−N(2)			80.7(1)	86.7(3)
P(1)−Ru(1)−O(1)			81.08(7)	81.00(18)
P(2)−Ru(1)−O(1)			177.89(7)	171.5(2)
O(2)−Ru(1)−N(1)				90.1(3)
O(2)−Ru(1)−N(2)				169.7(3)
P(1)−Ru(1)−O(2)				88.97(18)
P(2)−Ru(1)−O(2)				82.43(18)
O(1)−Ru(1)−O(2)				89.7(3)

forming an angle of 167.56(2)°. The plane of the diamine ligand is tilted from the equatorial plane by a dihedral angle of 42.8(1)°. In comparison to **3a**, the Ru−Cl distances are slightly shorter and the Ru−N bonds slightly longer. In the methoxyethyl chains of the phosphines, the P−C bonds deviate from an all-trans arrangement and, with P−C−C−O torsional angles of 151 and 144°, are almost partially eclipsed (anticlinal).

Syntheses and Characterization of the Cations [RuCl(P∼O)(P⌒O)(N⌒N)]X (4a−d,f) and [Ru(P⌒O)$_2$(N⌒N)]X$_2$ (5a−c,e−g). Complexes **3a−g** react with different chloride scavengers such as $AgSbF_6$, $AgBF_4$, and $TlPF_6$ in dichloromethane to give solutions from which the mono- and dicationic salts **4a−d,f**, and **5a−c,e−g** are isolated (Scheme 1). Depending on the amount of silver and thallium salt used, one or two chloride ions are abstracted by simultaneously closing one or two rings via ether coordination. In the case of **3d**, the conversion into **5d** remained incomplete, even after a prolonged reaction time and the presence of a large excess of silver salt. Only traces of **5d** are observed in addition to the main product **4d**. In these reaction steps, the advantage of the ether−phosphines becomes obvious, as they protect the vacant coordination sites and circumvent the need for further weakly coordinating ligands such as acetonitrile, THF, and acetone. The mono- and dicationic species **4a−d,f**, and **5a−c,e−g** are obtained as colored powders. In the solid state they are relatively insensitive, while in solution they are rather sensitive toward air. They readily decompose in the presence of water. Due to their polar composition they dissolve in moderately polar solvents such as dichloromethane.

The formation of only one η^2-P⌒O chelate ring generates two sets of resonances in the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of the monocationic complexes **4a−d,f**. In all cases, the signals caused by the ether−phosphine chelate are shifted downfield compared to the η^1-P∼O unit. This holds especially for the nuclei belonging to groups which are directly bound to the ruthenium-coordinated oxygen. Thus, chemical shift differences of 3−6 ppm in the ^{13}C{^{1}H} and of 0.1−0.5 ppm in the ^{1}H NMR spectra are observed for the CH_2OCH_3 fragments. The ^{31}P{^{1}H} NMR spectra contain AX patterns with $^2J_{PP}$ coupling constants typically found for cis-arranged phosphines.

The loss of symmetry which is caused by the 2-fold ring closure in **5a−c,e−g** results in two chemically inequivalent phosphine groups. As they are located in similar structural environments, their ^{31}P{^{1}H} NMR spectra display the typical splitting patterns of AB spectra. The small coupling constants ($^2J_{PP} \approx 35$ Hz) confirm the cis arrangement of both phosphine groups in the complexes **5a−c,e−g**. The chiral carbon center in the diamine ligand of **5c** generates a pair of diastereomeric complexes, which give rise to two AB multiplets in the ^{31}P{^{1}H} NMR spectrum. The additional low-field shifts of the ^{31}P resonances in the spectra of **5a−c,e−g** compared to those of **3a−g** are indicative of the formation of five-membered rings.[42] This is supported by the ^{13}C{^{1}H} NMR spectra. Due to the coordination of the ether oxygen, the ^{13}C signals of the carbon atoms of the methyl and methylene groups bound to the oxygen are shifted to lower field by approximately 10 ppm. In agreement with the ^{31}P{^{1}H} NMR spectra, two sets of signals are observed in the ^{13}C{^{1}H} NMR spectra of **5a−c,e−g** for the phosphine ligands. The spectra are completed by the characteristic ^{13}C resonances of the diamines in the alkane (**5a−c**) and aromatic (**5e−f**) regions, respectively.

Crystal Structures of 4b and 5a. The cationic complex **4b** shares some structural features with the isomer **A** of complex **3a**, insofar as one phosphine ligand is located in the equatorial plane defined by the chelating diamine ligand, while the other phosphine ligand resides in an axial position (Figure 2). Consequently, the ruthenium is displaced from the equatorial plane toward P(2) by 0.17 Å and the angles involving O(1) and cis ligands are significantly smaller than 90°. The diaminopropane chelate adopts a chair conformation, where the tip involving ruthenium is flattened (torsional angles about the Ru−N bonds are 19−22°) but C(11) is pushed more strongly out of plane (torsional angles about the C(11)−C(10) and C(11)−C(12) bonds in the range 71−74°). The five-membered chelate created by the η^2-phosphine forms a regular twisted ring. The two Ru−P distances differ from each other more than in the neutral compounds **3a**,**e**. The methoxyethyl chain of the η^1-phosphine is in an all-trans conformation, except for the P−C bond that adopts a gauche position with respect to the chain, with a P−C−C−O torsional angle of 71°.

In the dicationic complex **5a**, the phosphorus atoms differ also with respect to the equatorial plane defined by the chelating 1,2-diaminoethane. However, the out-of-plane displacement of ruthenium toward P(2) is not as strong (0.12 Å). Similar to **4b**, the η^2-phosphine chelate involving P(1) adopts a twist conformation, as does the ethylenediamine ring. In contrast, the η^2-phosphine involving P(2) adopts an envelope conformation, with C(6) forming the flap.

