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Synthesis of a Ruthenium(II) Complex Containing an [11]ane-P_2C^{NHC} (NHC = Imidazolidin-2-ylidene) Macrocycle

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Reaction of $[RuCl(Cp)(PPh_3)_2]$ with bis[di(2-fluorophenyl)phosphino]benzene, **3**, yields complex [RuCl(Cp)(**3**)], [**4**]. The chloro ligand in [**4**] can be exchanged for the 2-azidoethyl isocyanide ligand **2**, giving complex [Ru(Cp)(**2**)(**3**)]Cl, [**5**]Cl, which reacts with NH_4BF_4 to give [**5**]BF_4. The azido group of the coordinated isocyanide ligand in [**5**]Cl or [**5**]BF_4 can be reduced with $Zn/NH_4Cl/H_2O$ to give the complex with the 2-aminoethyl isocyanide ligand. This ligand is not stable but cyclizes by an intramolecular nucleophilic attack of the amino group at the isocyanide carbon atom to give an NH, NH-stabilized NHC ligand in complexes [**6**]X (X = Cl, [**6**]Cl; X = 0.5 $ZnCl_4$, [**6**]$_2$($ZnCl_4$); X = BF_4, [**6**]BF_4). Deprotonation of the NH,NH-stabilized NHC ligands in cations of type $[\mathbf{6}]^+$ leads to an intramolecular nucleophilic attack of the amido nitrogen atoms at the fluorinated phenyl groups of the diphosphine ligand under formation of the complex with the *facially* coordinated macrocyclic [11]ane-P_2C^{NHC} ligand [**1**]X (X = Cl, [**1**]Cl; X = 0.5 $ZnCl_4$, [**1**]$_2$($ZnCl_4$); X = BF_4, [**1**]BF_4). Formation of the macrocycle is facilitated by the steric pressure excerted by the cyclopentadienyl ligand. The molecular structures of [**4**], [**5**]BF_4, [**6**]$BF_4 \cdot CH_2Cl_2$, and [**1**]$Cl \cdot CH_2Cl_2 \cdot 0.5H_2O$ have been determined by X-ray diffraction.

Introduction

The coordination chemistry of *facially* coordinated macrocyclic tridentate N-donor ligands such as triazacyclononane (tacn) has been studied for some years,[1] but their P-donor analogues have only recently attracted attention when efficient synthetic procedures for the preparation of such ligands were developed. Initially, cyclic ligands with three P-donors have been prepared as mixtures of all possible diastereomers by a purely organic approach.[2] More recently, complexes with macrocyclic P-donor ligands in the *all-syn* conformation have been obtained by metal template-controlled procedures.[3] In selected cases it was possible to liberate the *facially* coordinated P_3-donor macrocycle from the metal center[4] and to coordinate it to another metal under conservation of the *all-syn* conformation.[4,5] The template synthesis proved advantageous since the separation of *syn* and *anti* ligand isomers could be avoided and the incorporation of different linkers within the macrocycle proved possible.[3]

Most template syntheses of P_3-macrocycles proceed via radical or base-induced intramolecular hydrophosphination of appropriately functionalized primary or secondary phosphines (Scheme 1, method A).[3] In addition, a template approach utilizing the nucleophilic attack of coordinated phosphides at halogenato functionalized aryl or alkyl phosphines has been developed (Scheme 1, method B)[6] next to more exotic methods such as olefin metathesis for the generation of very large P_3-macrocycles.[7]

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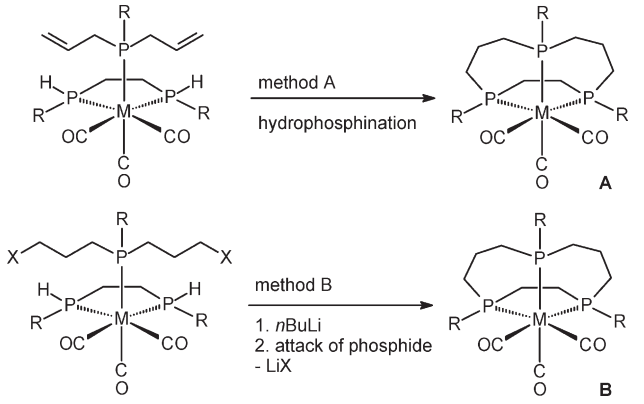
Scheme 1. Template Synthesis of P_3-Macrocycles

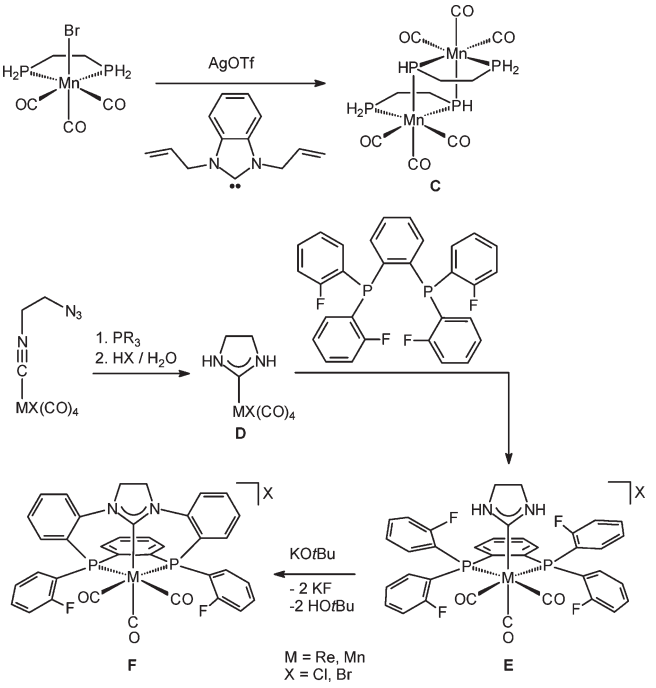


Due to the similarities in the coordination chemistry of N-heterocyclic carbenes[8] and phosphine ligands,[9] we became interested in the preparation of tridentate *facially* coordinated macrocyclic ligands incorporating simultaneously phosphine and NHC donor groups. Such ligands, if *facially* coordinated to an octahedral $\{M(CO)_3\}$ metal center, could lead to a discrimination in the reactivity of the carbonyl ligands, which would be located in *trans* position to either an NHC or a phosphine ligand.

