Interplay between Solvent and Counteranion Stabilization of Highly Unsaturated Rhodium(III) Complexes: Facile Unsaturation-Induced Dearomatization

Mark Gandelman,[a] Leonid Konstantinovski,[a] Haim Rozenberg,[b] and David Milstein*[a]

Abstract: Abstraction of the chloride ligand from the PCN-based chloromethylrhodium complex **2** by AgX ($X = BF_4^-$, $CF_3SO_3^-$) or a direct C–C cleavage reaction of the PCN ligand **1** with $[(coe)_2Rh(solv)_n]^+X^-$ (coe = cyclooctene) lead to the formation of the coordinatively unsaturated rhodium(III) complexes **3**. Compound **3a** ($X = BF_4^-$) exhibits a unique medium effect; the metal center is stabilized by reversible coordination of the bulky counteranion or solvent as a function of temperature. Reaction of $[(PCN)Rh(CH_3)(Cl)]$ with $AgBAr_f$ in diethyl ether leads to an apparent rhodium(III) 14-electron complex **4**, which is stabilized by reversible, weak coordination of a solvent molecule. This complex coordinates donors as weak as diethyl ether and dichloromethane. Upon substitution of the BF_4^- ion in $[(PCN)Rh(CH_3)]BF_4$ by the noncoordinating BAr_f^- ion in a noncoordinating medium, the resulting highly unsaturated intermediate undergoes a 1,2-metal-to-carbon methyl shift, followed by β-hydrogen elimination, leading to the Rh-stabilized methylene arenium complex **5**. This process represents a unique mild, dearomatization of the aromatic system induced by unsaturation.

Keywords: dearomatization · N,P ligands · rhodium · tridentate ligands · unsaturated complexes

Introduction

Coordinatively unsaturated metal complexes play central roles in many catalytic processes.[1] Vacant coordination sites can be stabilized by relatively weak coordination of a counteranion,[2] a solvent molecule,[3] or by agostic interactions with ligands on the metal center.[4] The interplay between the ligating features of a counteranion versus a solvent molecule is intriguing and can influence the reactivity of the complex. For example, it is known that in a number of systems this interplay has an important role in the mechanistic and energetic requirements of many processes, such as C–H activation,[5] alkene polymerization,[6] and CO/alkene copolymerization.[7] In general, the study of medium effects (e.g. counterions and solvents) on metal-mediated processes is an important but a relatively unexplored area.[8]

Of special interest are d^6 and d^8 14-electron metal complexes, which are postulated as intermediates in various metal-mediated processes, such as carbon–carbon[9] and carbon–hydrogen[10, 11] bond activation and functionalization. Formally 14-electron d^6 iridium,[4a] ruthenium,[3, 4b] and d^8 rhodium[4c, 12] complexes were reported. Also, examples of unsaturated platinum d^6 compounds are known.[13] However, the preparation and investigation of rhodium d^6 14-electron complexes, which are proposed as key intermediates in many Rh-catalyzed reactions, still remains a desirable goal.[14] Here we report on our efforts to isolate and study rhodium(III) 14-electron species. We have obtained a highly unsaturated Rh d^6 complex, which exhibits remarkable behavior: it is stabilized by weak coordination of either a solvent or a bulky anion as a function of the temperature. Donors as weak as dichloromethane and diethyl ether can reversibly coordinate to these species.[15] Based on these species, we demonstrate a unique, unsaturation-driven, dearomatization process caused by a simple counteranion exchange. This reaction proceeds by a 1,2-metal-to-carbon alkyl shift, which represents an important but scarcely studied process.[16]

[a] Prof. Dr. D. Milstein, M. Gandelman, Dr. L. Konstantinovski
Department of Organic Chemistry
The Weizmann Institute of Science
Rehovot, 76100 (Israel)
Fax: (+972) 8-9344142
E-mail: david.milstein@weizmann.ac.il

[b] Dr. H. Rozenberg
Unit of Chemical Research Support
The Weizmann Institute of Science
Rehovot, 76100 (Israel)

Results and Discussion

With the purpose of the generation of highly unsaturated Rh^{III} cationic complexes, we chose a system based on the tridentate aromatic phosphinoamine PCN ligand (**1**; see Scheme 1).[17] In general, it was demonstrated that analogous tridentate PCP- and NCN-based ligands can provide high stability for late

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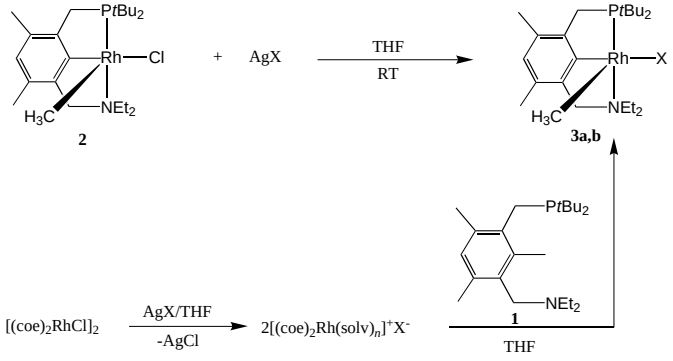
transition metal complexes and allow the isolation of "elusive" compounds, which are postulated as intermediates in a number of metal promoted transformations of aromatic compounds.[18]

Recently we reported the preparation of the chloromethylrhodium(III) complex **2**, which was obtained by rhodium insertion into an C_{aryl}–CH_3 bond of the PCN ligand **1**.[17] Upon reaction of compound **2** with $AgBF_4$ in THF at room temperature, precipitation of AgCl and quantitative formation of complex **3a** were observed (Scheme 1). Compound **3a** can also be obtained by direct reaction of ligand **1** with the



3a: X = BF_4

3b: X = OTf

Scheme 1. Synthesis of **3**. coe = cyclooctene; X = BF_4^- (**3a**), OTf (**3b**).