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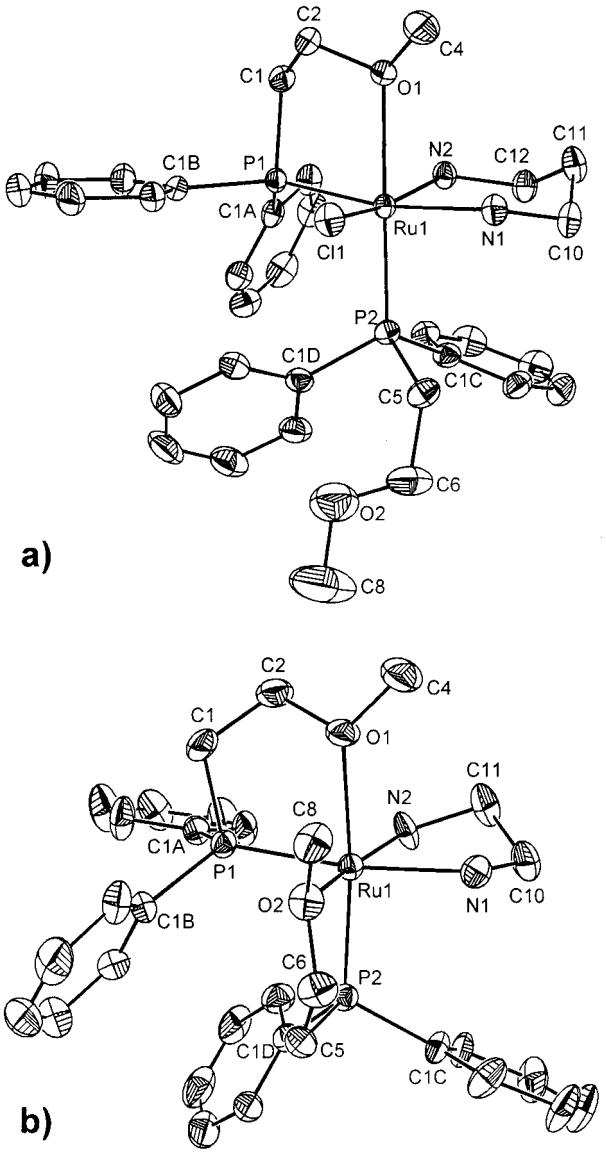

Figure 2. ORTEP plots of (a) **4b** and (b) **5a** shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

Conclusion

An efficient method to produce a large variety of neutral and cationic diamine(ether−phosphine)ruthenium(II) complexes was established. The geometry of these complexes is controlled via the cis diamines and the ether−phosphine ligands. Of importance is the exclusive cis arrangement of the weak Ru−O bonds in the complexes **5a**−**c**,**e**−**g**, since many of the transition-metal-catalyzed conversions require two available coordination sites cis to one another. Interestingly, in the case of the neutral complexes **3a**−**g** without Ru−O contacts, a sensitive interplay between the stereochemistry of the diamine ligand and electronic factors decide the geometry of the complex. Therefore, all three possible isomers are found in the solid state by X-ray analysis of the complexes **3a**−**g**. However, as catalysis is performed in solution or under solution-like conditions, this should have no impact on the selectivity and activity of the potential catalyst precursors **3a**−**g**, since in solution geometry **B** is exclusively formed. The transformation of this chemistry to automatization and parallelization is in progress.

Experimental Section

General Comments. All experiments were carried out under an atmosphere of argon by use of standard Schlenk techniques. Solvents were dried with appropriate reagents, distilled, degassed, and stored under argon.

$RuCl_3 \cdot 3H_2O$ was purchased from ChemPur; 1,8-diaminonaphthalene and $AgSbF_6$ were available from Fluka. $AgBF_4$, 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane, 1,2-phenylenediamine, 2,2′-bipyridine, 1,10-phenanthroline, and $TlPF_6$ were purchased from Merck or Strem.

The precursor $RuCl_2(PPh_3)_3$,[43] the ether−phosphine $Ph_2P(CH_2)_2OCH_3$,[44] and **2**[37] were synthesized according to literature methods.

Elemental analyses were performed with an Elemental Vario EL analyzer. FD mass spectra were taken on a Finnigan MAT 711 A instrument, modified by AMD and reported as mass/charge (*m*/*z*). The high-resolution $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DRX 250 spectrometer at 298 K. Frequencies and standards are as follows: $^{31}P\{^1H\}$ NMR, 101.25 MHz; $^{13}C\{^1H\}$ NMR, 62.90 MHz. The ^1H and ^{13}C chemical shifts were calibrated to deuterated solvent peaks, which are reported relative to TMS. All assignments are supported by ^{13}C 135DEPT experiments. ^{31}P chemical shifts were measured relative to 85% H_3PO_4 (δ 0).

General Procedure for the Preparation of the Neutral Complexes 3a−g. The corresponding dinitrogen ligand **a**−**g** (10% excess) was dissolved in 25 mL of dichloromethane and added dropwise to a stirred solution of **2** in 25 mL of dichloromethane. After the reaction mixture had been stirred for another 45 min at room temperature, the volume of the solution was concentrated to about 5 mL under reduced pressure. Addition of 80 mL of *n*-hexane caused the precipitation of a solid, which was filtered off (P3), washed three times with 25 mL portions of *n*-hexane, and dried under vacuum.

Complex 3a. Complex **2** (300 mg, 0.454 mmol) was treated with **a** (0.033 mL, 0.50 mmol) to give **3a**: yield 307 mg (94%) of a yellow powder. ^1H NMR ($CDCl_3$): δ 2.2−2.4 (m, 4H, PCH_2), 2.6−2.8 (m, 8H, CH_2NH_2), 2.9 (s, 6H, OCH_3), 2.9−3.0 (m, 4H, CH_2O), 7.1−7.7 (m, 20H, C_6H_6). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 38.8 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 25.2 (m,[45a] N = 27.0 Hz, PCH_2), 43.6 (s, NCH_2), 57.9 (s, OCH_3), 69.0 (s, CH_2O), 128.2 (m,[45b] N = 8.2 Hz, *m*-C_6H_5), 129.1 (s, *p*-C_6H_5), 132.7 (m,[45c] N = 8.2 Hz, *o*-C_6H_5), 134.4 (m,[45a] N = 35 Hz, *i*-C_6H_5). FD-MS: *m*/*z* 720.6 (M^+). Anal. Calcd for $C_{32}H_{42}Cl_2N_2O_2P_2Ru$: C, 53.34; H, 5.87; N, 3.89; Cl, 9.84. Found:[25] C, 52.87; H, 5.53; N, 3.71; Cl, 9.87.

