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Preparation of 2-Alkylidene-Substituted 1,3,4,5-Tetramethylimidazolines and Their Reactivity Towards Rh^I Complexes and $B(C_6F_5)_3$

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In addition to the known 1,3,4,5-tetramethyl-2-methyleneimidazoline (**1a**), which exhibits a highly polarized exocyclic C–C bond, a series of novel 2-alkylidene-substituted 1,3,4,5-tetramethylimidazolines **1b–e** were synthesized and characterized. The molecular structures of **1b**, **1d**, and **1e** were determined by X-ray diffraction analysis and revealed an increase in the polarization of the exocyclic C–C bond with increasing steric demand of the 2-substituent. On the basis of their ylidic nature, **1a–e** show enhanced basicity and reactivity towards Lewis acidic centers. Treatment of **1a** and **1b** with $[\{RhCl(cod)\}_2]$ or $B(C_6F_5)_3$ afforded complexes of the type [(**L**)RhCl(cod)] (**4a**,**b**), [(**L**)RhCl$(CO)_2$] (**7a**,**b**) (**L** = **1a**,**b**) or classical Lewis acid/base adducts [(**1a**)$B(C_6F_5)_3$] (**8a**) and [(**1b**)$B(C_6F_5)_3$] (**8b**). In contrast, complexes [(**L**)RhCl(cod)] with **1c** and **1d** as ligands are not stable, and imidazolium dichlororhodate salts **6a** and **6b** were isolated instead. Rhodium–alkyl complexes **5a** and **5b** are assumed to be intermediates in this decomposition process, and **5a** was characterized by X-ray diffraction analysis. Furthermore, treatment of **1c** and **1d** with $B(C_6F_5)_3$ did not afford classical Lewis adducts, and instead imidazolium hydridoborate salts **9a** and **9b** are formed by hydride abstraction. Surprisingly, we found that **1e** does not react with $[\{RhCl(cod)\}_2]$ and forms an abnormal Lewis adduct **10** when treated with $B(C_6F_5)_3$.

Introduction

The introduction of a functional group X (X = CH_2,[1,2] SiR_2,[3] NH,[4] PH,[5] O,[6] S,[7] Se,[8,9] Te[2,8,10]) at the 2-position of N-heterocyclic carbenes (NHC) of the imidazolin-2-ylidene type affords compounds in which the ylidic resonance structure **B** makes a major contribution to the electronic structure (Figure 1). This is a result of the effective stabilization of the positive charge by the imidazolium ring.[4b,11–13] For example, when X = CH_2 the bonding can be described as a donor–acceptor interaction between an imidazolin-2-ylidene and a carbenoid fragment, with substantial π backbonding of the carbenoid moiety (see **A** in Figure 1).[14] Consequently, 2-alkylidene-substituted imidazolidines **C**[15–18] and benzimidazolines **D**[19,20] (Figure 2) contain highly polarized C–C bonds with remarkably nucleophilic terminal carbon atoms. The resulting enhanced electron density at the exocyclic α-carbon atoms is usually reflected by pronounced high-field shifts of their ^{13}C NMR spectroscopic resonances.[18,20] It was found that the ^{13}C NMR spectroscopic signals of the α-carbon atoms correlate with their π-electron density and therefore with their reactivity towards electrophiles, which was studied to some extent.[21–24] The introduction of substituents with an increasing steric demand at the α-carbon atom results in a shift of the corresponding ^{13}C NMR spectroscopic resonances to lower field relative to 2-methylene derivatives. This effect was attributed to an increasingly pyramidal geometry at the ring nitrogen atoms because of steric interaction between the N and α-C substituents.[20]

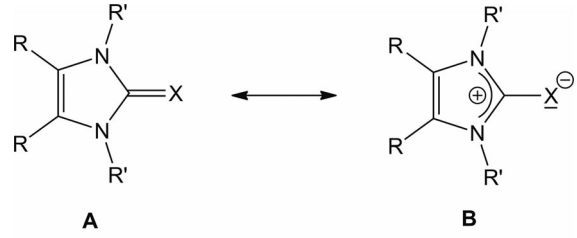

Figure 1. Mesomeric structures **A** and **B** for imidazolin-2-ylidenes bearing an exocyclic moiety X in the 2-position.