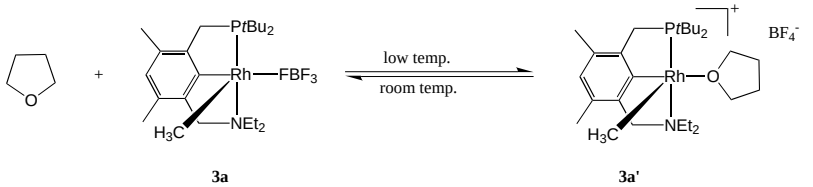
cationic rhodium precursor $[(coe)_2Rh(solv)_n]^+BF_4$[19] (coe = cyclooctene) at room temperature, resulting in facile carbon–carbon bond activation to give the product **3a**. The C–C bond activation by cationic rhodium species with a PCP type system was recently communicated.[20]

Complex **3a** was characterized by multinuclear NMR techniques. It gives rise to a doublet centered at $\delta =$ 73.21 ppm ($^1J_{Rh,P} = 160.2$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum. In the ^1H NMR spectrum the signal corresponding to CH_3Rh appears at $\delta = 1.75$ ppm as a doublet of doublets due to coupling with phosphorous and rhodium ($^2J_{Rh,H} = 2.9$ Hz, $^3J_{P,H} = 1.2$ Hz). In the $^{13}C\{^1H\}$ NMR spectrum the CH_3Rh group gives rise to a doublet of doublets centered at $\delta =$ 0.08 ppm ($^1J_{Rh,C} = 35.1$ Hz, $^2J_{P,C} = 7.2$ Hz) and the *ipso*-carbon atom exhibits a doublet of doublets at $\delta = 171.12$ ppm ($^1J_{Rh,C} = 29.1$ Hz, $^2J_{P,C} = 3.6$ Hz). The chemical shifts of the CH_3Rh group in both ^1H NMR and $^{13}C\{^1H\}$ NMR spectra are characteristic of a methyl group *trans* to a vacant coordination site.[9a, 17, 20] No signals due to coordinated solvent are observed. Moreover, elemental analysis shows that solvent is absent in the solid state as well. The IR spectrum shows no signals assignable to coordinated N_2. The BF_4^- ion appears as a very broad singlet at $\delta =$ –164.40 ppm in the ^{19}F NMR spectrum, measured in THF. Taking into consideration that free (not coordinated) BF_4^- appears at $\delta = -151$ ppm as a singlet in the ^{19}F NMR spectrum,[21] we conclude that the tetrafluoroborate anion in complex **3a** is coordinated to the Rh center (through a fluorine atom). This conclusion is in agreement with the recently published PCO-based rhodium(III) cationic complex, in which coordination of BF_4^- through a fluorine atom was proven by X-ray crystallography.[22] The presence of a coordinated tetrafluoroborate in **3a** is also supported by its chemical behavior (vide infra). The broadness of the signal in the ^{19}F NMR spectrum of **3a** indicates that the coordinated tetrafluoroborate anion undergoes a dynamic process.

Additional information about BF_4^- coordination is obtained from the IR spectrum. The bound BF_4^- ion gives rise to three weak bands at 1183, 1107, and 941 cm^{-1}, which is in good agreement with literature IR data for BF_4^- coordination to the metal center through one of its fluorine atoms.[23, 25] It has been suggested that the frequency difference between bands due to coordinated and free BF_4^- (ca. 1055 cm^{-1}) reflects the amount by which the B–F bonding is perturbed; for the lowest lying band this shows the weakening of the B–F bond due to the competing Lewis acidity of the metal.[23b] The values observed for **3a** are quite close to those of free BF_4^- (contrary to the examples of strongly coordinated BF_4^-[23b]) and confirm weak coordination of this group.

To study the dynamic behavior of **3a**, the ^{19}F NMR of the complex in THF was measured at low temperatures. Interestingly, as the temperature was lowered, the peak area of the coordinated tetrafluoroborate at $\delta = -164.4$ ppm decreases and a peak at the chemical shift of free BF_4^- ($\delta =$ –151.2 ppm) appears. The assumption that the new peak is due to free BF_4^- was confirmed by adding a small amount of $Bu_4N^+BF_4^-$ to the solution of complex **3a**, which resulted in the expected proportional increase in the signal at $\delta =$ –151.2 ppm. This indicates that a new complex, not stabilized by BF_4^- coordination, is formed as the temperature is lowered. At –30 °C the integration ratio between the complex with a coordinated BF_4^- ion and the one with a noncoordinated BF_4^- ion is 1:1 according to ^{19}F NMR spectroscopy, while at –90 °C the species with a free BF_4^- is dominant (1:9 ratio).

Remarkably, the described phenomena do not take place when the NMR measurements of complex **3a** are performed in the noncoordinating solvent 2,5-dimethyltetrahydrofuran (mixture of *cis and trans* isomers), the broad signal at $\delta =$ –164.4 ppm in the ^{19}F NMR spectrum remaining unchanged on varying the temperature. Therefore, we conclude that a THF molecule coordinates to the Rh^{III} center at low temperature, replacing the weakly coordinated BF_4^- ligand and resulting in complex **3a′** (Scheme 2). This process is reversible and the equilibrium can be shifted completely back to **3a** by elevating the temperature up to 25 °C.



Scheme 2. Stabilization of the cationic Rh center by BF_4^- or THF coordination tuned by temperature.

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The exchange between bound and free BF_4^- was studied by spin-saturation transfer experiments in the noncoordinating solvent 2,5-dimethyltetrahydrofuran. When complex **3a** is mixed with $Bu_4N^+BF_4^-$ in this solvent, the ^{19}F NMR spectrum exhibits two signals, at $\delta = -151.2$ ppm and $\delta = -164.4$ ppm, for the free and coordinated (complex **3a**) tetrafluoroborate, respectively. Spin-saturation experiments were performed between $-70\,^\circ C$ and $10\,^\circ C$, and the response of the signal of coordinated BF_4^- upon saturation of free BF_4^- (saturation transfer difference) was monitored. These experiments show that the coordinated BF_4^- ion is in a relatively fast equilibrium with the free BF_4^- ion even at low temperatures,[24] and that this exchange does not require solvent coordination to the metal center. Interestingly, the exchange was faster upon increasing the concentration of $Bu_4N^+BF_4^-$.