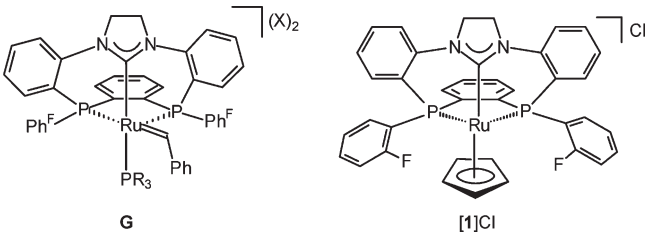
Our first experiments with the template-controlled hydrophosphination method (Scheme 2, top) using a diallyl-functionalized benzannulated carbene ligand[10] did not lead to the desired *facial* diphosphine-NHC complex. The free NHC ligand is basic enough to deprotonate the coordinated diphosphine under formation of complexes of type **C** (Scheme 2).[11]

We have therefore developed an alternative template synthesis starting with complexes of 2-azido-functionalized isocyanides,[12] which upon reduction of the azido function by a Staudinger reaction followed by hydrolysis[13] cyclize to yield the complexes of type **D** with an NH,NH-stabilized NHC ligand (Scheme 2, bottom).[14] Subsequently, a fluorinated diphenylphosphine was introduced, giving complexes of type **E**. Deprotonation of the NHC ligand led to an attack of the NHC nitrogen atoms at the fluorinated diphosphine under formation of the complexes **F** with the [11]ane-P_2C^{NHC} ligand (Scheme 2, bottom).[15]

Scheme 2. Template Synthesis of [11]ane-P_2C^{NHC} Macrocycles



Scheme 3



We became particularly interested in ruthenium complexes like **G** (Scheme 3) with an [11]ane-P_2C^{NHC} ligand since they could find application as olefin metathesis catalysts in analogy with the well-known complexes of type $[RuCl_2(PCy_3)(CHPh)(NHC)]$ (type II Grubbs catalysts).[16] Dissociation of the monodentate phosphine ligand in **G** would, however, generate a cationic species that might exhibit catalytic properties different from the original Grubbs type II catalyst. In this contribution we describe the generation of a macrocyclic [11]ane-P_2C^{NHC} ligand at Ru^{II} leading to complex [**1**]Cl (Scheme 3).

Results and Discussion

We have previously studied the cyclization of 2-azidoethyl isocyanide **2** at a Ru^{II} template center.[17] In contrast to

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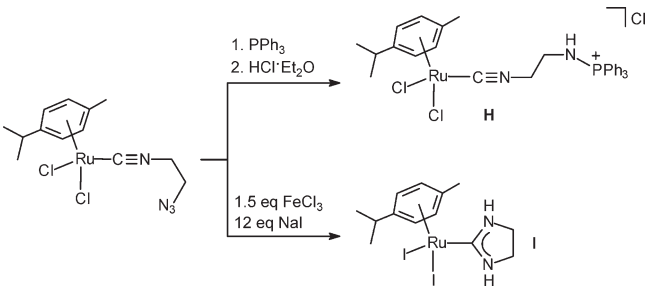
Scheme 4. Reduction and Cyclization of 2-Azidoethyl Isocyanide at Ru^{II}



previous observations,[14] the Staudinger reaction followed by hydrolysis at the azido group of the 2-azidoethyl isocyanide ligand in [$Ru(Cl)_2$(*p*-cymene)(**2**)] did not yield the complex with the NH,NH-stabilized NHC ligand (Scheme 4). Instead, protonation of the intermediate phosphinimine-substituted isocyanide ligand leading to complex **H** was observed. The hydrolysis/cyclization reaction of the isocyanide ligand might be competing with the protonation reaction. This is particularly likely when M→CNR back-bonding deactivates the coordinated isocyanide for an intramolecular nucleophilic attack.[18]

Reduction of the azido group followed by cyclization to yield complex **I** was achieved with a $FeCl_3$/NaI mixture (Scheme 4).[19] The required large excess of NaI led to an exchange of the halogenato ligands at the ruthenium atom, resulting in the isolation of the diiodo complex. Complex **I**, however, proved unsuitable for the generation of a macrocycle since its reaction with chelating diphosphines led invariably to decomposition or mixtures of reaction products.

In order to obtain a Ru^{II} complex of type **E** (Scheme 2) bearing a diphosphine and the NH,NH-stabilized NHC ligand in the *facial* orientation essential for a subsequent linkage, we decided to introduce the diphosphine ligand first, followed by generation of the carbene ligand at the metal center. Complex [$RuCl(Cp)(PPh_3)_2$] has been shown to react with chelating diphosphines in boiling toluene within 24 h under substitution of the monodentate phosphine ligands.[20] Reaction of [$RuCl(Cp)(PPh_3)_2$] with the less reactive fluorinated diphosphine **3**[15a] required 48 h but yielded complex [RuCl(Cp)(**3**)], [**4**], in an excellent yield of 97% (Scheme 5). The high yield observed with the fluorinated diphosphine **3** contrasts the observation made when a nonfluorinated diphosphine such as bis(diphenylphosphino)benzene (dppbz) was used, where after a reaction time of 24 h a product mixture composed of [RuCl(Cp)(dppbz)] (57%) and [Ru(Cp)(dppbz)PPh_3]Cl (27%) was obtained.[21] While diphosphine **3** is less reactive than dppbz in the substitution reaction with [$RuCl(Cp)(PPh_3)_2$], it is a better π-acceptor

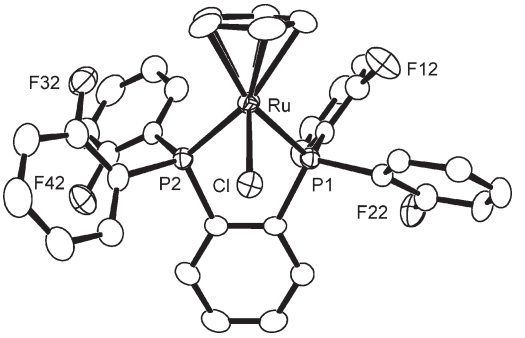
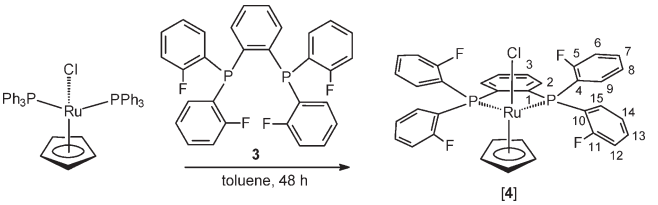


Figure 1. Molecular structure of [**4**] (50% displacement ellipsoids, hydrogen atoms have been omitted). Selected bond lengths (Å) and angles (deg): Ru−P1 2.2652(9), Ru−P2 2.2512(9), Ru−Cl 2.4454(8); P1−Ru−P2 82.97(3), Pl−Ru−C1 85.75(3), P2−Ru−C1 83.52(3).