Usually, 2-alkylidene-substituted compounds that bear *N*-alkyl groups are obtained by deprotonation of the corresponding 2-alkylimidazolium salts with strong bases such as NaH and KH.[18,20,25] Recently, Wangelin et al. presented a simple protocol for the synthesis of *N*-aryl- and *N*-alkyl-substituted 2-alkylideneimidazolines from imidazolium halides and alkyl halides in the presence of potassium *tert*-butoxide (2 equiv.) as base.[26,27] The use of unsaturated

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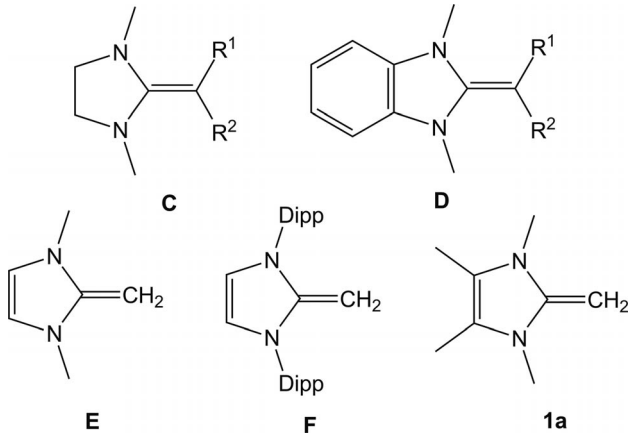


Figure 2. Examples of 2-alkylidene-substituted imidazolidines **C**, benzimidazolines **D**, and imidazolines **E**, **F**, and **1a**.

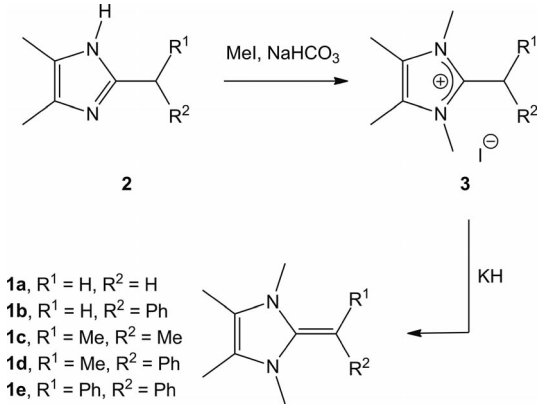
alkyl halides leads to the introduction of conjugated 2-substituents (e.g., alkene, diene, enyne, and styryl moieties), in which the α- and γ-positions are highly nucleophilic.[26] In a synthetic and theoretical study, the reactivity towards benzyl bromides of NHCs with different basicity, nucleophilicity, and steric properties was investigated. In general, derivatives with *N*-alkyl groups, especially bulky *tert*-butyl groups, are less stable than *N*-aryl-(2,6-diisopropylphenyl)-substituted 2-alkylideneimidazolines.[27] Furthermore, Mayr et al. were able to demonstrate experimentally and theoretically that 2-alkylidene-substituted derivatives obtained from unsaturated NHCs are significantly more nucleophilic than those derived from saturated NHCs.[28] It should also be noted that these compounds can be regarded as the deoxy counterparts of Breslow-type intermediates,[27] which have only recently been isolated by Berkessel and coworkers.[29]