Interestingly, the signal of the bound tetrafluoroborate anion of **3a** in the noncoordinating solvent, 2,5-dimethyltetrahydrofuran is very broad in the ^{19}F NMR spectrum. The broadness of the signal can be explained by fast intramolecular rotation of BF_4^-, which takes place by fast coordination/decoordination of the fluorine atoms (complete dissociation of BF_4^- is unlikely, vide infra). Therefore, it was impossible to distinguish between the coordinated and uncoordinated fluorine atoms of the bound BF_4^- ion in ^{19}F NMR spectra even at low temperatures. Traditionally, the BF_4^- ion is considered as a "noncoordinating" ligand and examples of binding of this anion to a metal are not common. We are aware of only two other examples of BF_4^- coordination to a rhodium center.[25] The BF_4^- ion coordinates to **3a** to stabilize the very unsaturated rhodium(III) 14-electron complex, although the dynamic behavior of the anion indicates, most likely, a relatively weak coordination.

Complex **3** represents a unique example, in which stabilization of a highly unsaturated, formally 14-electron Rh^{III} center, either by a weakly coordinated anion (BF_4^-) or a loosely bound solvent molecule (THF) is *controlled by the temperature selected*. At low temperature THF coordination is favored over BF_4^- coordination, while at room temperature the ligation of BF_4^- to Rh^{III} in **3a** is preferred, although the opposite order of the donor strengths was reported for molybdenum and tungsten complexes (THF > BF_4^-).[2a] A likely explanation for the observed temperature dependence is that THF coordination is enthalpically favored, THF being a better ligand than BF_4^-, whereas BF_4^- coordination is favored entropically, because it results in lower charge separation.

Complex **3b**, in which the unsaturated rhodium(III) center is stabilized by another weakly coordinating ligand, the trifluoromethylsulfonate (triflate, OTf^-) ion, was prepared in a similar way to compound **3a**. Abstraction of the chloride from complex **2** by AgOTf in THF results in quantitative formation of compound **3b**. Complex **3b** can also be synthesized by direct reaction of the PCN ligand with the monomeric cationic precursor $[(coe)_2Rh(solv)_n]^+OTf^-$ (Scheme 1). Complex **3b** exhibits NMR spectra similar to those of **3a**, including characteristic shifts and splitting patterns for the CH_3Rh group in both ^1H and $^{13}C\{^1H\}$ NMR spectra and for the *ipso*-carbon atom in the $^{13}C\{^1H\}$ NMR spectrum. No signals for coordinated solvent were found at room temperature, suggesting that the OTf^- ion is bound to the metal center.[26]

The molecular structure of complex **3b** was confirmed by an X-ray diffraction study.[27] Orange prismatic crystals were obtained by slow diffusion of pentane into a concentrated solution of **3b** in THF at room temperature. The rhodium atom is located in the center of a distorted square pyramid with the methyl group occupying the position *trans* to the empty coordination site (Figure 1).

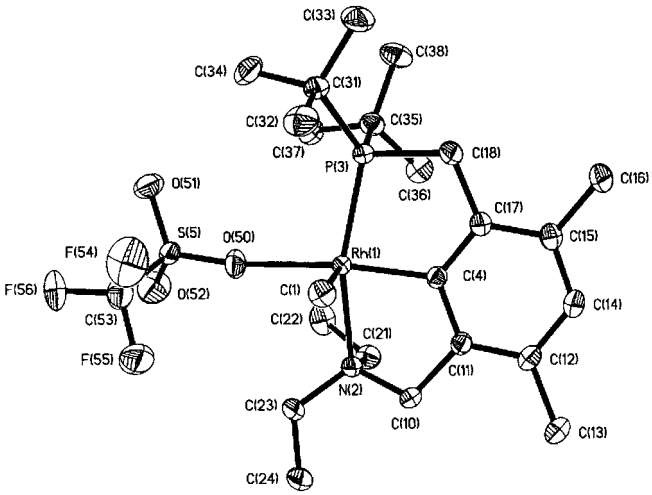

Figure 1. Strucuture of **3b** (ORTEP drawing, 50% of probability; hydrogen atoms are omitted for clarity).

The triflate ligand is located in the position *trans* to the aromatic ring. Noteworthy, although **3b** has an additional vacant coordination site, $CF_3SO_3^-$ prefers to bind through one oxygen atom, rather than by η^2-coordination.[28] The N–Rh bond (2.184(15) Å) is shorter than the P–Rh bond (2.274(6) Å), which forces the rhodium atom to tilt toward the amine ligand. This results in a certain asymmetry of the PCN system in **3b**. Selected bond lengths and angles are given in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for **3b**.

Rh(1)–N(2)	2.1844(15)	Rh(1)–P(3)	2.2739(6)
Rh(1)–C(4)	1.9607(16)	Rh(1)–O(50)	2.2373(14)
Rh(1)–C(1)	2.0339(17)		
C(4)-Rh(1)-C(1)	87.30(7)	N(2)-Rh(1)-O(50)	92.43(6)
C(4)-Rh(1)-N(2)	81.87(6)	C(4)-Rh(1)-P(3)	83.98(5)
C(1)-Rh(1)-N(2)	93.81(7)	C(1)-Rh(1)-P(3)	98.25(6)
C(4)-Rh(1)-O(50)	173.70(6)	N(2)-Rh(1)-P(3)	160.91(4)
C(1)-Rh(1)-O(50)	90.42(7)	O(50)-Rh(1)-P(3)	102.17(4)

Interestingly, in contrast to the BF_4^- ion in **3a**, the OTf^- ligand in **3b** remains coordinated regardless of the temperature, indicating stronger binding of OTf^- than BF_4^-. This fact is in agreement with Beck's series of donor strengths for weakly coordinating ligands.[2a]

Since the unsaturated rhodium(III) cationic complexes described above can coordinate anions such as triflate and tetrafluoroborate, we decided to use the very bulky non-

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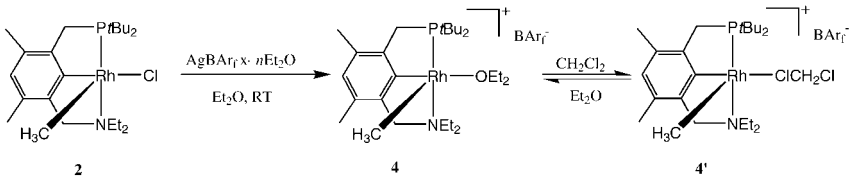
coordinating anion tetrakis(3,5-bis(trifluoromethyl)phenyl)-borate (BAr_f^-).[29] Upon reaction of $AgBAr_f \cdot n((CH_3CH_2)_2O)$[30] with complex **2** in diethyl ether at room temperature, silver chloride precipitation and quantitative formation of complex **4** were observed (Scheme 3).[31]



2 4 4'

Scheme 3. Synthesis of solvent-stabilized **4**.