Scheme 5. Synthesis of Complex 4[a]



[a] The numbering refers to the assignment of the NMR resonances.

once coordinated to the metal center, and thus ligand scrambling was not observed.

Complex [**4**] was characterized by NMR spectroscopy and X-ray diffraction. As expected, only one signal was observed in the $^{31}P\{^1H\}$ NMR spectrum of [**4**] at δ = 62 ppm, while the ^{19}F NMR spectrum exhibited two resonances, at δ = −100 and −101 ppm. The occurrence of these two resonances is caused by the presence of two sets of fluorophenyl rings oriented toward different parts of the pseudotetrahedral coordination sphere.

An X-ray diffraction study confirmed the connectivity in [**4**] (Figure 1). The metric parameters found in [**4**] fall in the range previously observed for related ruthenium complexes. The P−Ru−P bite angles in [**4**] (82.97(3)°) and in the ruthenium complex with the nonfluorinated bis(diphenylphosphino)benzene (dppbz) ligand [Ru(Cp)(dppbz)PPh_3]Cl (82.87(2)°) exhibit almost identical values.[21]

Substitution of the chloro ligand in [**4**] by a slight excess of 2-azidoethyl isocyanide **2** in refluxing methanol yields compound [Ru(Cp)(**2**)(**3**)]Cl, [**5**]Cl, in excellent yield (Scheme 6). Anion exchange with NH_4BF_4 in methanol gave [**5**]BF_4. In the $^{13}C\{^1H\}$ NMR spectrum the resonance for the isocyanide carbon atom of [**5**]Cl was observed at δ = 151.7 ppm ($^2J_{CP}$ = 18 Hz), slightly downfield from the isocyanide carbon resonance in complex [$Ru(Cl)_2$(*p*-cymene) (**2**)] at δ = 142.4 ppm (Scheme 4).[17] Coupling between the isocyanide nitrogen atom and the adjacent carbon atoms, which is typical for free alkyl isocyanides, was not observed for the coordinated isocyanide ligand in [**5**]Cl.[22]

The wavenumber of the C≡N stretching frequency in the IR spectrum of [**5**]Cl (ν(KBr) = 2152 cm^{-1}) is lower than the value recorded for [$Ru(Cl)_2$(*p*-cymene)(**2**)] (ν(KBr) = 2199 cm^{-1}).

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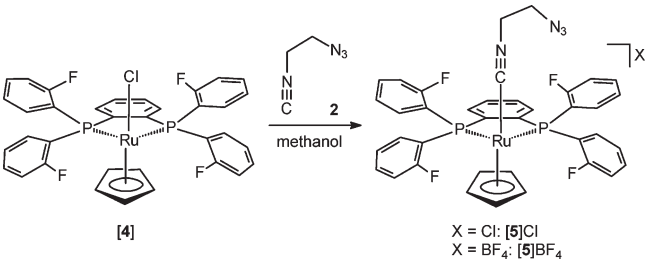
Scheme 6. Synthesis of Compounds [5]Cl and [5]BF_4



Apparently, the 2-azidoethyl isocyanide ligand receives more d→π* back-bonding from the ruthenium atom in complex cation $[\mathbf{5}]^+$ than in the neutral complex [Ru(Cl)$_2$(*p*-cymene)(**2**)]. This assumption, however, is easily explained by the presence of two strongly donating ligands in the complex cation $[\mathbf{5}]^+$, while the neutral complex contains much weaker donor ligands. Strong back-bonding to the isocyanide is undesirable, as it deactivates the isocyanide carbon atom for a nucleophilic attack.

The trend in the IR data appears to contradict the trend observed for the $^{13}C\{^1H\}$ NMR data, which show a downfield shift for the resonance of the isocyanide carbon atom in [**5**]Cl (δ = 151.7 ppm) relative to the equivalent resonance in [Ru(Cl)$_2$(*p*-cymene)(**2**)] (δ = 142.4 ppm), while the IR spectra indicate an enhanced back-bonding in [**5**]Cl relative to [Ru(Cl)$_2$(*p*-cymene)(**2**)]. The ligand sets in the two Ru^{II} isocyanide complexes are different, and it appears that the isocyanide carbon atom in [**5**]Cl reaches into the deshielding region of the phenylene rings, while such a long-range interaction does not exist for [Ru(Cl)$_2$(*p*-cymene)(**2**)].

While numerous recrystallization attempts with compound [**5**]Cl did not yield crystals suitable for an X-ray diffraction study, such crystals could be obtained from a methanol solution of [**5**]BF_4. The monoclinic unit cell of [**5**]BF_4 contains two formula units located on crystallographic mirror planes (Figure 2). Substitution of the chloro ligand in [**4**] for the isocyanide ligand in [**5**]BF_4 does not lead to significantly different metric parameters for the ruthenium complexes. The bite angle of the diphosphine ligand (84.83(7)°) in [**5**]BF_4 is only marginally enlarged compared to [**4**] (82.97(3)°). Only the Ru−P distance in the cationic complex $[\mathbf{5}]^+$ (2.2803(14) Å) is slightly longer than the corresponding bond lengths in the neutral complex [**4**] (2.2652(9) and 2.2512(9) Å).