Kuhn et al. have investigated the reactivity of **1a** towards a wide range of compounds of main-group elements such as boranes, electrophilic carbon, silicon, and tin substrates, and also with respect to adduct formation with iodine.[25,30] Recently, Rivard et al. demonstrated that the *N*-aryl-substituted compound **F** was sufficiently Lewis basic to stabilize main-group hydrides in unusually low oxidation states.[31] So far, only a few examples of organometallic complexes that bear 2-alkylidene imidazolines as ligands are known. In 1979, Kaska et al. investigated the complexation of 1,3-dimethyl-2-methyleneimidazolidine **C** ($R^1 = R^2 = H$) to Zeise's dimer [{Pt(C_2H_4)Cl_2}$_2$]. The release of ethylene resulted in the formation of a mixture of complexes in which the ligand is bound in a η^1 and η^2 fashion.[16] Structural evidence for the end-on coordination mode of **1a** was established by Schumann et al. and Kuhn et al. In complexes [(**1a**)M(CO)$_5$] (M = Mo, W),[32] [(**1a**)Ln{N(SiMe$_3$)$_2$}$_3$] (Ln = La, Nd), and [(**1a**)Y(C_8H_8)Cp*] (Cp* = pentamethylcyclopentadiene),[33] ligand **1a** exclusively shows coordination of the α-carbon atom to the metal atom in solution and in the solid state. Binding through the α-carbon atom was also found more recently in the 16-electron cycloheptatrienyl zirconium allyl complex [(η^7-C_7H_7)Zr{C_3H_3(tms)$_2$}(**1a**)] (tms = trimethylsilyl).[34] Fürstner et al. also proved the terminal coordination mode for ligand **E** by isolating complexes [(PPh_3)Au(**E**)]SbF_6 and [(**E**)RhCl(CO)$_2$].[35] The IR data of complexes [(**1a**)M(CO)$_5$] (M = Mo, W) and [(**E**)RhCl(CO)$_2$] revealed that 2-methylene-substituted 1,3-dimethyl- and 1,3,4,5-tetramethylimidazolines outperform standard N-heterocyclic carbenes in terms of their donor capacity.[35] Therefore, we were interested in the synthesis and characterization of derivatives based on the known 1,3,4,5-tetramethyl-2-methyleneimidazoline (**1a**),[25] in which simple alkyl and aryl substituents are introduced at the exocyclic α-carbon atom. In particular, we wished to explore the reactivity of the resulting sterically encumbered and highly nucleophilic compounds as ligands and potential carbon mimics of phosphane ligands in transition-metal complexes.

Results and Discussion

Preparation and Characterization of 2-Alkylidene-1,3,4,5-tetramethylimidazolines

The 2-methylene derivative **1a** was synthesized according to the procedure published by Kuhn et al. by deprotonation of 1,2,3,4,5-pentamethylimidazolium iodide (**3a**) with KH (Scheme 1).[25] For the synthesis of **1b**–**e**, the known iodides **3b** and **3c** were prepared by methylation of the corresponding imidazoles **2**, and this procedure was also used to obtain the iodides **3d** and **3e** in high yields (85–94%).[36] Deprotonation of **3b**–**e** with KH was accomplished in solutions in diethyl ether or THF, and, after removal of all insoluble materials by filtration through Celite, compounds **1a**–**e** could be obtained as colorless (**1a** and **1c**) or yellow to orange (**1b**, **1d**, and **1e**) crystalline solids, which could be stored at room temperature under an inert atmosphere for several months. However, a colorless sample of compound **1c** turned into a yellow oily material within two days at room temperature and was therefore stored at –30 °C.



Scheme 1. Synthesis of 2-alkylidene-1,3,4,5-tetramethylimidazolines (**1**).

Compounds **1a**–**e** are soluble in hexane and pentane and show excellent solubility in diethyl ether, toluene, and THF. In the chlorinated solvents dichloromethane and chloroform, immediate decomposition is observed, as indicated by

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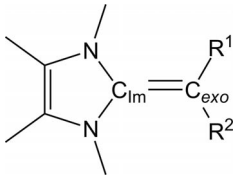
a color change of the solutions from colorless or yellow to brown.[18] NMR spectra of **1a**–**e** were recorded in C_6D_6, and the ^{13}C NMR spectroscopic chemical shifts of the exocyclic C–C bonds are summarized in Table 1. As observed for the imidazolidine and benzimidazoline derivatives **C** and **D**, an increasing steric demand of the substituents results in a low-field shift of the ^{13}C NMR spectroscopic resonances for the exocyclic α-carbon atoms.[18,20] Accordingly, the introduction of a phenyl group in the α position induces a low-field shift of $\delta \approx 25$ ppm in **1b** relative to **1a** (δ = 40.2 ppm).[37a] The substitution of the hydrogen atom in **1b** by a methyl group in **1d** has no further influence on the chemical shift of the α-carbon atom. Not only the steric but also the electronic properties of the exocyclic substituents might have an impact on the chemical shift of the α-carbon atom, which is correlated with its electron density.[20] The symmetrically substituted derivatives **1c** and **1e** exhibit the largest ^{13}C NMR spectroscopic shifts of the α-carbon atoms to lower field (δ = 71.4 and 75.6 ppm). The substitution pattern in the exocyclic positions has hardly any effect on the chemical shifts of the C2-ring carbon atoms. For unsymmetrically substituted 2-alkylideneimidazolidines **C** and benzimidazolines **D** ($R^1 \neq R^2$), different chemical shifts for the diastereotopic *N*-methyl groups were observed, which implies that there is hindered rotation around the exocyclic C–C bond at room temperature on the NMR spectroscopic timescale.[18] In contrast, **1b** and **1d** exhibit a single resonance for both *N*-methyl groups in the ^1H NMR spectra at δ = 2.62 and 2.68 ppm (in C_6D_6), respectively. Therefore, a variable-temperature (VT) ^1H NMR spectroscopic study was performed for **1d**, as a typical representative of compounds **1**. The spectra were recorded in [D_8]-toluene and display the broadening and separation of the initial singlet at δ = 2.69 ppm for the *N*-methyl groups into two singlets below a coalescence temperature of –78 °C (Figure 3). The rotational barrier was calculated to be approximately 9.5 kcal mol^{-1} (39.4 kJ mol^{-1}).[38] In contrast, resolution of the 4,5-methyl resonances was not observed down to –96 °C.