The NMR data of complex **4** are similar to that of **3a** and **3b**, indicating the similarity in their structure. In addition, the characteristic signals of the BAr_f^- ion are observed in both ^1H and $^{13}C\{^1H\}$ NMR spectra, and the ^{19}F NMR spectrum shows a sharp singlet at $\delta = -62.5$ ppm due to the free BAr_f^- ion. To address the question of solvent coordination to the rhodium center in **4**, the following experiment was performed. Complex **4** was prepared in diethyl ether and the solvent was evaporated to dryness, followed by dissolution in CD_2Cl_2 and measurement of the ^1H NMR spectrum. In addition to the characteristic signals of complex **4**, the spectrum shows the presence of one equivalent of diethyl ether (by integration). Thus, we can conclude that a molecule of diethyl ether is coordinated to the rhodium center in complex **4** even in the solid state, and that it is substituted by a molecule of dichloromethane when **4** is dissolved in it. In agreement with this, the $^{31}P\{^1H\}$ NMR spectrum exhibits a doublet at $\delta = 74.1$ ppm ($^1J_{Rh,P} = 155.7$ Hz) in CH_2Cl_2, while in diethyl ether a doublet at $\delta = 77.3$ ppm with $^1J_{Rh,P} = 159.5$ Hz is observed. Coordination of one diethyl ether molecule in complex **4** in the solid state was confirmed by elemental analysis (see Experimental Section). Moreover, solvent coordination in **4** is supported also by comparing its reactivity with that of the complex prepared in the absence of any coordinating solvent (vide infra).

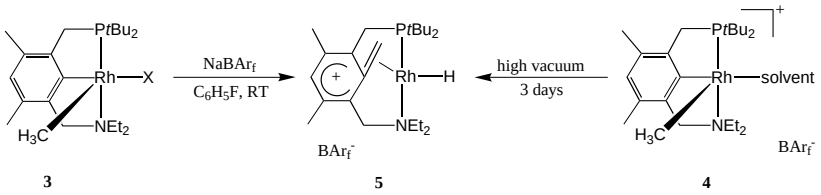
The ability of **4** to coordinate CH_2Cl_2 was demonstrated in a similar fashion. Upon evaporation of the CH_2Cl_2 solvent to dryness and redissolving the solid **4** in THF, the ^1H NMR spectrum of the THF solution shows a singlet at $\delta = 5.65$ ppm, which integrated 1:1 to the complex, assignable to one free molecule of CH_2Cl_2, replaced by the better-coordinating THF ligand. The $^{31}P\{^1H\}$ NMR spectrum of complex **4** in THF differs from that in diethyl ether or dichloromethane and exhibits a doublet at $\delta = 73.02$ ppm with $^1J_{Rh,P} = 157.3$ Hz. The coordination of the solvents in **4** is reversible (Scheme 3).

Thus, **4** represents an interesting complex, which closely mimics a highly unsaturated rhodium(III) 14-electron reactive intermediate, dissolved in solvents such as diethyl ether or dichloromethane. The solvent molecule stabilizes this species by very weak labile coordination. This is a very rare case of dichloromethane and diethyl ether coordination to a rhodium center. Because of its poor ligating ability, CH_2Cl_2 complexes of late transition metals are rare.[3, 15, 32] Notably, in Beck's series of weakly coordinating ligands dichloromethane and diethyl ether were classified as the weakest ones.[2a]

Complex **4** is stable in solution at room temperature and it is similar to complex **3a′**, which is solvent-trapped only at very low temperature. Thus, at room temperature, the choice of a counteranion (BF_4^- or BAr_f^-) controls the mode of stabilization of the cationic rhodium species, either by an anion (in **3a**) or by a solvent (in **4**).

1,2-Metal-to-carbon methyl shift: facile dearomatization: Complexes **3** and **4** were obtained in the presence of weakly coordinating anions or/and solvents. In an effort to study such complexes in a noncoordinating medium, we tried to exchange the BF_4^- ion in complex **3** for the BAr_f^- ion in fluorobenzene.[33]

Addition of $NaBAr_f$[34] to an orange solution of **3** in fluorobenzene leads to a gradual color change to green, accompanied by the precipitation of NaX (X = BF_4, OTf). Analysis of the reaction mixture by NMR spectroscopy shows the quantitative conversion of complex **3** to the hydride complex **5** (Scheme 4).



3 5 4

3a: X=BF_4

3b: X=OTf

Scheme 4. Thermodynamically favorable dearomatization, caused by simple counteranion exchange.

Complex **5** was unequivocally characterized by multinuclear NMR spectroscopy. The NMR spectra show a very characteristic picture of a dearomatized compound with a methylene arenium frame, which is similar to the NMR data for the only other known metal stabilized methylene arenium system, which is based on the PCP ligand.[16e, 35] The $^{31}P\{^1H\}$ NMR spectrum shows a doublet at $\delta = 43.29$ ppm ($^1J_{Rh,P} = 116.5$ Hz), which is strongly upfield shifted in comparison to that of the aromatic compound **3** ($\Delta\delta \approx 30$ ppm). The RhH appears at $\delta = -27.4$ ppm in the ^1H NMR spectrum as a doublet of doublets ($^1J_{Rh,H} = 62.5$, $^2J_{P,H} = 23.7$ Hz), the chem-