The isocyanide C−N−C angle in $[\mathbf{5}]^+$ (169.8(10)°) is smaller than the corresponding angle in [Ru(Cl)$_2$(*p*-cymene)-(**2**)] (175.7(5)°).[17] Like the wavenumbers for the C≡N stretching vibration, this indicates an increased d→π* back-bonding to the isocyanide ligand in the cationic complex $[\mathbf{5}]^+$ in comparison to [Ru(Cl)$_2$(*p*-cymene)(**2**)].

The next step in the preparation of the [11]ane-P_2C^{NHC} macrocycle is the reduction of the azido function of the coordinated 2-azidoethyl isocyanide in $[\mathbf{5}]^+$ to a primary amine, which is supposed to cyclize to the NH,NH-stabilized carbene ligand in $[\mathbf{6}]^+$ (Scheme 7). Various methods for the reduction azide → primary amine in organic compounds have been reported.[23] The situation is more complicated for an azide that is part of a coordinated ligand, as in complexes with 2-azidoethyl isocyanide, as the azide reduction must not affect the metal complex. We have shown that the Staudinger

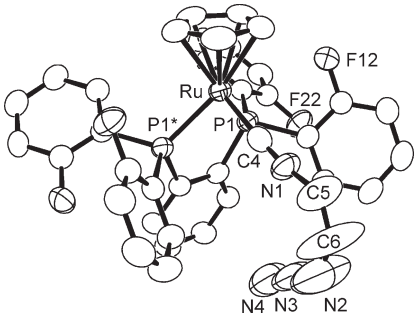


Figure 2. Molecular structure of the cation $[\mathbf{5}]^+$ in [**5**]BF_4 (50% displacement ellipsoids, hydrogen atoms have been omitted). The asymmetric unit contains one-half of the cation, related to the other half by a crystallographic mirror plane. Selected bond lengths (Å) and angles (deg): Ru−P1 2.2803(14), Ru−C4 1.942(9), N1−C4 1.169(11), N1−C5 1.381(14), N2−C6 1.24(2), N2−N3 1.26(2), N3−N4 1.13(2); P1−Ru−P1* 84.83(7), P1−Ru−C4 87.6(2), Ru−C4−N1 174.4(7), C4−N1−C5 169.3(10), C6−N2−N3 134(2), N2−N3−N4 176(2).

reaction followed by hydrolysis of the intermediate phosphinimine can be used for the conversion of the azido function into a primary amine,[14] although this method has failed in selected cases.[17] Alternatively, azide reduction was achieved with $FeCl_3$/NaI followed by an aqueous workup.[17] We have recently carried out a systematic study regarding the conversion of coordinated 2-azido-substituted isocyanides into 2-amino isocyanides at $\{Ru(Cp)(PR_3)_2\}^+$ templates.[24] From this study a mixture of Zn/NH_4Cl/H_2O emerged as a suitable reducing agent.[25]

Reaction of [**5**]Cl with 1.3 equiv of Zn dust, 2.3 equiv of NH_4Cl, and a small amount of water in boiling methanol for 24 h gave complex cation $[\mathbf{6}]^+$ as a mixture of the salts [**6**]Cl and [**6**]$_2$[$ZnCl_4$]. The reaction can be followed by mass spectroscopy showing the disappearance of the peak for $[\mathbf{5}]^+$ (m/e = 781) and the appearance of a new peak at m/e = 755. This latter peak is caused by the intermediate complex cation with the 2-aminoethyl isocyanide ligand or by the isomeric carbene complex cation $[\mathbf{6}]^+$. The actual nature of the reaction product was established spectroscopically. The IR spectrum of the reaction product shows no absorptions due to the N_3 and C≡N groups in $[\mathbf{5}]^+$. The resonance for the isocyanide carbon atom of $[\mathbf{5}]^+$ at δ = 151.7 ppm ($^2J_{CP}$ = 18 Hz) was also absent in the $^{13}C\{^1H\}$ NMR spectrum of the reaction product, and a new resonance at δ = 199.7 ppm ($^2J_{CP}$ = 15.2 Hz) typical for the carbene carbon atom in Ru^{II} NHC complexes[17,24] was detected instead. In addition, the typical resonance for the NH protons of the carbene ligand was found in the ^1H NMR spectrum at δ = 6.26 ppm. The spectroscopic data indicate immediate cyclization of the 2-aminoethyl isocyanide upon reduction of the azido function in [**5**]Cl. No indication for an equilibrium between the isocyanide and the NHC complex was found. Such equilibria have previously been observed in the template-controlled cyclization of 2-hydroxyphenyl isocyanides[18a−e] and during the synthesis of complexes with acyclic diaminocarbene ligands.[18f]

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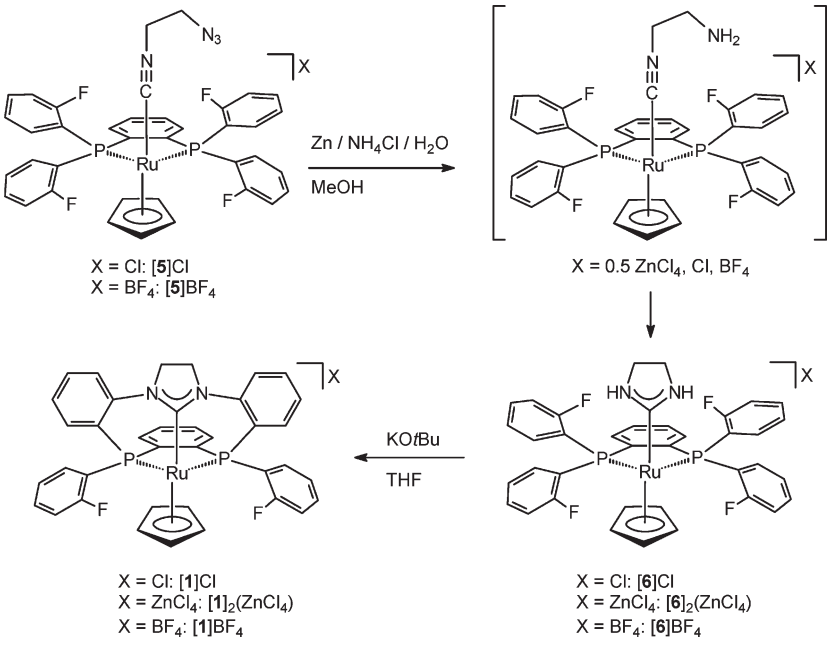
Scheme 7. Reduction of the Azido Group in [5]$^+$ followed by Cyclization to Give Cation [6]$^+$ and Synthesis of Complex Cation [1]$^+$ Bearing the Macrocyclic [11]ane-P_2C^{NHC} Ligand