Complex 3b. Compound **2** (300 mg, 0.454 mmol) was treated with **b** (0.042 mL, 0.50 mmol) to give **3b**: yield 320 mg (96%) of a yellow powder. ^1H NMR ($CDCl_3$): δ 1.6 (m, 2H, NCH_2CH_2), 2.2−2.4 (m, 4H, PCH_2), 2.9 (s, 6H, OCH_3), 2.8−3.0 (m, 12H, NH_2CH_2, CH_2O), 7.2−7.7 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 42.7 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 26.8 (m,[45a] N = 28.0 Hz, PCH_2), 29.9 (s, NCH_2CH_2), 39.5 (s, NCH_2), 58.0 (s, OCH_3), 70.0 (s, CH_2O), 128.6 (m,[45b] N = 7.6 Hz, *m*-C_6H_5), 129.6 (s, *p*-C_6H_5), 134.0 (m,[45c] N = 7.2 Hz, *o*-C_6H_5), 134.6 (m,[45a] N = 32.7 Hz, *i*-C_6H_5). FD-MS: *m*/*z* 734.6 (M^+). Anal. Calcd for $C_{33}H_{44}Cl_2N_2O_2P_2Ru$: C, 53.95; H, 6.04; N, 3.81; Cl, 9.65. Found:[46] C, 53.29; H, 6.15; N, 3.58; Cl, 9.32.

(43) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945.

(44) Lindner, E.; Meyer, S.; Wegner, P.; Karle, B.; Sickinger, A.; Steger, B. *J. Organomet. Chem.* **1987**, *335*, 59.

(45) A part of an AXX′ pattern: (a) $N = |^1J_{PC} + {}^3J_{PC}|$; (b) $N = |^3J_{PC} + {}^5J_{PC}|$; (c) $N = |^2J_{PC} + {}^4J_{PC}|$.

(46) Although high temperature and catalyst was used to determine the C, H analyses, some of the carbon values remained low. This is probably due to incomplete combustion, which may be caused by ruthenium.

Complex 3c. Complex **2** (300 mg, 0.454 mmol) was treated with **c** (0.043 mL, 0.50 mmol) to give **3c**: yield 304 mg (91%) of a yellow powder. ^{1}H NMR ($CDCl_3$): δ 0.9 (d, $^3J_{HH}$ = 4.5 Hz, 3H, CHC*H*$_3$), 1.9−2.2 (m, 1H, C*H*CH$_3$), 2.4−3.3 (m, 14H, PCH$_2$, CH$_2$O, NH$_2$, NH$_2$CH$_2$), 2.9 (br, 6H, OCH$_3$), 7.2−7.8 (m, 20H, C$_6$H$_5$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 39.1, 38.9 (AB pattern, $^2J_{PP}$ = 36.7 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 20.4 (s, C*C*H$_3$), 25.4 (m, PCH$_2$), 49.6 (s, NCH), 50.9 (s, NCH$_2$), 58.0 (s, OCH$_3$), 69.1 (d, $^2J_{PC}$ = 4.0 Hz, CH$_2$O), 128.1 (d, $^3J_{PC}$ = 4.9 Hz, *m*-C$_6$H$_5$), 128.2 (d, $^3J_{PC}$ = 6.4 Hz, *m*-C$_6$H$_5$), 129.0, 129.3 (2s, *p*-C$_6$H$_5$), 132.3, 133.2 (2d, $^2J_{PC}$ = 6.4 Hz, *o*-C$_6$H$_5$), 134.8−133.8 (m, *i*-C$_6$H$_5$). FD-MS: *m*/*z* 734.6 (M$^+$). Anal. Calcd for $C_{33}H_{44}Cl_2N_2O_2P_2Ru$: C, 53.95; H, 6.04; N, 3.81; Cl, 9.65. Found: C, 53.53; H, 5.75; N, 3.75; Cl, 9.38.

Complex 3d. Complex **2** (300 mg, 0.454 mmol) was treated with **d** (54 mg, 0.50 mmol) to give **3d**: yield 206 mg (59%) of a pale yellow powder. ^{1}H NMR ($CDCl_3$): δ 2.2−2.4 (m, 4H, PCH$_2$), 2.9 (m, 6H, OCH$_3$), 2.9−3.0 (m, 4H, CH$_2$O), 4.5 (s, 4H, NH$_2$), 6.8−7.0 (m, 4H, C$_6$H$_4$), 7.1−7.7 (m, 20H, C$_6$H$_5$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 40.7 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 25.2 (m,[45a] *N* = 26.5 Hz, PCH$_2$), 58.0 (s, OCH$_3$), 69.1 (m,[45b] *N* = 5.0 Hz, CH$_2$O), 127.3 (s, C3, C6), 127.8 (s, C4, C5), 128.4 (m,[45b] *N* = 8.5 Hz, *m*-C$_6$H$_5$), 129.4 (s, *p*-C$_6$H$_5$), 132.8 (m,[45c] *N* = 8.4 Hz, *o*-C$_6$H$_5$), 134.2 (m,[45a] *N* = 36.3 Hz, *i*-C$_6$H$_5$), 140.1 (s, C1, C2). ^{31}P{^{1}H} NMR ($CDCl_3$) for the C_1 isomer: δ 37.6 (d, $^2J_{PP}$ = 34.9 Hz), 47.5 (d, $^2J_{PP}$ = 34.9 Hz). FD-MS: *m*/*z* 768.7 (M$^+$), 660.5 (M$^+$ − C$_6$H$_8$N$_2$). Anal. Calcd for $C_{36}H_{42}Cl_2N_2O_2P_2Ru$: C, 56.25; H, 5.51; N, 3.64; Cl, 9.22. Found:[46] C, 55.64; H, 5.97; N, 3.82; Cl, 8.94.