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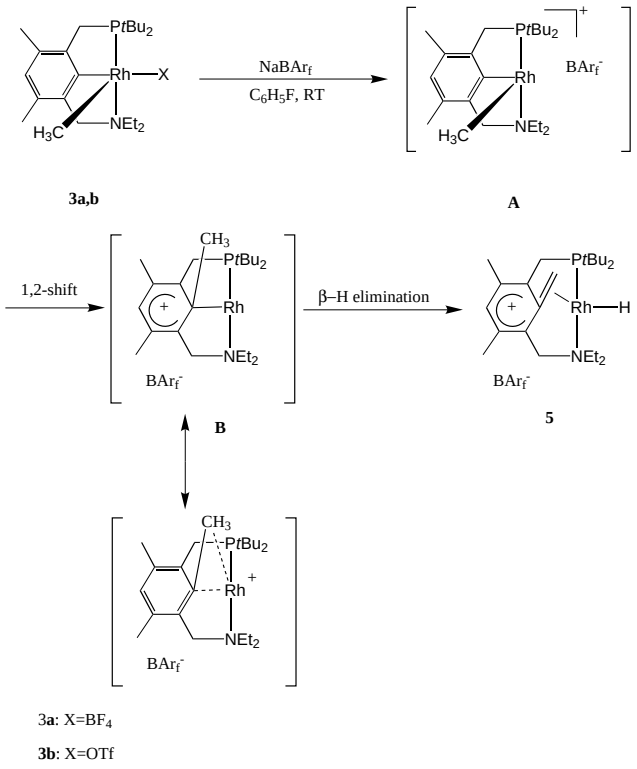
ical shift being characteristic of a hydride ligand located *trans* to the occupied coordination site. The protons of a coordinated double bond ($C{=}CH_2$) give rise to a pair of broad doublet of doublets at $\delta = 4.67$ and 4.11 ppm. The different chemical shift of these protons is a result of their magnetic inequivalence caused by lack of a symmetry plane passing through the double bond and rhodium atom. In the same spectrum, the ring-bound hydrogen atom exhibits a single resonance at $\delta = 8.51$ ppm, the downfield shift being characteristic of a positively charged arenium species.[36] The $^{13}C\{^1H\}$ NMR spectrum shows a pair of doublet of doublets at $\delta =$ 95.34 ($Rh{-}(C{=}CH_2)$) and 38.60 ppm ($Rh{-}(C{=}CH_2)$) due to the coordinated methylene group. In the same spectrum the *ortho*- and *para*- carbon atoms show three singlets at $\delta =$ 152.39, 147.34, and 144.82 ppm, which indicates a relatively high degree of the positive charge localization at these carbon atoms.[36]

A plausible mechanism for the formation of the methylene arenium complex **5** is described in Scheme 5. It is conceivable that the initial exchange of the X^- ($X = BF_4$, OTf) ion by



Scheme 5. Possible mechanism of the dearomatization process by way of a 1,2-metal-to-carbon methyl shift.

BAr_f^- followed by the precipitation of NaX leads to the formation of complex **A**. Compound **A** must be very unstable, because it represents a very unsaturated Rh^{III} complex, formally a 14-electron complex, which is not stabilized by the medium (in contrast to **3** and **4**). Therefore, a 1,2-methyl shift to give the more electron-rich Rh^I methyl arenium complex **B** may take place. Such an apparent 1,2-methyl shift upon reducing electron density at the metal center by CO coordination was recently reported.[16e] Complex **B** can be represented by two resonance forms, one having the positive charge on the dearomatized ring of the ligand and the second one having it on the rhodium atom, including an agostic interaction of the C–C bond with the metal center. In the case of the stable PCP-based methyl arenium Rh–carbonyl complex it was shown that the positive charge is concentrated mainly on the metal center. Intermediate **B** is a Rh^I 14-electron complex, which is expected to be unstable. Examples of isolated monovalent rhodium 14-electron complexes are scarce.[4c, 12] Having a methyl group in the β-position, **B** can easily undergo β-hydrogen elimination to give the rhodium(I) 16-electron methylene arenium compound **5**.

The transformation of complex **3** to **5** (Scheme 4) cannot be reversed by addition of an excess of NaX or of a coordinating solvent to **5**. The reason for this is, most likely, a high kinetic barrier for migratory insertion of the hydride to the *trans*-located double bond, although one example of such a process is known.[37] Thus, formation of compound **5** represents a unique, facile, thermodynamically driven dearomatization process caused by a simple exchange of counteranions, which takes place at room temperature. Metal-stabilized methylene arenium species, which are very rare, were previously prepared by reaction of PCP-based Rh or Ir methyl chloride complexes, analogous to **3**, with a strong acid, such as HOTf.[16e] In that case the dearomatization process of the aromatic ring is driven by H_2 liberation. Here, the dearomatization process (of intermediate **A**) itself is thermodynamically favorable: the highly unstable rhodium(III) 14-electron intermediate loses its aromaticity to form a more stable 16-eelectron Rh^I complex. In addition, this system represents a remarkable example, in which it is possible to follow and control a transformation of trivalent rhodium 14 electron complexes. Usually, such species undergo uncontrollable decomposition.

Interestingly, complex **5** can be alternatively obtained by leaving compound **4** under high vacuum for three days (Scheme 4). The coordinated diethyl ether molecule is removed by this treatment, resulting in species **A** (Scheme 5), which undergoes the previously described transformation.

Finally, taking into consideration the observation that the exchange rate involving BF_4^- is enhanced upon increasing the concentration of this anion, and the described 1,2-methyl-shift chemistry (even traces of dearomatization product were not observed in the BF_4^-/THF system), we believe that the mechanism of the ligand exchange in complex **3a** is associative rather than dissociative, although a dissociative mechanism may also be possible.

Summary

Synthesis, characterization, medium effects, and reactivity studies of highly unsaturated rhodium(III) cationic complexes, which mimic "elusive" 14-electron intermediates of metal-catalyzed reactions are presented in this work. Complex **3** represents a unique example, in which a highly coordinatively unsaturated rhodium center is stabilized by a counteranion or solvent molecule *as a function of temperature*. Complex **4** is an apparent Rh^{III} 14-electron compound stabilized by reversible,

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weak coordination of a solvent molecule. Rare examples of coordination of dichloromethane and diethyl ether to the rhodium center are presented. When the cationic unsaturated complex **3** is forced to be in a noncoordinating medium (solvent, anion) the highly unsaturated 14-electron rhodium(III) species undergoes a unique 1,2-metal-to-carbon methyl shift. Followed by β-hydrogen elimination, the whole process results in a dearomatized methylene arenium system. This process represents a mild, thermodynamically favorable dearomatization of the aromatic system driven by unsaturation.

Experimental Section

General procedures: All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with a MO 40–2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All non-deuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glove box over 4 Å molecular sieves. Commercially available reagents were used as received. The complex $[\{Rh(coe)_2Cl\}_2]$,[38] was prepared according to a literature procedure.