Table 1. ^{13}C NMR spectroscopic data of the exocyclic C_{Im}–C_{exo} bonds in **1a**–**e**.[a]



	C_{Im}	C_{exo}
1a[37]	153.6	40.2
1b	150.4	65.4
1c	153.5	71.4
1d	153.7	65.2
1e	152.0	75.6

[a] Recorded in C_6D_6.

To further investigate the structural impact of the substituents in the exocyclic α position, we tried to obtain single crystals for X-ray diffraction analysis. Compounds **1b**, **1d**, and **1e** crystallize from saturated solutions in diethyl ether (**1b**), pentane (**1d**), or toluene (**1e**) at –30 °C. Colorless prisms of **1c** were also obtained from pentane solutions at –30 °C, but the crystals liquefied rapidly when we tried to isolate them for X-ray diffraction analysis. The molecular structure of **1b** (Figure 4, top) reveals the polarized character of the exocyclic C–C bond with a C1–C8 bond length of 1.3833(15) Å, which is 0.02 Å longer than that reported for **1a**.[37] The methyl carbon C7 bound to N2 lies 0.53 Å out of the imidazole plane (including the exocyclic C8 atom) and points away from the phenyl moiety (see also Table 2). This steric congestion is also reflected by the interplanar angle of 40.2° between the five- and six-membered rings and by the torsion angle N2–C1–C8–C9 of 25.73(19)°.

In **1d**, the C1–C8 bond is even longer at 1.3990(11) Å, and both *N*-methyl groups are displaced to opposite sides of the imidazole plane by 0.47 (C6) and 0.28 Å (C7). This results in torsion angles of 33.58(13)° (N1–C1–C8–C10) and 32.31(12)° (N2–C1–C8–C9) and an angle of 45.9° between the planes of the five- and six-membered rings. At 1.4078(13) Å, compound **1e** exhibits the longest exocyclic C1–C8 bond in this series. An even longer C–C bond was reported for 2-cyclopentadienylidene-1,3,4,5-tetramethylimidazole (1.430 Å), in which the negative charge is additionally stabilized by the cyclopentadienyl (Cp) moiety,

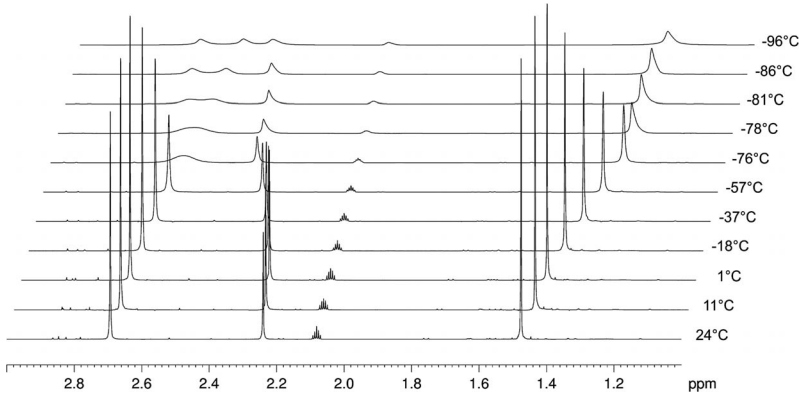


Figure 3. Variable-temperature ^1H NMR spectrum of **1d** in [D_8]toluene (signal for the residual hydrogen atoms at δ = 2.08 ppm).