Complex 3e. Compound **2** (300 mg, 0.454 mmol) was treated with **e** (79 mg, 0.50 mmol) to give **3e**: yield 299 mg (84%) of a tawny powder. ^{1}H NMR ($CDCl_3$): δ 2.3−2.4 (m, 4H, PCH$_2$), 2.9 (s, 6H, OCH$_3$), 2.9−3.1 (m, 4H, CH$_2$O), 5.1 (s, 4H, NH$_2$), 6.4−7.5 (m, 6 H, C$_{10}$H$_6$), 7.3−7.7 (m, 20H, C$_6$H$_5$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 43.9 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 25.7 (m,[45a] *N* = 26.3 Hz, PCH$_2$), 58.2 (s, OCH$_3$), 69.5 (s, CH$_2$O), 121.7 (s, C2, C7), 125.2 (s, C8a), 126.0 (s, C4, C5), 126.9 (s, C3, C6), 128.8 (m,[45b] *N* = 8.5 Hz, *m*-C$_6$H$_5$), 129.8 (s, *p*-C$_6$H$_5$), 133.7 (m,[45c] *N* = 7.8 Hz, *o*-C$_6$H$_5$), 134.2 (s, C4a), 136.1 (m,[45a] *N* = 44.8 Hz, *i*-C$_6$H$_5$), 136.8 (s, C1, C8). FD-MS: *m*/*z* 783.3 (M$^+$ − Cl), 660.5 (M$^+$ − C$_{10}$H$_{10}$N$_2$). Anal. Calcd for $C_{40}H_{44}Cl_2N_2O_2P_2Ru$: C, 58.68; H, 5.42; N, 3.42; Cl, 8.66. Found:[46] C, 57.89; H, 5.43; N, 3.52; Cl, 9.03.

Complex 3f. Complex **2** (300 mg, 0.454 mmol) was treated with **f** (78 mg, 0.50 mmol) to give **3f**: yield 323 mg (87%) of a auburn powder. ^{1}H NMR ($CDCl_3$): δ 2.5−2.6 (m, 4H, PCH$_2$), 2.8 (s, OCH$_3$), 2.8−3.0 (m, 4H, CH$_2$O), 6.6−8.7 (m, 28H, C$_{10}$H$_8$, C$_6$H$_5$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 30.5 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.8 (m,[45a] *N* = 29.1 Hz, PCH$_2$), 57.8 (s, OCH$_3$), 69.4 (s, CH$_2$O), 122.2 (s, C4, C4′), 123.9 (s, C6, C6′), 128.0 (m,[45b] *N* = 8.5 Hz, *m*-C$_6$H$_5$), 129.3 (s, *p*-C$_6$H$_5$), 133.3−134.1 (m, *i*-C$_6$H$_5$, *o*-C$_6$H$_5$), 136.0 (s, C5, C5′), 156.6 (s, C3, C3′), 158.7 (s, C1, C1′). ^{31}P{^{1}H} NMR ($CDCl_3$) for the C_1 isomer: δ 29.3 (d, $^2J_{PP}$ = 30.2 Hz), 33.4 (d, $^2J_{PP}$ = 30.2 Hz). FD-MS: *m*/*z* 816.7 (M$^+$). Anal. Calcd for $C_{40}H_{42}Cl_2N_2O_2P_2Ru$: C, 58.83; H, 5.18; N, 3.43; Cl, 8.68. Found:[46] C, 58.14; H, 5.32; N, 3.52; Cl, 8.69.

Complex 3g. Compound **2** (300 mg, 0.454 mmol) was treated with **g** (90 mg, 0.50 mmol) to give **3g**: yield 351 mg (92%) of a deep red powder. ^{1}H NMR ($CDCl_3$): δ 2.5−2.7 (m, 4H, PCH$_2$), 2.8 (s, OCH$_3$), 2.8−3.0 (m, CH$_2$O), 7.0−9.0 (m, 28H, C$_6$H$_5$, C$_{12}$H$_8$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 30.5 (s). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 26.7 (m,[45a] *N* = 29.2 Hz, PCH$_2$), 57.6 (s, OCH$_3$), 69.2 (s, CH$_2$O), 123.1 (s, C3, C8), 126.8 (s, C5, C6), 127.8 (m,[45b] *N* = 8.5 Hz, *m*-C$_6$H$_5$), 129.1 (s, *p*-C$_6$H$_5$), 130.0 (s, C4a, C6a), 133.4 (m,[45a] *N* = 34.2 Hz, *i*-C$_6$H$_5$), 134.1 (br m,[45c] *o*-C$_6$H$_5$), 135.1 (s, C4, C7), 149.2 (s, C10a, C10b), 156.0 (s, C2, C9). FD-MS: *m*/*z* 840.7 (M$^+$). Anal. Calcd for $C_{42}H_{42}Cl_2N_2O_2P_2Ru$: C, 60.00; H, 5.03; N, 3.33; Cl, 8.43. Found:[46] C, 59.36; H, 5.34; N, 3.64, Cl, 8.69.

General Procedure for the Preparation of the Monocationic Complexes 4a−c,f. Use of TlPF$_6$. TlPF$_6$ (5% excess) was added to a solution of the neutral complexes **3a**−**g** in 25 mL of dichloromethane and stirred for 24 h. After filtration through silica the solution was concentrated to about 5 mL under reduced pressure. The corresponding cationic complex was precipitated by addition of 100 mL of diethyl ether, filtered off (P3), washed three times with 25 mL portions of diethyl ether, and dried under vacuum.

Use of AgBF$_4$. A solution of AgBF$_4$ (5% excess) in 25 mL of dichloromethane was added to a solution of the neutral complexes **3a**−**g** in 25 mL of dichloromethane and stirred for 4 h. After filtration through silica the solution was concentrated to a small volume. Adding 100 mL of diethyl ether caused the precipitation of a solid, which was filtered off (P3), washed three times with 25 mL portions of diethyl ether, and dried under vacuum.