The spectroscopic features of [**6**]$^+$ parallel those of the rhenium(I) complex cation **E** (Scheme 2), both containing the NH,NH-stabilized NHC ligand and the fluorinated diphosphine.[15] In both, the chemical shifts of the resonances for the diphosphine ligand are essentially identical in the ^{1}H, $^{13}C\{^1H\}$ NMR, and ^{19}F NMR spectra. The resonances in the $^{31}P\{^1H\}$ NMR spectra, however, differ somewhat (δ = 22 ppm for **E** (M = Re),[15a] δ = 72 ppm for [**6**]$^+$).

The formation of cation [**6**]$^+$ under the given reaction conditions proceeded under formation of salts containing two different anions ([**6**]Cl and [**6**]$_2$[$ZnCl_4$], Scheme 7), which were difficult to separate. The mixture of salts was also difficult to crystallize. We therefore studied the azide reduction with [**5**]BF_4 as the starting material, hoping that the presence of the tetrafluoroborate anion would lead to compound [**6**]BF_4, which we believed would be easier to crystallize. Reaction of [**5**]BF_4 with Zn/NH_4Cl/H_2O under the same conditions used for the reduction of [**5**]Cl led as expected to the formation of [**6**]BF_4. The yield, however, was significantly lower, and unreacted [**5**]BF_4 was identified by NMR spectroscopy in the reaction mixture after 24 h. Apparently, the azide reduction is sensitive to the type of counterion present in [**5**]X. The reasons for this behavior have not been investigated yet. In spite of the low yield, compound [**6**]BF_4 could be crystallized from dichloromethane. It can also be obtained by anion exchange with NH_4BF_4 from the salt mixture [**6**]Cl/[**6**]$_2$[$ZnCl_4$]$_2$.

Crystals of [**6**]$BF_4\cdot CH_2Cl_2$ were investigated by X-ray diffraction methods. The molecular structure of the cation [**6**]$^+$ is depicted in Figure 3. Transformation of the 2-azidoethyl isocyanide ligand in [**5**]$^+$ to the NH,NH-stabilized NHC ligand in [**6**]$^+$ does not significantly change the other metric parameters in the cations. The Ru−C62 bond lengths of 2.032(4) Å compare well with the value found for the Ru−$C_{carbene}$ separation of 2.031(4) Å in [Ru(I)$_2$-(*p*-cymene)(NH,NH-NHC)].[17]

As demonstrated for the formation of triphosphamacrocycles[6] and for the first complexes with the [11]ane-P_2C^{NHC} macrocycle **F**,[15] the nucleophilic aromatic substitution of fluoride has been shown to be an efficient method for template-controlled macrocycle formation (Scheme 2). The same reaction also worked for the macrocycle formation in complex cation [**6**]$^+$. Deprotonation of the NHC nitrogen atoms in [**6**]Cl/[**6**]$_2$[$ZnCl_4$] with 2 equiv of KO*t*Bu in THF at room temperature yielded complex cation [**1**]$^+$ with the [11]ane-P_2C^{NHC} macrocycle after a reaction time of 24 h (Scheme 7). Use of less than 2 equiv of KO*t*Bu gave a mixture of complexes with only one new $N_{carbene}-C_{phenyl}$ bond (formal elimination of 1 equiv of HF, m/z = 735) and two new $N_{carbene}-C_{phenyl}$ bonds (formal elimination of 2 equiv of HF, m/z = 715). The complex cation [**1**]$^+$ can also be obtained by the same reaction starting from [**6**]BF_4. As was previously observed for complexes of type **F** (Scheme 2), formation of the macrocycle in [**1**]$^+$ leads to an upfield shift to δ = 62 ppm in the $^{31}P\{^1H\}$ NMR spectrum (δ = 72 ppm in [**6**]$^+$), and two resonances are observed for the CH_2 protons of the carbene ring due to their locked position in the complex cation.

Crystals of [**1**]Cl$\cdot CH_2Cl_2\cdot 0.5H_2O$ were grown from a mixture of salts [**1**]Cl/[**1**]$_2$[ZnCl] in dichloromethane. The X-ray structure analysis confirms the formation of the complex cation [**1**]$^+$ with the macrocyclic ligand at the ruthenium(II) template atom (Figure 4).

Upon formation of the macrocycle, the Ru−$C_{carbene}$ bond shortens slightly from 2.032(4) Å in [**6**]$^+$ to 1.996(5) Å in [**1**]$^+$, while the P1−Ru−P2 angle expands slightly. Additional metric parameters in [**6**]$^+$ and [**1**]$^+$ are essentially identical, indicating a stress-free formation of the macrocycle.

The relatively short reaction time for the formation of the macrocycle in [**1**]$^+$ (24 h) compared to the analogous rhenium(I) complex (**E** in Scheme 2, 5 days)[15] is remarkable. We attribute this behavior to the influence of the ancillary ligands in the two complexes. In the template-controlled formation of [12]ane-P_3 macrocycles from trisphosphine complexes the additional ligands at the template metal played an important role. It was argued that at the

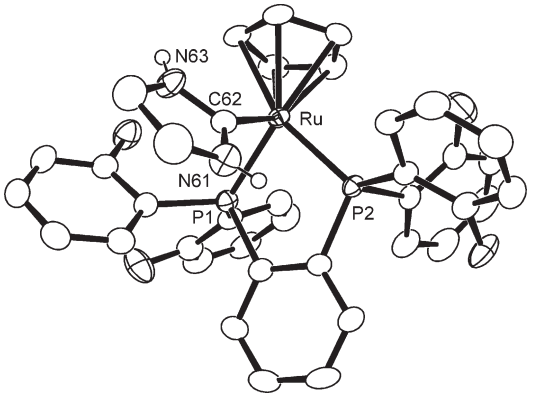


Figure 3. Molecular structure of the cation $[\mathbf{6}]^+$ in $[\mathbf{6}]BF_4 \cdot CH_2Cl_2$ (50% displacement ellipsoids, hydrogen atoms have been omitted except for those bound to the NHC nitrogen atoms). Selected bond lengths (Å) and angles (deg): Ru−P1 2.2601(8), Ru−P2 2.2584(8), Ru−C62 2.032(4); P1−Ru−P2 83.77(3), P1−Ru−C62 84.53(10), P2−Ru−C62 96.34(10), N61−C62−N63 106.0(3).