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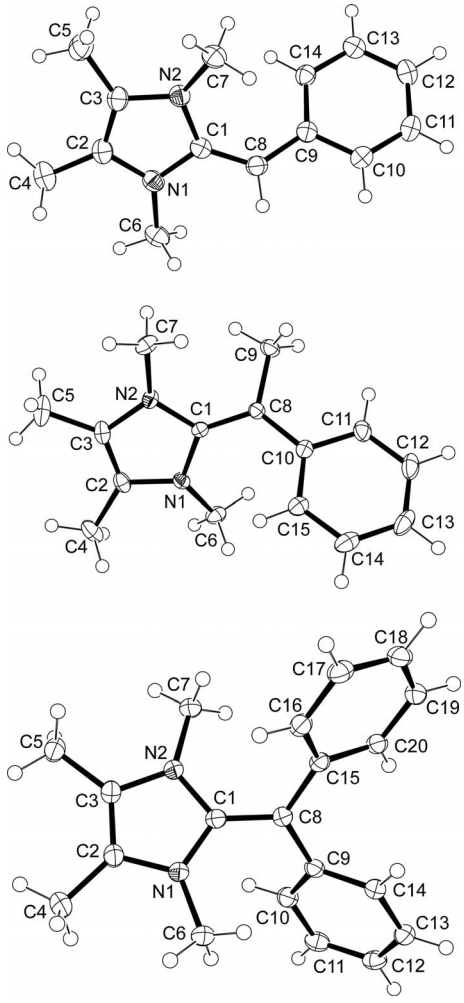
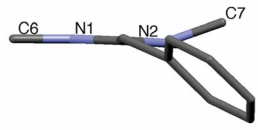
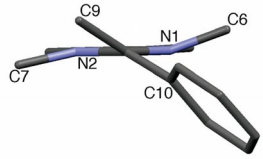
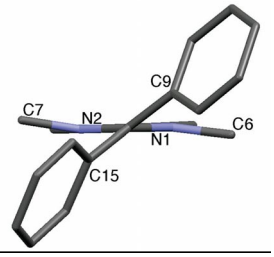


Figure 4. ORTEP drawings of **1b** (top), **1d** (center), and **1e** (bottom) with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [°] for **1b**: N1–C1 1.3750(14), N2–C1 1.3830(14), C1–C8 1.3833(15), C8–C9 1.4413(16); C1–C8–C9 129.06(10), N1–C1–N2 105.45(9), N2–C1–C8–C9 of 25.73(19), C6–N1–C1–C8 5.45(16), C7–N2–C1–C8 23.11(17). For **1d**: N1–C1 1.3813(10), N2–C1 1.3789(10), C1–C8 1.3990(11), C8–C10 1.4513(11), C8–C9 1.5137; C1–C8–C10 123.01(7), C1–C8–C9 119.16(7), C10–C8–C9 117.83(7), N2–C1–N1 104.78(7), N1–C1–C8–C10 33.58(13), N2–C1–C8–C9 32.31(12), C7–N2–C1–C8 14.89(13), C6–N1–C1–C8 21.13(13). For **1e**: N1–C1 1.3765(12), N2–C1 1.3739(12), C1–C8 1.4078(13), C8–C9 1.4707(12), C8–C15 1.4658(13); C1–C8–C9 119.16(8), C1–C8–C15 120.82(8), N2–C1–N1 104.72(8), N2–C1–C8–C15 37.89(15), N1–C1–C8–C9 36.23(14), C7–N2–C1–C8 10.67(15), C6–N1–C1–C8 10.42(16).

thereby affording a highly ylidic fulvalene.[39] The displacement of the *N*-methyl groups from the imidazole plane by 0.21 (C6) and 0.25 (C7) Å is less pronounced in **1e** than in **1b** and **1d**; however, the alkylidene moiety in **1e** exhibits the greatest deviation from coplanar alignment with the imidazole plane as indicated by torsion angles of 36.23(14) (N1–C1–C8–C9) and 37.89(15)° (N2–C1–C8–C15). The three aromatic rings in **1e** are orientated in a propeller-like fashion with angles of 61.3 and 60.5° between the imidazole and phenyl rings.

Table 2. Bond lengths of the exocyclic C1–C8 bonds, angle sums of the ring N atoms, and capped-stick models of **1a**–**e**.