Complex 4a. Complex **3a** (300 mg, 0.416 mmol) was treated with TlPF$_6$ (153 mg, 0.437 mmol) to give **4a**: yield 252 mg (73%) of a yellow powder. ^{1}H NMR (CD_2Cl_2): δ 0.9−1.5 (m, 2H, CH$_2$P), 2.1−2.8 (m, 10H, CH$_2$NH$_2$, CH$_2$P), 2.9 (s, 3H, OCH$_3$), 2.9−3.1 (m, 2H, CH$_2$O), 3.6 (s, 3H, OCH$_3$), 3.7−4.0 (m, 2H CH$_2$O), 6.5−8.1 (m, 20H, C$_6$H$_5$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 57.5 (d, $^2J_{PP}$ = 37.8 Hz), 48.5 (d, $^2J_{PP}$ = 37.8 Hz), −143.3 (sept, $^1J_{PF}$ = 712.1 Hz, PF$_6^-$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 28.6 (d, $^1J_{PC}$ = 28.5 Hz, PCH$_2$), 32.2 (d, $^1J_{PC}$ = 25.6 Hz, PCH$_2$), 43.7, 45.5 (2s, NCH$_2$), 58.5, 61.3 (2s, OCH$_3$), 68.6, 73.9 (2s, CH$_2$O), 128.6 (d, $^3J_{PC}$ = 10.0 Hz, *m*-C$_6$H$_5$), 129.1(d, $^3J_{PC}$ = 10.0 Hz, *m*-C$_6$H$_5$), 129.9 (d, $^3J_{PC}$ = 10.0 Hz, *m*-C$_6$H$_5$), 130.0 (d, $^3J_{PC}$ = 10.0 Hz, *m*-C$_6$H$_5$), 130.8−130.9 (br, *p*-C$_6$H$_5$), 131.6 (d, $^2J_{PC}$ = 9.0 Hz, *o*-C$_6$H$_5$), 131.9 (d, $^2J_{PC}$ = 9.0 Hz, *o*-C$_6$H$_5$), 133.0 (d, $^2J_{PC}$ = 9.0 Hz, *o*-C$_6$H$_5$), 134.1 (d, $^1J_{PC}$ = 44.1 Hz, *i*-C$_6$H$_5$), 135.1 (d, $^2J_{PC}$ = 10.0 Hz, *o*-C$_6$H$_5$), 138,1 (d, $^1J_{PC}$ = 37.7 Hz, *i*-C$_6$H$_5$). FD-MS: *m*/*z* 685.2 (M$^+$ − PF$_6$). Anal. Calcd for $C_{32}H_{42}ClF_6N_2O_2P_3Ru$: C, 46.30; H, 5.10; N, 3.37. Found: C, 45.92; H, 5.37; N, 3.39.

Complex 4b. Complex **3b** (300 mg, 0.408 mmol) was treated with TlPF$_6$ (150 mg, 0.429 mmol) to give **4b**: yield 238 mg (69%) of a yellow powder. ^{1}H NMR (CD_2Cl_2): δ 0.6−4.2 (br m, 16H, CH$_2$P, H$_2$NCH$_2$CH$_2$CH$_2$NH$_2$, CH$_2$O), 2.9, 3.8 (2s, 6H, OCH$_3$), 6.3−8.2 (m, 20H, C$_6$H$_5$). ^{31}P{^{1}H} NMR (CD_2Cl_2): isomer a (94%), δ 54.3 (d, $^2J_{PP}$ = 36.5 Hz), 47.8 (d, $^2J_{PP}$ = 36.5 Hz), −143.3 (sept, $^1J_{PF}$ = 711.8 Hz, PF$_6^-$); isomer b (6%), δ 63.4 (d, $^2J_{PP}$ = 32.4 Hz), 32.4 (d, $^2J_{PP}$ = 32.4 Hz), −143.3 (sept, $^1J_{PF}$ = 711.8 Hz, PF$_6^-$). ^{13}C{^{1}H} NMR (CD_2Cl_2): isomer a, δ 27.5 (d, $^1J_{PC}$ = 27.5 Hz, PCH$_2$), 28.8 (s, NCH$_2$*C*H$_2$), 30.8 (d, $^1J_{PC}$ = 26.0 Hz, PCH$_2$), 41.4, 43.1 (2s, NCH$_2$), 58.3, 61.7 (2s, OCH$_3$), 68.2, 74.0 (2s, CH$_2$O), 128.7 (d, $^3J_{PC}$ = 9.2 Hz, *m*-C$_6$H$_5$), 129.2 (d, $^3J_{PC}$ = 9.0 Hz, *m*-C$_6$H$_5$), 130.1 (br, *m*-C$_6$H$_5$), 131.0 (br, *p*-C$_6$H$_5$), 131.2 (br, *p*-C$_6$H$_5$), 132.0 (d, $^2J_{PC}$ = 8.0 Hz, *o*-C$_6$H$_5$), 132.4 (d, $^2J_{PC}$ = 8.0 Hz, *o*-C$_6$H$_5$), 133.3 (d, $^2J_{PC}$ = 9.0 Hz, *o*-C$_6$H$_5$), 134.9 (d, $^2J_{PC}$ = 9.0 Hz, *o*-C$_6$H$_5$), 136.2 (d, $^1J_{PC}$ = 41.0 Hz, *i*-C$_6$H$_5$). FD-MS: *m*/*z* 699.2 (M$^+$ − PF$_6$). Anal. Calcd for $C_{33}H_{44}ClF_6N_2O_2P_3Ru$: C, 46.95; H, 5.25; N, 3.32. Found: C, 47.27; H, 4.95; N, 3.31.