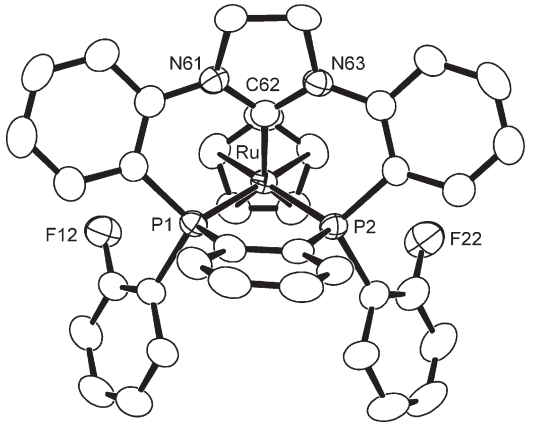


Figure 4. Molecular structure of the cation $[\mathbf{1}]^+$ in $[\mathbf{1}]Cl \cdot CH_2Cl_2 \cdot 0.5H_2O$ (50% displacement ellipsoids, hydrogen atoms omitted). Selected bond lengths (Å) and angles (deg): Ru−P1 2.2221(12), Ru−P2 2.2257(12), Ru−C62 1.996(5), C62−N61 1.370(6), C62−N63 1.356(6); P1−Ru−P2 84.89(4), P1−Ru−C62 83.76(12), P2−Ru−C62 82.98(13), N61−C62−N63 107.1(4).

$\{CpFe\}^+$ template, in contrast to $\{M(CO)_3\}$ templates (M = Cr, Mo), the cyclopentadienyl ligand exerts a certain amount of steric pressure, favoring an orientation of the phosphines that is suitable for the subsequent linkage.[4b] The same appears to be true for $[\mathbf{6}]^+$, where the cyclopentadienyl ligand favors the orientation of the NH,NH-stabilized NHC ligand in an orientation suitable for its subsequent linkage to the phenyl groups of the phosphine.

Conclusion

We have demonstrated that an NH,NH-stabilized NHC ligand can be generated at a Ru^{II} center bearing the 2-azidoethyl isocyanide ligand by reduction of the azido function with $Zn/NH_4Cl/H_2O$. The template-controlled cyclization of the intermediate 2-aminoethyl isocyanide occurs in spite of the presence of strongly electron donating ligands at the metal center. The reactive NH,NH-stabilized NHC ligand can be deprotonated while coordinated to the metal center and reacts with a *o*-fluorinated bis(diphenylphosphino)benzene at the Ru^{II} template to give the air- and water-stable complex [**1**]Cl with the macrocyclic [11]ane-P_2C^{NHC} ligand. Complexes of type $[\mathbf{1}]^+$ have been prepared in our search for new olefin metathesis catalysts of type $[Ru([11]ane\text{-}P_2C^{NHC})(CHPh)PR_3]^{2+}$. While the Ru^{II}-template-controlled formation of the macrocycle is possible, the substitution of the cyclopentadienyl ligand in $[\mathbf{1}]^+$ for an alkylidene and a phosphine has not been achieved yet. We are currently studying the formation of the [11]ane-P_2C^{NHC} macrocycle at $\{Ru(indenyl)\}^+$ and $\{Ru(pentadienyl)\}^+$ templates, where the removal of the π-perimeters is more easily achieved.

Experimental Section

General Comments. *Caution! Aliphatic azides are high-energy density materials. Vigorous heating of 2-azidoethyl isocyanide can cause an explosive decomposition, and appropriate care is advised when handling organic azides.* All preparations were carried out under an argon atmosphere using conventional Schlenk techniques. Solvents were dried and degassed by standard methods prior to use. The preparation of isocyanide **2**,[17] diphosphine **3**,[15a] and $[RuCl(Cp)(PPh_3)_2]$[26] has been described. NMR spectra were recorded with a Bruker Avance I 400 NMR spectrometer. IR spectra were measured with a Bruker Vector 22 spectrometer. MALDI mass spectra were obtained with a Varian MAT 212 spectrometer. Consistent microanalytical data were difficult to obtain due to the presence of fluoride in all complexes. MALDI and ESI HRMS data are provided instead. In addition ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^{19}F NMR spectra are provided for all compounds in the Supporting Information.

[RuCl(Cp)(3)], [4]. A solution of $[RuCl(Cp)(PPh_3)_2]$ (280 mg, 0.39 mmol) and diphosphine **3** (400 mg, 0.77 mmol) in toluene (20 mL) was heated under reflux for 48 h. The solvent was removed under reduced pressure, and the solid obtained was washed with diethyl ether (2 × 10 mL) to give a yellow solid. Yield: 270 mg, (0.38 mmol, 97%). For assignment of the resonances in the NMR spectra see Scheme 5. ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (m, 2H, Ar−H15), 8.03 (m, 2H, Ar−H2), 7.47 (m, 2H, Ar−H3), 7.43 (m, Ar−H13), 7.25 (m, 2H, Ar−H7), 7.20 (m, 2H, Ar−H14), 7.07 (m, 2H, Ar−H12), 6.97 (m, 2H, Ar−H6), 6.60 (m, 2H, Ar−H8), 6.17 (m, 2H, Ar−H9), 4.79 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.2 (d, $^1J_{CF}$ = 247 Hz, C11), 162.3 (d, $^1J_{CF}$ = 248 Hz, C5), 142.5 (pseudo-t, $^1J_{CP}$ = 42.7 Hz, $^2J_{CP}$ = 42.7 Hz, C1), 137.0 (m, C15), 134.2 (m, C9), 132.7 (m, C2), 132.2 (d, $^3J_{CF}$ = 8.4 Hz, C13), 131.6 (d, $^3J_{CF}$ = 8.4 Hz, C7), 130.8 (C3), 126.2 (m, C4), 123.6 (m, C14), 123.4 (m, C8), 121.4 (m, C10), 115.6 (d, $^2J_{CF}$ = 23.8 Hz, C6), 115.2 (d, $^2J_{CF}$ = 23.8, C12), 81.6 (Cp). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 62. ^{19}F NMR (376 MHz, $CDCl_3$): δ −100, −101. MS (MALDI) *m*/*z* (%): 720 (100) $[M - Cl]^+$.