	C1–C8 [Å]	Angle sums at N1 and N2 [°]	Capped-stick depictions
1b	1.383	359.9 354.1	
1d	1.399	355.9 358.4	
1e	1.407	359.4 358.8	

As further illustrated in Table 2, an increasing steric demand of the substituents at the exocyclic α-carbon atoms causes the *N*-methyl groups to deviate from the imidazole plane and therefore force the nitrogen atoms into a more pyramidalized geometry. In addition, the substituents in the 2-position are increasingly rotated out of the imidazole ring plane in the order **1a** > **1b** > **1c** > **1d**, which is associated with an increase in the C1–C8 bond lengths.

Rhodium(I) Complexes of 2-Alkylidene-1,3,4,5-tetramethylimidazolines

To investigate the reactivity of 2-alkylidene-1,3,4,5-tetramethylimidazolines as potential ligands towards transition metals, we chose to treat **1a**–**e** with [{RhCl(cod)}$_2$] (cod = 1,5-cyclooctadiene) to obtain complexes of the type [(**1**)RhCl(cod)] (**4**) (Scheme 2). Complexes **4a** and **4b** immediately precipitate from hexane/toluene mixtures and can be isolated by filtration as yellow solids in very good yields (90–98%). In contrast, the reaction of **1c** with [{RhCl(cod)}$_2$] in toluene/hexane leads after 30 min to a color change of the solution from yellow to brown, and precipitation of dark brown materials was observed. In further experiments, therefore, the solvent was removed after 20 min, and the residue was washed with pentane to yield complex **4c** as a light yellow solid in moderate yield (64%).

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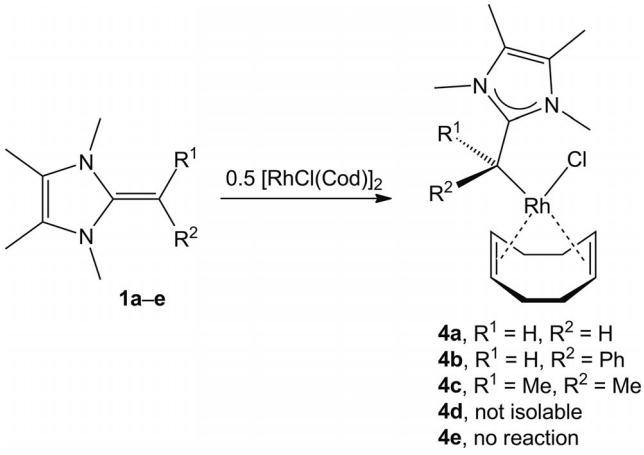

Scheme 2. Preparation of complexes [(**1**)RhCl(cod)] (**4**).

Complexes **4a** and **4c** are insoluble in hexane, but dissolve sufficiently in toluene, whereas **4b** is only soluble in more polar solvents such as THF, acetone, or dichloromethane. Therefore, NMR spectra were recorded in [D_8]-THF, and they show the expected shift of the resonances for the exocyclic α-carbon atoms to higher field (Table 3). The coupling constants of the coordinated α-carbon atoms are significantly smaller (21.8–23.9 Hz) than $C_{carbene}$–Rh coupling constants observed for [(NHC)RhCl(cod)] complexes.[40–45]

Table 3. ^{13}C NMR spectroscopic resonances [ppm] and coupling constants J [Hz] of C_{exo}, C_{Im}, and *trans*-coordinated CH_{cod} carbon atoms in complexes **4a**–**c**.[a]

	Rh(C_{exo}–C_{Im}) [$^1J_{C,Rh}$]	Rh(C_{exo}–C_{Im})	*trans*-CH_{cod} [$^1J_{C,Rh}$]
4a	19.8 [21.8]	163.1	87.0 [8.5]
4b	33.2 [21.8]	160.1	85.6, 85.8 [8.8]
4c	25.9 [23.9]	164.9	87.1 [8.1]

[a] Recorded in [D_8]THF.

Crystals of complexes **4a** and **4b** suitable for X-ray diffraction analysis could be obtained from saturated solutions in THF at –30 °C. The molecular structures are shown in Figure 5 and confirm binding of the ligands **1a** and **1b** through the exocyclic α-carbon atoms to the metal atom, which is coordinated in a distorted square-planar fashion. Relative to the free ligands **1a** and **1b**, the exocyclic C1–C8 bonds are elongated by 0.08 Å in both **4a** and **4b**. At the same time, the N1–C1 and N2–C1 bonds are 0.03 Å shorter in the complexes than in the free ligands, thus indicating a higher degree of charge separation and imidazolium character of the metal-bound 2-alkylideneimidazolines. The sterically more demanding ligand **1b** generates a longer Rh–C8 bond in complex **4b** [2.163(2) Å] than in **4a** [2.150(2) Å]. As expected, complex **4b** exhibits a center of chirality at C8.