Complex 4c. Compound **3c** (300 mg, 0.408 mmol) was treated with AgBF$_4$ (83 mg, 0.429 mmol) to give **4c**: yield 218 mg (68%) of a yellow powder. ^{1}H NMR (CD_2Cl_2): δ 0.4−4.3 (m, 33H, CH$_2$P, H$_2$NCH$_2$CHNH$_2$, CH$_2$O), 0.8 (d, $^2J_{HH}$ = 6.3 Hz, 3H, CHC*H*$_3$), 1.1 (d, $^2J_{HH}$ = 6.6 Hz, 6H, CHC*H*$_3$), 3.0 (s, 3H, OCH$_3$), 3.1 (s, 6H, OCH$_3$), 3.6 (s, 3H, OCH$_3$), 3.7 (s, 6H, OCH$_3$), 6.2−8.3 (m, 20H, C$_6$H$_5$). ^{31}P{^{1}H} NMR (CD_2Cl_2): isomer a (55%), δ 59.1 (d, $^2J_{PP}$ = 37.2 Hz), 48.2 (d, $^2J_{PP}$ = 37.2 Hz); isomer b (25%), δ 57.6 (d, $^2J_{PP}$ = 37.2 Hz), 47.8 (d, $^2J_{PP}$ = 37.2 Hz); isomer c (20%), δ 56.8 (d, $^2J_{PP}$ = 36.3 Hz), 49.9 (d, $^2J_{PP}$ = 36.3 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 18.2, 18.6, 20.0 (3s, CH*C*H$_3$), 30.0−32.6 (m, PCH$_2$), 51.2 (br, NCH$_2$), 52.2 (br, NCH), 58.7, 60.7, 61.0 (3s, OCH$_3$), 68.8, 68.9, 73.8 (3s, CH$_2$O), 128.4−137.0 (C$_6$H$_5$). FD-MS: *m*/*z* 699.2 (M$^+$ − BF$_4$). Anal. Calcd for $C_{33}H_{44}BClF_4N_2O_2P_2Ru$: C, 50.43; H, 5.64; N, 3.56. Found: C, 49.97; H, 5.73; N, 3.32.

Complex 4d. Compound **3d** (300 mg, 0.390 mmol) was treated with AgBF$_4$ (79 mg, 0.410 mmol) to give **4d**: yield 337

Table 2. Crystal Data and Summary of Data Collection and Refinement for 3a,e, 4b, and 5a

	3a·0.5C_7H_8	**3e**·CH_2Cl_2	**4b**(PF_6)	**5a**(SbF_6)$_2$
formula	$C_{32}H_{42}Cl_2N_2O_2P_2Ru$·0.5$C_7H_8$	$C_{40}H_{44}Cl_2N_2O_2P_2Ru$·$CH_2Cl_2$	$C_{33}H_{44}ClF_6N_2O_2P_3Ru$	$C_{32}H_{42}F_{12}N_2O_2P_2RuSb_2$
fw	766.65	903.61	844.13	1121.19
cryst size, mm^3	0.3 × 0.2 × 0.1	0.3 × 0.2 × 0.2	0.1 × 0.1 × 0.1	0.3 × 0.2 × 0.1
temp, K	173(2)	173(2)	173(2)	173(2)
cryst class	monoclinic	triclinic	monoclinic	orthorhombic
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	*Pbca* (No. 61)
a, Å	31.03(1)	9.492(2)	13.730(3)	15.348(5)
b, Å	13.108(7)	13.070(3)	11.869(4)	15.163(6)
c, Å	18.054(4)	16.724(5)	23.342(3)	34.98(1)
α, deg	100.44(2)	90.03(2)	106.52(1)	
β, deg		93.62(2)		
γ, deg		99.65(1)		
V, Å^3	7221(5)	2041.1(9)	3647(2)	8141(5)
Z	8	2	4	8
d_{calcd}, g/cm^3	1.410	1.470	1.537	1.830
μ, mm^{-1}	0.704	0.762	0.698	1.849
F(000)	3176	928	1728	4384
θ range, deg	2.11−24.98	2.01−27.50	2.03−24.99	2.22−27.51
index ranges	$-1 \le h \le 36$	$-1 \le h \le 12$	$-1 \le h \le 16$	$-1 \le h \le 19$
	$-1 \le k \le 15$	$-16 \le k \le 16$	$-1 \le k \le 14$	$-1 \le k \le 19$
	$-21 \le l \le 21$	$-21 \le l \le 21$	$-27 \le l \le 27$	$-1 \le l \le 45$
no. of data collected	7295	11 036	8022	11 052
R_{int}	0.0489	0.0665	0.0296	0.0508
no. of unique data/ restraints/params	6285/10/385	9345/0/470	6399/0/434	9320/0/479
GOF on F^2	1.771	1.845	1.614	1.936
R1, wR2 ($I > 2\sigma(I)$)[a]	0.0551, 0.1380	0.0402, 0.1007	0.0406, 0.0982	0.0602, 0.1387
R1, wR2 (all data)	0.0830, 0.1606	0.0456, 0.1064	0.0488, 0.1061	0.1183, 0.1764
largest diff peak, hole, e/Å^3	1.204, −1.450	1.520, −1.129	2.748, −0.727	1.103, −1.259

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$; $w = [\exp(5(\sin^2\theta)/\lambda^2)]/[\sigma^2(F_o^2) + bP + (aP)^2]$; $P = [F_o^2 + 2F_c^2]/3$.

mg (92%) of a dark brown powder which was contaminated with traces of **5d**. ^{1}H NMR (CD_2Cl_2): δ 2.1−4.6 (m, 12H, CH_2P, CH_2O, NH_2), 3.1 (s, 3H, OCH_3), 3.9 (s, 3H, OCH_3), 6.4−7.8 (m, 24H, C_6H_5, $C_6N_2H_4$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 42.7 (d, $^2J_{PP}$ = 32.6 Hz), 56.1 (d, $^2J_{PP}$ = 32.6 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 24.5 (d, $^1J_{PC}$ = 30.3 Hz, PCH_2), 29.7 (d, $^1J_{PC}$ = 24.3 Hz, PCH_2), 53.6, 62.5 (2s, OCH_3), 63.8, 74.0 (2s, CH_2O), 120.3−135.3 (C_6H_5, $C_6N_2H_4$). FAB-MS: *m*/*z* 731.1 ($M^+ - BF_4$). Anal. Calcd for $C_{39}H_{50}BClF_4N_2O_2P_2Ru$: C, 54.21; H, 5.83; N, 3.24. Due to the presence of **5d**, complex **4d** does not analyze well.