[Ru(Cp)(2)(3)]Cl, [5]Cl. A mixture of [**4**] (250 mg, 0.35 mmol) and 2-azidoethyl isocyanide **2** (44 mg, 0.46 mmol) in methanol (10 mL) was heated under reflux for 3 h. The solvent was removed under reduced pressure and the colorless solid washed with diethyl ether (2 × 10 mL). Yield: 270 mg (0.33 mmol, 92%). For assignment of the resonances in the NMR spectra see Scheme 5. ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (m, 2H, Ar−H2), 7.60(m, 2H, Ar−H3), 7.581 (m, 2H, Ar−H15), 7.45 (m, 2H, Ar−H9), 7.27 (m, 2H, Ar−H14), 7.21 (m, 2H, Ar−H12), 7.06 (m, 2H, Ar−H13), 7.05 (m, 2H, Ar−H8), 7.05 (m, 2H, Ar−H6), 7.02 (m, 2H, Ar−H7), 4.98 (s, 5H, Cp), 3.04 (s br, 4H, $CNCH_2CH_2N_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.8 (d, $^1J_{CF}$ = 248.8, C11), 162.2 (dd, $^1J_{CF}$ = 259.9 Hz,

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Table 1. Crystallographic Data for the Complexes [4], [5]BF_4, [6]$BF_4 \cdot CH_2Cl_2$, and [1]$Cl \cdot CH_2Cl_2 \cdot 0.5H_2O$

parameter	[4]	[5]BF_4	[6]$BF_4 \cdot CH_2Cl_2$	[1]$Cl \cdot CH_2Cl_2 \cdot 0.5H_2O$
formula	$C_{35}H_{25}ClF_4P_2Ru$	$C_{38}H_{29}N_4BF_8P_2Ru$	$C_{39}H_{33}N_2BCl_2F_8P_2Ru$	$C_{39}H_{32}N_2Cl_3F_2O_{0.5}P_2Ru$
cryst size [mm]	0.20 × 0.10 × 0.05	0.25 × 0.15 × 0.05	0.30 × 0.08 × 0.05	0.20 × 0.20 × 0.08
M_r	720.01	867.47	926.39	844.01
a [Å]	14.5918(2)	10.0935(7)	9.7875(3)	20.0186(5)
b [Å]	11.0255(2)	16.0492(12)	26.0823(8)	22.1164(7)
c [Å]	19.0144(3)	10.9204(9)	15.3468(5)	18.4397(7)
α [deg]	90	90.0	90.0	90.0
β [deg]	98.439(1)	93.071(5)	105.080(2)	107.580(2)
γ [deg]	90	90.0	90.0	90.0
V [Å^3]	3025.95(8)	1766.5(2)	3782.8(2)	7782.7(4)
Z	4	2	4	8
space group	$P2_1/n$	$P2_1/m$	$P2_1/n$	$C2/c$
ρ_{calcd} [g cm^{-3}]	1.580	1.631	1.627	1.437
μ [mm^{-1}]	0.762	5.142	6.095	6.270
2θ range [deg]	3.3−55.9	8.1−134.9	6.9−135.8	6.1−135.8
data collected	20 093	15 792	32 583	30 499
no. unique data, R_{int}	7184, 0.066	3205, 0.079	6711, 0.064	6859, 0.064
no. obsd data [$I \geq 2\sigma(I)$]	4678	2850	6109	5711
R	0.0455	0.0609	0.0426	0.0522
wR	0.0951	0.1538	0.1103	0.01469
no. of variables	388	262	502	450

$^2J_{CP}$ = 8.4 Hz, C5), 151.7 (t, $^2J_{CP}$ = 18 Hz, C≡N), 141.5 (m, C1), 134.2 (d, $^2J_{CP}$ = 8.6 Hz, C15), 133.9 (m, C9), 133.1 (m, C2 and C7), 132.3 (d, $^3J_{CP}$ = 3.5 Hz, C3), 131.5 (C13), 125.3 (m, C14), 124.7 (C8), 121.8 (m, C4), 121.2 (m, C10), 116.7 (d, $^2J_{CF}$ = 22.6 Hz, C6), 116.7 (d, $^2J_{CF}$ = 22.0 Hz, C12), 86.2 (Cp), 49.6 (CH_2N_3), 44.3 (CH_2NC). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 61. ^{19}F NMR (376 MHz, $CDCl_3$): δ −97, −98. IR (KBr): ν 2152 (s, CN), 2136 (sh, N_3), 2099 (s, N_3). MS (MALDI) m/z (%): 781 (100) [M − Cl]$^+$. MS (ESI HRMS) m/z (%): 781.0855 (100) [**5**]$^+$ (calcd for [**5**]$^+$ 781.0852).

[Ru(Cp)(2)(3)]BF_4, [5]BF_4. The tetrafluoroborate salt was obtained by anion exchange with NH_4BF_4. The ^1H, ^{13}C, and ^{31}P NMR are not affected by the anion exchange.