^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded at 400, 100, 162, and 376 MHz, respectively, using a Bruker AMX-400 NMR spectrometer. All spectra were recorded at 23 °C. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents ($\delta = 3.58$ ppm, tetrahydrofuran; $\delta = 5.32$ ppm, dichloromethane). In ^{13}C{^{1}H} NMR measurements the signals of $[D_8]$THF ($\delta = 67.5$ ppm) and CD_2Cl_2 ($\delta = 53.8$ ppm) were used as a reference. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. ^{19}F NMR chemical shifts were referenced to C_6F_6 ($\delta = -163$ ppm). Screw-cap 5 mm NMR tubes were used in the NMR follow-up experiments. Abbreviations used in the description of NMR data are as follows: b, broad; s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet, v, virtual. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Germany.

Complex 3a: Method A: Mixing a solution of the PCN-based Rh-methyl chloride complex **2** (30 mg, 0.060 mmol) in THF (2 mL) with a solution of $AgBF_4$ (11.7 mg, 0.060 mmol) in THF resulted in the formation of complex **3a** and AgCl after 3 min. The solution of **3a** was separated from AgCl by filtration and the solvent was evaporated, to yield **3a** as a brown solid (31 mg; 95%).

Complex 3a: Method B: A solution of $[\{Rh(coe)_2Cl\}_2]$ (30 mg, 0.042 mmol) in THF (2 mL) was mixed with a solution of $AgBF_4$ (16.3 mg, 0.084 mmol) in THF at room temperature, resulting in the formation of the cationic rhodium precursor $[(coe)_2Rh(solv)_n]BF_4$ and an AgCl precipitate. The precipitate was removed by filtration and the filtrate containing the cationic rhodium monomer was filtered out and added to a solution of the PCN ligand **1** (30 mg, 0.083 mmol) in THF. The color changed to brown within 3 min and ^{31}P{^{1}H} NMR spectroscopy showed quantitative formation of **2** as a single product.

Characterization of 3a: ^{31}P{^{1}H} NMR ($[D_8]$THF): $\delta = 73.21$ ppm (d, $J_{Rh,P} = 160.2$ Hz); ^{1}H NMR ($[D_8]$THF): $\delta = 6.57$ (s, 1H; Ar), 3.77 (m, 1H; Ar-CH_2-N), 3.45 (m, 1H; Ar-CH_2-N), 2.99 (m, 1H; CH$_3$-CH_2-N), 2.81 (m, 1H; Ar-CH_2-P), 2.76 (m, 1H; Ar-CH_2-P), 2.67 (m, 1H; CH$_3$-CH_2-N), 2.48 (m, 1H; CH$_3$-CH_2-N), 2.22 (m, 1H; CH$_3$-CH_2-N), 2.16 (s, 3H; Ar-CH_3), 2.03 (s, 3H; Ar-CH_3), 1.75 (dd, $J_{Rh,H} = 2.9$ Hz, $J_{P,H} = 1.2$ Hz, doublet in ^{1}H{^{31}P} NMR, 3H; RhCH$_3$), 1.19 (d, $J_{P,H} = 13.5$ Hz, singlet in ^{1}H{^{31}P} NMR, 9H; (CH$_3$)$_3$C-P), 1.13 (d, $J_{P,H} = 13.4$ Hz, singlet in ^{1}H{^{31}P} NMR, 9H; (CH$_3$)$_3$C-P), 1.09 (t, $J_{H,H} = 7.2$ Hz, 3H; CH_3-CH$_2$-N), 0.81 ppm (t, $J_{H,H} = 7.2$ Hz, 3H; CH_3-CH$_2$-N); ^{13}C{^{1}H} NMR ($[D_8]$THF): $\delta = 171.12$ (dd, $J_{Rh,C} = 29.1$, $J_{PC,cis} = 3.6$ Hz; C_{ipso}, Rh–Ar), 145.25 (dd, $J_{P,C} = 11.3$, $J_{Rh,C} = 2.9$ Hz; Ar), 140.07 (s; Ar), 138.56 (s; Ar), 131.91 (dd, $J_{P,C} = 15.7$, $J_{Rh,C} = 1.8$ Hz; Ar), 130.62 (s; Ar), 61.65 (bs; Ar-CH_2-N), 48.91 (bs; CH$_3$-CH_2-N), 48.00 (bd, $J_{Rh,C} = 1.8$ Hz; CH$_3$-CH_2-N), 36.11 (d, $J_{P,C} = 19.33$ Hz; Ar-CH_2-P), 35.07 (d, $J_{P,C} = 2.4$ Hz; (CH$_3$)$_3$C-P), 34.84 (d, $J_{P,C} = 2.3$ Hz; (CH$_3$)$_3$C-P), 30.70 (d, $J_{P,C} = 3.4$ Hz; (CH$_3$)$_3$C-P), 28.86 (d, $J_{P,C} = 2.6$ Hz; (CH$_3$)$_3$C-P), 20.57 (s; CH$_3$-Ar), 19.43 (s; CH$_3$-Ar), 11.16 (s; CH$_3$-CH$_2$-N), 6.40 (s; CH$_3$-CH$_2$-N), 0.08 ppm (dd, $J_{Rh,C} = 35.1$ Hz, $J_{P,C} = 7.2$ Hz; Rh-CH$_3$). (Assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT). ^{19}F{^{1}H} NMR ($[D_8]$THF): $\delta = -164.40$ ppm (s; BF_4); elemental analysis (%): calcd: C 49.92, H 7.67; found: C 50.93, H 8.02.