Complex 4f. Compound **3f** (300 mg, 0.367 mmol) was treated with $AgBF_4$ (75 mg, 0.386 mmol) to give **4f**: yield 281 mg (88%) of a orange powder. ^{1}H NMR (CD_2Cl_2): δ 2.2−4.3 (m, 8H, CH_2P, CH_2O), 2.8 (s, 3H, OCH_3), 2.9 (s, 3H, OCH_3), 6.5−10.0 (m, 28H, C_6H_5, $C_{10}N_2H_8$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 45.9 (d, $^2J_{PP}$ = 34.0 Hz), 42.9 (d, $^2J_{PP}$ = 34.0 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 27.7 (d, $^1J_{PC}$ = 30.3 Hz, PCH_2), 32.0 (d, $^1J_{PC}$ = 24.3 Hz, PCH_2), 58.4, 61.6 (2s, OCH_3), 68.4 (d, $^2J_{PC}$ = 5.4 Hz, CH_2O), 74.2 (s, CH_2O), 123.3−159.1 (C_6H_5, $C_{10}N_2H_8$). FD-MS: *m*/*z* 781.3 ($M^+ - BF_4$). Anal. Calcd for $C_{40}H_{42}BClF_4N_2O_2P_2Ru$: C, 55.35; H, 4.88; N, 3.23. Found:[46] C, 54.68; H, 4.53; N, 2.89.

General Procedure for the Preparation of the Dicationic Complexes 5a−c,e−g. A solution of the neutral complex **3a**−**c**,**e**−**g** in 25 mL of dichloromethane was added to $AgBF_4$, $AgSbF_6$, or $TlPF_6$ (300% excess) and stirred for 4 h. After filtration through silica the solvent was reduced to 5 mL under reduced pressure. The corresponding dicationic complex was precipitated by addition of 100 mL of diethyl ether, filtered off (P3), and washed three times with 25 mL portions of diethyl ether.

Complex 5a. Compound **3a** (300 mg, 0.416 mmol) was treated with $AgSbF_6$ (429 mg, 1.249 mmol) to give **5a**: yield 331 mg (71%) of a yellow powder. ^{1}H NMR (CD_2Cl_2): δ 0.5−5.2 (m, 16H, PCH_2, CH_2NH_2, CH_2O) 3.5, 4.0 (2s, 6H, OCH_3), 6.4−7.9 (m, 20H, C_6H_6). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 67.4 (d, $^2J_{PP}$ = 35 Hz), 51.3 (d, $^2J_{PP}$ = 35 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 28.8 (d, $^1J_{PC}$ = 31.6 Hz, PCH_2), 30.9 (d, $^1J_{PC}$ = 24.7 Hz, PCH_2), 42.0, 48.5 (2s, NCH_2), 64.2, 65.5 (2s, OCH_3), 74.8, 77.7 (2s, CH_2O), 129.4−133.1 (C_6H_5). FD-MS: *m*/*z* 885.5 ($M^+ - SbF_6$). Anal. Calcd for $C_{32}H_{42}B_2F_8N_2O_2P_2Ru$: C, 46.68; H, 5.14; N, 3.40. Found: C, 47.00; H, 4.79; N, 3.42.

Complex 5b. Complex **3b** (300 mg, 0.408 mmol) was treated with $TlPF_6$ (428 mg, 1.225 mmol) to give **5b**: yield 265 mg (68%) of a yellow powder. ^{1}H NMR (CD_2Cl_2): δ 1.0−4.5 (m, 18H, PCH_2, $H_2NCH_2CH_2CH_2NH_2$, CH_2O), 3.5, 4.0 (2s, 6H, OCH_3), 6.4−8.0 (m, 20H, C_6H_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 67.3 (d, $^2J_{PP}$ = 34.8 Hz), 44.5 (d, $^2J_{PP}$ = 34.8 Hz), −143.2 (sept, $^1J_{PF}$ = 713 Hz, PF_6^-). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 26.9 (s, NCH_2CH_2), 27.9 (d, $^1J_{PC}$ = 25.6 Hz, PCH_2), 28.0 (d, $^1J_{PC}$ = 32.7 Hz, PCH_2), 40.0, 43.9 (2s, NCH_2), 62.1, 63.0 (2s, OCH_3), 73.1, 75.2 (2s, CH_2O), 127.4−134.5 (C_6H_5). FD-MS: *m*/*z* 808.7 ($M^+ - PF_6$). Anal. Calcd for $C_{33}H_{44}F_{12}N_2O_2P_4Ru$: C, 41.56; H, 4.65; N, 2.94. Found: C, 41.64; H, 4.79; N, 2.57.

Complex 5c. Complex **3c** (300 mg, 0.408 mmol) was treated with $AgBF_4$ (238 mg, 1.225 mmol) to give **5c**: yield 202 mg (59%) of a yellow powder. ^{1}H NMR (CD_2Cl_2): δ 0.6, 1.0, 1.1 (3d, $^3J_{HH}$ = 5.7, 5.6, 6.3 Hz, 9H, $CHCH_3$), 0.7−5.0 (m, 39H, PCH_2, CH_2O, $H_2NCH_2CHNH_2$), 3.2, 3.3, 3.4, 3.8, 3.9, 4.0 (6s, 18H, OCH_3), 6.3−7.7 (m, 60H, C_6H_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): isomer a (43%), δ 69.4 (d, $^2J_{PP}$ = 35.2 Hz), 51.8 (d, $^2J_{PP}$ = 35.2 Hz); isomer b (35%), δ 68.4 (d, $^2J_{PP}$ = 35.4 Hz), 51.8 (d, $^2J_{PP}$ = 35.4 Hz); isomer c (22%), δ 66.9 (d, $^2J_{PP}$ = 37.3 Hz), 53.3 (d, $^2J_{PP}$ = 37.3 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 17.9, 18.5, 18.6 (s, CCH_3), 28.5−31.2 (m, PCH_2), 46.7, 48.3, 55.8 (s, NCH_2), 49.9, 57.3, 59.7 (s, NCH), 63.8, 64.0, 65.1 (s OCH_3), 67.8, 74.5, 77.3 (s, CH_2O), 128.9−134.4 (C_6H_5). FD-MS: *m*/*z* 750.5 ($M^+ - BF_4$). Anal. Calcd for $C_{33}H_{44}B_2F_8N_2O_2P_2Ru$: C, 47.34; H, 5.30; N, 3.35. Found:[46] C, 46.83; H, 5.62; N, 2.96.