[Ru(Cp)(3)(NH,NH-NHC)]Cl, [6]Cl. A suspension of [**5**]Cl (180 mg, 0.22 mmol), zinc dust (19 mg, 0.29 mmol), and NH_4Cl (27 mg, 0.29 mmol, 2.3 equiv) in methanol (20 mL) was treated with 0.1 mL of degassed water. The mixture was subsequently heated under reflux for 24 h. The solvent was removed and the solid residue was extracted with dichloromethane (20 mL). Removal of the solvent gave a yellow solid. This solid consisted of the salts [**6**]Cl and [**6**]$_2$[$ZnCl_4$], which could not be separated. Yield: 160 mg (94% for pure [**6**]Cl or 87% for pure[**6**]$_2$[$ZnCl_4$]; the real value lies in between these two extremes). For assignment of the resonances in the NMR spectra see Scheme 5. ^1H NMR (400 MHz, DMSO-d_6): δ 8.09 (m, 2H, Ar−H15), 7.80 (m, 2H, Ar−H2), 7.64 (m, 2H, Ar−H3), 7.47 (m, 2H, Ar−H13), 7.43 (2H, Ar−H7), 7.33 (m, 2H, Ar−H12), 7.31 (m, 2H, Ar−H14), 7.20 (m, 2H, Ar−H6), 6.91 (m, 2H, Ar−H8), 6.36 (m, 2H, Ar−H9), 6.26 (s br, 2H, NH), 4.96 (s, 5H, Cp), 2.76 (s, 4H, NCH_2CH_2N). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 199.7 (t, $^2J_{CP}$ = 15.2 Hz, NCN), 162.6 (d, $^1J_{CF}$ = 246.1 Hz, C11), 161.4 (d, $^1J_{CF}$ = 247.1 Hz, C5), 141.3 (m, C1), 134.5 (m, C15), 133.5 (m, C9 and C2), 133.4 (d, $^3J_{CF}$ = 9.7 Hz, C13), 133.1 (d, $^3J_{CF}$ = 8.6 Hz, C7), 132.3 (C3), 124.8 (m, C4), 124.2 (m, C8 and C14), 121.0 (m, C10), 116.0 (d, $^2J_{CF}$ = 23.4 Hz, C6), 115.2 (d, $^2J_{CF}$ = 22.9 Hz, C12), 86.2 (Cp), 44.0 (NCH_2CH_2N). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 72. ^{19}F NMR (376 MHz, $CDCl_3$): δ −99, −101. MS (MALDI) m/z (%): 755 (100) [M − Cl]$^+$. MS (ESI HRMS) m/z (%): 755.0916 (100) [**6**]$^+$ (calcd for [**6**]$^+$ 755.0947).

[Ru(Cp)(3)(NH,NH-NHC)]Cl, [6]BF_4. The salt [**6**]BF_4 was obtained by azide reduction of [**5**]BF_4 using the reaction conditions employed for the reduction of the azido function in [**5**]Cl/[**5**]$_2$[$ZnCl_4$]. It can also be obtained by anion exchange in [**6**]Cl/[**6**]$_2$[$ZnCl_4$] using NH_4BF_4.

[Ru(Cp)([11]ane-P_2C^{NHC})]Cl, [1]Cl. A suspension of [**6**]X (X = Cl or 0.5 $ZnCl_4$) (165 mg, 0.21 mmol for pure [**6**]Cl) and KO*t*Bu (47 mg, 0.42 mmol) in THF (20 mL) was stirred for 24 h. After solvent removal, the residue was extracted with dichloromethane. Removal of the solvent afforded a mixture of [**1**]Cl and [**1**]$_2$[$ZnCl_4$] as a yellow solid. Yield: 110 mg (0.147 mmol, 70% relative to [**1**]Cl, 0.134 mmol, 64% relative to [**1**]$_2$[$ZnCl_4$]; the real value lies in between these two extremes). ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (m, 2H, Ar−H15), 7.44 (m, 4H, Ar−H2 and Ar−H3), 7.39 (m, 4H, Ar−H12 and Ar−H7), 7.31 (m, 2H, Ar−H13), 7.15 (m, 2H, Ar−H14), 7.14 (m, 2H, Ar−H6), 7.01 (m, 2H, Ar−H8), 6.66 (br, 2H, Ar−H9), 4.96 (m, 2H, NC*H*H−C*H*HN), 4.71 (s, 5H, Cp), 3.39 (m, 2H, NCH*H*−CH*H*N). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 204.3 (br, NCN), 162.9 (dd, $^1J_{CF}$ = 249.5 Hz, $^2J_{CP}$ = 2.3 Hz, C5), 145.0 (d, $^2J_{CP}$ = 12.8 Hz, C11), 133.9 (d, $^3J_{CF}$ = 8.0, C7), 132.8 (br, C15), 132.7 (C3), 132.3 (br, C9), 132.2 (br, C1), 131.5 (m, C2), 128.9 (C13), 125.1 (dd, $^4J_{CF}$ = 8.5 Hz, $^3J_{CP}$ = 3.0 Hz, C8), 124.9 (m, C4), 124.6 (d, $^3J_{CP}$ = 7.6 Hz, C14), 121.9 (d, $^3J_{CP}$ = 6.8 Hz, C12), 121.2 (m, C10), 116.8 (dd, $^2J_{CF}$ = 22.9 Hz, $^3J_{CP}$ = 3.2 Hz, C6), 84.6 (Cp), 50.2 (NCH_2CH_2N). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 62. ^{19}F NMR (376 MHz, $CDCl_3$): δ −96. MS (MALDI) m/z (%): 715 (100) [M − Cl]$^+$. MS (ESI HRMS) m/z (%): 715.0808 (100) [**1**]$^+$ (calcd for [**1**]$^+$ 715.0822).

X-ray Diffraction Studies. X-ray diffraction data for [**4**], [**5**]BF_4, [**6**]$BF_4 \cdot CH_2Cl_2$, and [**1**]$Cl \cdot CH_2Cl_2 \cdot 0.5H_2O$ were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 223(2) K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) for [**4**] or Cu- Kα radiation (λ = 1.54178 Å) for [**5**]BF_4, [**6**]$BF_4 \cdot CH_2Cl_2$, and [**1**]$Cl \cdot CH_2Cl_2 \cdot 0.5H_2O$. Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[27] program package. For further crystal and data collection details see Table 1. Structure solutions were found with the SHELXS-97[28] package using the heavy-atom method and were refined with SHELXL-97[29] against F^2 using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

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Supporting Information Available: X-ray crystallographic files for complexes [**4**], [**5**]BF_4, [**6**]$BF_4 \cdot CH_2Cl_2$, and [**1**]$Cl \cdot CH_2Cl_2 \cdot 0.5H_2O$ in CIF format and ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, and ^{19}F NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.