Complex 3b: Compound **3b** was prepared similarly to **3a** using AgOTf instead of $AgBF_4$. In method A 15 mg AgOTf (0.061 mmol) was used, and in method B 20.6 mg AgOTf (0.042 mmol) was used. ^{31}P{^{1}H} NMR ($[D_8]$THF): $\delta = 72.53$ ppm (d, $J_{Rh,P} = 160.2$ Hz); ^{1}H NMR ($[D_8]$THF): $\delta = 6.61$ ppm (s, 1H; Ar), 3.73 (m, 1H; Ar-CH_2-N), 3.42 (m, 1H; Ar-CH_2-P), 3.33 (m, 1H; CH$_3$-CH_2-N), 3.05 (m, 1H; Ar-CH_2-N), 2.74 (m, 1H; Ar-CH_2-P), 2.70 (m, 1H; CH$_3$-CH_2-N), 2.55 (m, 1H; CH$_3$-CH_2-N), 2.41 (m, 1H; CH$_3$-CH_2-N), 2.10 (s, 3H; Ar-CH_3), 1.97 (s, 3H; Ar-CH_3), 1.67 (dd, $J_{Rh,H} = 2.2$, $J_{P,H} = 1.3$ Hz, doublet in ^{1}H{^{31}P} NMR, 3H; Rh-CH$_3$), 1.15 (d, $J_{P,H} = 13.4$ Hz, singlet in ^{1}H{^{31}P} NMR, 9H; (CH$_3$)$_3$C-P), 1.07 (d, $J_{P,H} = 13.5$ Hz, singlet in ^{1}H{^{31}P} NMR, 9H; (CH_3)$_3$C-P), 0.96 (t, $J_{H,H} = 7.5$ Hz, 3H; CH_3-CH$_2$-N), 0.75 ppm (t, $J_{H,H} = 7.2$ Hz, 3H; CH_3-CH$_2$-N); ^{13}C{^{1}H} NMR ($[D_8]$THF): $\delta = 156.15$ (dd, $J_{Rh,C} = 30.1$, $J_{P,C,cis} = 3.4$ Hz; C_{ipso}, Rh-Ar), 143.35 (dd, $J_{P,C} = 11.8$, $J_{Rh,C} = 3.2$ Hz; Ar), 141.81 (s; Ar), 141.33 (s; Ar), 129.81 (dd, $J_{P,C} = 16.2$, $J_{Rh,C} = 1.9$ Hz; Ar), 128.62 (s; Ar), 60.17 (d, $J_{P,C} = 1.5$ Hz; Ar-CH$_2$-N), 47.38 (bs; CH$_3$-CH_2-N), 46.71 (bs; CH$_3$-CH_2-N), 34.16 (d, $J_{P,C} = 21.0$ Hz; Ar-CH_2-P), 33.72 (d, $J_{P,C} = 2.4$ Hz; (CH$_3$)$_3$C-P), 33.58 (d, $J_{P,C} = 1.9$ Hz; (CH$_3$)$_3$C-P), 28.83 (d, $J_{P,C} = 3.3$ Hz; (CH$_3$)$_3$C-P), 26.86 (d, $J_{P,C} = 2.7$ Hz; (CH$_3$)$_3$C-P), 18.50 (s; CH$_3$-Ar), 17.41 (s; CH$_3$-Ar), 9.69 (s; CH$_3$-CH$_2$-N), 4.69 (d, $J_{P,C} = 2.2$ Hz; CH$_3$-CH$_2$-N), −3.13 ppm (dd, $J_{Rh,C} = 35.0$, $J_{P,C} = 7.5$ Hz; Rh-CH$_3$); ^{19}F{^{1}H} NMR ($[D_8]$THF): $\delta = -78.11$ ppm (s; SO_3CF_3); elemental analysis (%): calcd: C 44.88, H 6.34; found: C 45.17, H 7.02.

Complex 4: To a solution of complex **2** (30 mg, 0.06 mmol) in diethyl ether (3 mL) (or *tert*-butyl methyl ether) was added $AgBAr_f \cdot n\,Et_2O$ (58.3 mg, 0.06 mmol) in diethyl ether (3 mL). The mixture was stirred at room temperature for 30 min, after which the precipitated AgCl was filtered through celite. Removal of the solvent from the filtrate by evaporation left complex **4** (78.9 mg, 94%). When dry complex **4** was dissolved in CD_2Cl_2, compound **4′** was obtained. ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta = 74.10$ ppm (d, $J_{Rh,P} = 155.7$ Hz); ^{1}H NMR (CD_2Cl_2): $\delta = 7.72$ (bs, 8H; *o*-B(3,5-C$_6H_3$(CF$_3$)$_2$)$_4$), 7.57 (bs, 4H; *p*-B(3,5-C$_6H_3$(CF$_3$)$_2$)$_4$), 6.69 (s, 1H; Ar), 3.91 (m, 1H; Ar-CH$_2$-N), 3.46 (q, 4H; (CH$_3$-CH_2)$_2$O, free molecule), 3.20–2.91 (overlapping multiplets, 4H, CH$_3$-CH_2-N; 1H, Ar-CH_2-N; 2H, Ar-CH_2-P), 2.28 (s, 3H; Ar-CH_3), 2.19 (s, 3H; Ar-CH_3), 1.45 (dd, $J_{Rh,H} = 2.7$, $J_{P,H} = 1.3$ Hz, doublet in ^{1}H{^{31}P} NMR, 3H; Rh-CH$_3$), 1.30 (d, $J_{P,H} = 13.7$ Hz, singlet in ^{1}H{^{31}P} NMR, 9H; (CH$_3$)$_3$C-P), 1.27 (d, $J_{P,H} = 12.9$ Hz, singlet in ^{1}H{^{31}P} NMR, 9H; (CH$_3$)$_3$C-P), 1.20 (t, $J_{H,H} = 7.1$ Hz, 3H; CH_3-CH$_2$-N), 1.16 (t, $J_{H,H} = 7.0$ Hz, 6H; (CH_3-CH$_2$)$_2$O, free molecule), 1.15 ppm (t, $J_{H,H} = 7.3$ Hz, 3H; CH_3-CH$_2$-N); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 162.20$ (q, $J_{B,C} = 49.6$ Hz; *ipso*-B(Ar′$_4$)), 154.15 (m, C_{ipso}; Rh-Ar),144.82 (m; Ar), 142.53 (s; Ar), 135.20 (bs; *o*-B(*Ar*′$_4$)), 134.52 (s; Ar), 132.49 (s; Ar), 129.21 (bq, $^2J_{F,C} = 29.5$ Hz; *m*-B(Ar′$_4$)), 129.11 (s; Ar), 125.1 (q, $^1J_{F,C} = 272.1$ Hz; CF$_3$), 117.89 (m; *p*-B(*Ar*′$_4$)), 66.17 (s; (CH$_3$-CH$_2$)$_2$O, free molecule), 61.95 (bs; Ar-CH_2-N), 49.34 (bs; CH$_3$-CH_2-N), 49.00 (bs; CH$_3$-CH_2-N), 37.22 (d, $^1J_{P,C} = 19.1$ Hz; (CH$_3$)$_3$C-P), 35.88 (d, $^1J_{P,C} = 14.2$ Hz; (CH$_3$)$_3$C-P), 31.31 (d, $^2J_{P,C} = 1.3$ Hz; (CH$_3$)$_3$C-P), 29.19 (d, $J_{P,C} = 1.7$ Hz; (CH$_3$)$_3$C-P), 21.01 (s; CH$_3$-Ar), 19.99 (s; CH$_3$-Ar), 15.32 (s; (CH$_3$-CH$_2$)$_2$O, free molecule), 12.18 (s; CH$_3$-CH$_2$-N), 7.11 (s; CH$_3$-CH$_2$-N), −0.79 ppm (dd, $^1J_{Rh,C} = 37.3$ Hz, $J_{P,C} = 7.2$ Hz; Rh-CH$_3$). (Assignment of ^{13}C{^{1}H} NMR signals was confirmed by ^{13}C DEPT). ^{19}F{^{1}H} NMR (CD_2Cl_2): $\delta = -62.5$ ppm (s; CF$_3$); elemental analysis (%) for complex **4** obtained from a diethyl ether solution: calcd: C 50.54, H 4.35; found: C 50.62, H 4.54.