As mentioned above, complex **4c** is not indefinitely stable in solution, as indicated by a color change from yellow to dark brown and by precipitation of insoluble materials on standing. Since coordination of **1c** through the α-carbon atom to Rh^I was unambiguously confirmed by ^1H and ^{13}C

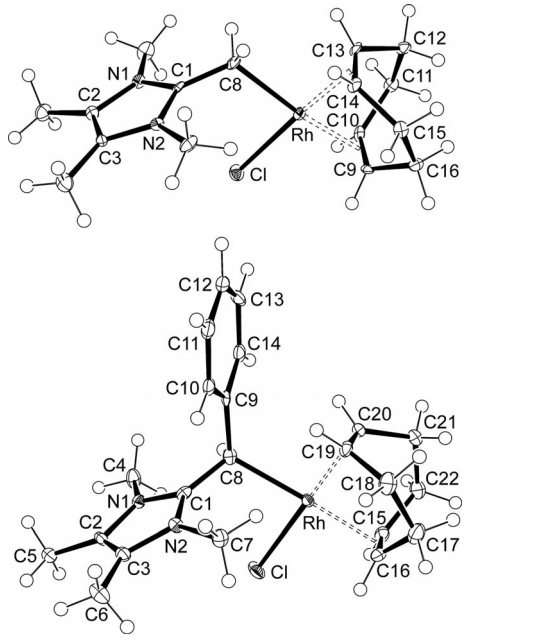

Figure 5. ORTEP drawings of **4a** and **4b** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [°] for **4a**: C1–C8 1.438(4), N1–C1 1.340(3), N2–C1 1.342(3), Rh–C8 2.150(2), Rh–C9 2.184(3), Rh–C10 2.158(3), Rh–C13 2.101(3), Rh–C14 2.098(3); C1–C8–Rh 116.91(19), C8–Rh–Cl 92.21(8), C13–Rh–C8 88.53(11), C14–Rh–C8 89.31(12). For **4b**: C1–C8 1.464(3), N1–C1 1.356(3), N2–C1 1.345(2), Rh–C8 2.163(2), C8–C9 1.511(3), Rh–C15 2.169(2), Rh–C16 2.171(2), Rh–C19 2.1002(19), Rh–C20 2.099(2); C1–C8–Rh 110.78(14), C8–Rh–Cl 85.13(6), C8–Rh–C19 93.09(8), C8–Rh–C20 96.12(8).

NMR spectroscopy (see above), we also tried to crystallize complex **4c** to determine its X-ray crystal structure. Therefore, we prepared saturated solutions of **4c** in toluene/THF mixtures, which were immediately stored at –30 °C. The yellow solutions turned dark brown within a few hours. Nevertheless, after two weeks, we were able to separate a few yellow needles, which were suitable for X-ray diffraction analysis. Surprisingly, the resulting molecular structure indicated the formation of the rhodium(I)–alkyl complex **5a** (Figure 6), which contains a zwitterionic imidazoliumalkyl ligand with an sp^3-hybridized C8 carbon atom and an exocyclic C1–C8 single bond of 1.501(4) Å. Coordination to rhodium occurs through the β-carbon atom C9, with a Rh–C9 bond length 2.083(3) Å that is significantly shorter than the Rh–C8 distances established for **4a** and **4b**. We assume that **5a** was derived from **4c** by a 1,2-hydrogen shift, which is likely to proceed through a rhodium hydride intermediate **Int**, which involves β-hydride elimination and olefin reinsertion (Scheme 3).[46,47] Another attempt to crystallize complex **4c** from a solution in THF at –30 °C yielded after about two months − together with insoluble dark material − a few pale yellow needles that were suitable for X-ray diffraction analysis. Crystal structure determination revealed the formation of **6a** as one of the decomposition products, which contains a 2-isopropylimidazolium cation and [$RhCl_2$(cod)]$^-$ anion (Scheme 3).[48,49]