Complex 5d. Complex **5d** could not be isolated. It was observed as traces in the ^{31}P{^{1}H} NMR spectrum of **4d**. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 69.0 (d, $^2J_{PP}$ = 35.8 Hz), 54.3 (d, $^2J_{PP}$ = 35.8 Hz).

Complex 5e. Compound **3e** (300 mg, 0.366 mmol) was treated with $AgBF_4$ (213 mg, 1.099 mmol) to give **5e**: yield 216 mg (64%) of a brown powder. ^{1}H NMR (CD_2Cl_2): δ 0.9−5 (m, 12H, PCH_2, CH_2O, NH_2), 3.7 (br, 6H, OCH_3), 5.9−8.0 (m, 26H, C_6H_5, $C_{12}H_6$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 57.3 (d, $^2J_{PP}$ = 35.6 Hz), 52.2 (d, $^2J_{PP}$ = 35.6 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ

28.9 (d, $^1J_{PC}$ = 27.0 Hz, PCH_2), 30.0 (d, $^1J_{PC}$ = 29.9 Hz, PCH_2), 64.9, 66.1 (2s, OCH_3), 74.2, 74.4 (2s, CH_2O), 120.2−136.5 (C_6H_5, $C_{10}H_6$). FD-MS: *m*/*z* 747.82 ($M^+ - 2BF_4$). Anal. Calcd for $C_{40}H_{44}B_2F_8N_2O_2P_2Ru$: C, 52.14; H, 4.81; N, 3.04. Found:[46] C, 51.52; H, 4.43; N, 3.12.

Complex 5f. Complex **3f** (300 mg, 0.367 mmol) was treated with $AgBF_4$ (214 mg, 1.102 mmol) to give **5f**: yield 233 mg (69%) of a yellow powder. ^{1}H NMR (CD_2Cl_2): δ 1.8−4.6 (m, 8H, PCH_2, CH_2O), 2.8, 3.6 (2s, 6H, OCH_3), 6.4−8.5 (m, 28H, C_6H_5, $C_{10}H_8$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 57.5 (d, $^2J_{PP}$ = 31.1 Hz), 40.3 (d, $^2J_{PP}$ = 31.1 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 25.4 (d, $^1J_{PC}$ = 30.6 Hz, PCH_2), 28.2 (d, $^1J_{PC}$ = 24.9 Hz, PCH_2), 62.4, 64.7 (2s, OCH_3), 75.5, 75.8 (2s, CH_2O), 124.6−158.0 (C_6H_5, $C_8H_6N_2$). FD-MS: *m*/*z* 832.6 ($M^+ - BF_4$). Anal. Calcd for $C_{40}H_{42}B_2F_8N_2O_2P_2Ru$: C, 52.26; H, 4.60; N, 3.05. Found:[46] C, 51.41; H, 4.27; N, 3.49.

Complex 5g. Complex **3g** (300 mg, 0.357 mmol) was treated with $AgBF_4$ (208 mg, 1.071 mmol) to give **5g**: yield 209 mg (62%) of an auburn powder. ^{1}H NMR (CD_2Cl_2): δ 1.6−4.6 (m, 8H, PCH_2, CH_2O), 2.6, 3.7 (2s, 6H, OCH_3), 5.8−9.0 (m, 28H, C_6H_5, $C_{12}H_8$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 57.3 (d, $^2J_{PP}$ = 31.6 Hz), 41.8 (d, $^2J_{PP}$ = 31.6 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 25.3 (d, $^1J_{PC}$ = 31.4 Hz, PCH_2), 28.2 (d, $^1J_{PC}$ = 24.9 Hz, PCH_2), 62.4, 64.9 (2s, OCH_3), 75.4, 76.2 (2s, CH_2O), 126.1−158.7 (C_6H_5, $C_{12}H_8N_2$). FD-MS: *m*/*z* 787.8 ($M^+ - 2BF_4 + H_2O$). Anal. Calcd for $C_{42}H_{42}B_2F_8N_2O_2P_2Ru$: C, 53.47; H, 4.49; N, 2.97. Found:[46] C, 52.71; H, 4.25; N, 3.32.

X-ray Structural Analyses for Complexes 3a,e, 4b, and 5a. Crystals were obtained by slow diffusion of diethyl ether into a toluene solution of **3a** or dichloromethane solutions of **3e**, **4b**, and **5a**. Selected crystals were mounted on a P4 Siemens diffractometer by using perfluorinated polyether (Riedel de Haen) as protecting agent. Graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) was used for the measurement of intensity data in the ω-scan mode. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction via ψ-scans was applied for **3a**. The structures were solved by direct methods with SHELXS-86.[47a] Refinement was carried out with full-matrix least-squares methods based on F^2 in SHELXL-97[47b] with anisotropic thermal parameters for all non-hydrogen atoms, except the disordered toluene in **3a**. Hydrogen atoms were included at calculated positions using a riding model. Crystal data and a summary of data collection and refinement details are given in Table 2.

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Supporting Information Available: Further details of the X-ray structure determinations, including bond distances and angles and thermal parameters, for **3a**,**e**, **4b**, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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