Complex 5: To a solution of **3a** (30 mg, 0.054 mmol) or **3b** (30 mg, 0.049 mmol) in fluorobenzene (3 mL) was added $NaBAr_f$ (48 mg, 0.054 mmol) or (43 mg, 0.049 mmol), respectively. The mixture was stirred for 3 h at room temperature. A color change from orange to deep green and precipitation of NaX (X = BF_4 for **3a** and OTf for **3b**) took place, and ^{31}P{^{1}H} NMR spectroscopy revealed quantitative formation of **5**. The precipitated NaX was separated by filtration through a cotton pad and the solvent was removed from the filtrate under vacuum. The resulting solid

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was washed with pentane and benzene and redissolved in dichloromethane. Evaporation of the solvent gave pure **5** as a green solid.
$^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 43.29$ ppm (d, $^1J_{P,Rh} = 116.45$ Hz); ^1H NMR (CD_2Cl_2): $\delta = 8.51$ (s, 1H; Ar-*H*), 7.62 (bs, 8H; *o*-B(3,5-$C_6H_3(CF_3)_2)_4$), 7.46 (bs, 4H; *p*-B(3,5-$C_6H_3(CF_3)_2)_4$), 4.67 (dd, 1H, $J_{P,H} = 7.2$, $J_{Rh,H} = 4.3$ Hz, doublet in $^1H\{^{31}P\}$ NMR; C=CH_2), 4.25 (d, 1H, $J_{Rh,H} = 4.0$ Hz; Ar-CH_2-N), 4.11 (dd, 1H, $J_{P,H} = 5.6$, $J_{Rh,H} = 3.1$ Hz, doublet in $^1H\{^{31}P\}$ NMR; C=CH_2), 3.47 (m, 1H; Ar-CH_2-P), 3.44 (d, 1H, $J_{Rh,H} = 4.5$ Hz; Ar-CH_2-N), 3.16–2.93 (overlapping multiplets, 4H, CH_3-CH_2-N; 1H, Ar-CH_2-P), 2.45 (s, 3H; Ar-CH_3), 2.43 (s, 3H; Ar-CH_3), 1.41 (d, $J_{P,H} = 14.7$ Hz, singlet in $^1H\{^{31}P\}$ NMR, 9H; (CH_3)$_3$C-P), 1.28 (t, $J_{H,H} = 7.2$ Hz, 3H; CH_3-CH_2-N), 1.22 (t, $J_{H,H} = 7.4$ Hz, 3H; CH_3-CH_2-N), 1.16 (d, $J_{P,H} = 13.2$ Hz, singlet in $^1H\{^{31}P\}$ NMR, 9H; (CH_3)$_3$C-P), −27.40 ppm (dd, $J_{Rh,H} = 62.5$, $J_{P,H} = 23.7$ Hz, 1H, doublet in $^1H\{^{31}P\}$ NMR; Rh-H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 162.12$ (q, $J_{B,C} = 49.8$ Hz; *ipso*-B(Ar′$_4$)), 152.39 (s; Ar), 147.34 (s; Ar), 144.82 (s; Ar), 146.39 (s; Ar), 142.53 (s; Ar), 140.65 (s; Ar), 139.36 (s; Ar), 135.20 (m; *o*-B(Ar′$_4$)), 129.20 (qq, $J_{F,C} = 29.5$, $J_{B,C} = 2.8$ Hz; *m*-B(Ar′$_4$)), 124.96 (q, $^1J_{F,C} = 272.3$ Hz; CF_3), 117.82 (septet, $J_{F,C} = 4.1$ Hz; *p*-B(Ar′$_4$)), 95.34 (dd, $J_{Rh,C} = 7.2$, $J_{P,C} = 3.6$ Hz; *C*=CH_2), 68.41 (bs; Ar-*C*H_2-N), 52.33 (bs; CH_3-*C*H_2-N), 50.77 (bs; CH_3-*C*H_2-N), 38.60 (dd, $J_{Rh,C} = 14.8$, $J_{P,C} = 1.3$ Hz; C=*C*H_2), 32.35 (d, $J_{P,C} = 5.6$ Hz; (CH_3)$_3$*C*-P), 32.09 (d, $^1J_{P,C} = 4.6$ Hz; (CH_3)$_3$*C*-P), 30.32 (d, $J_{P,C} = 2.7$ Hz; (CH_3)$_3$C-P), 29.37 (d, $J_{P,C} = 1.6$ Hz; (CH_3)$_3$C-P), 19.083 (s; *C*H_3-Ar), 18.55 (s; *C*H_3-Ar), 12.00 (s; *C*H_3-CH_2-N), 9.73 ppm (s; *C*H_3-CH_2-N). (Assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): $\delta = -62.8$ (s, CF_3).

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