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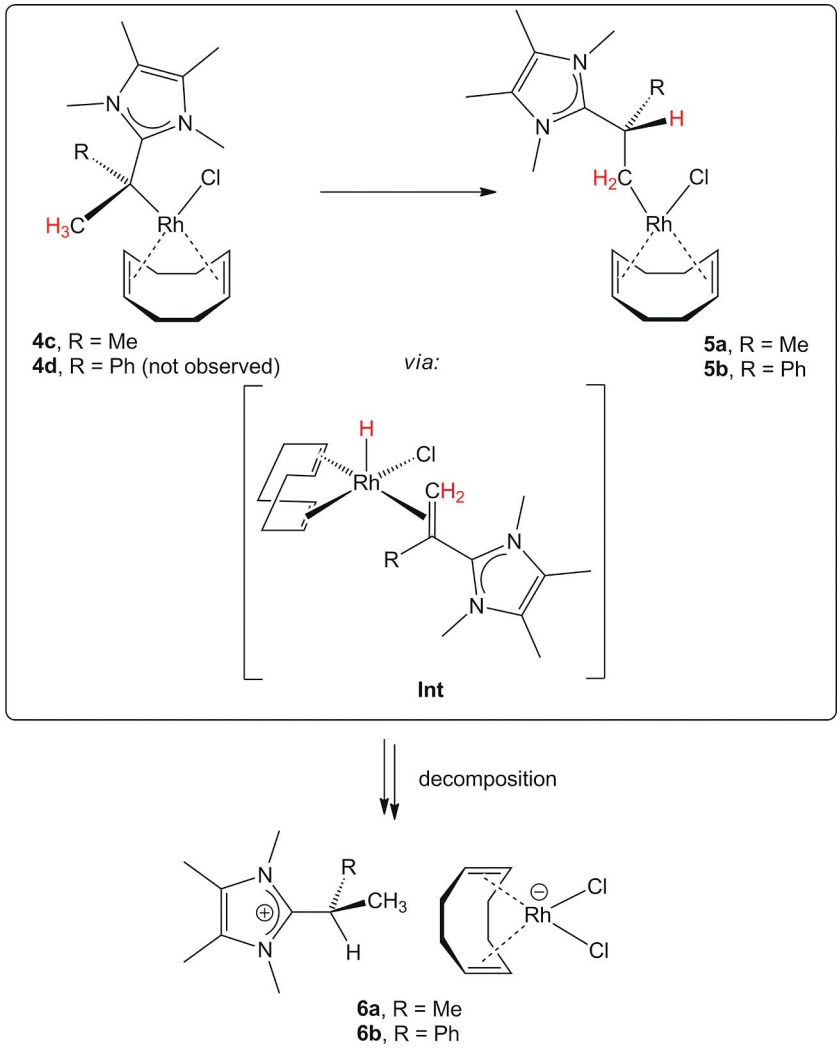

Scheme 3. Decomposition of complexes **4c** and **4d**.

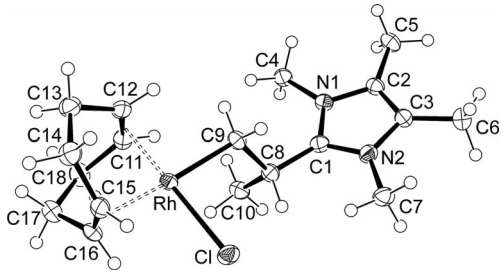

Figure 6. ORTEP drawing of **5a** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Rh–C9 2.083(3), Rh–C11 2.084(3), Rh–C12 2.102(3), Rh–C15 2.188(3), Rh–C16 2.209(3), C1–C8 1.501(4), N1–C1 1.352(4), N2–C1 1.340(4); C8–C9–Rh 114.59(19), C1–C8–C9 110.4(2).

The reaction of [{RhCl(cod)}$_2$] with **1d** in a hexane/toluene mixture led to precipitation of a light yellow solid within a couple of minutes, which was isolated by filtration. The elemental analysis suggested the presence of a complex with the chemical composition of complex **4d**. The compound is insoluble in C_6D_6 and only poorly soluble in [D_8]-THF. In the chlorinated solvents $CDCl_3$ and CD_2Cl_2, rapid decomposition was observed, indicated by a color change from yellow to brown. We repeated the reaction several times and tried to analyze the resulting product by NMR spectroscopy in [D_8]THF. Only the starting materials were present in solution, except for one measurement, in which we identified, among others, compound **5b**.[50] The ^{13}C NMR spectrum shows a doublet at δ = 42.6 ppm, which can be assigned to a rhodium-bound CH_2 group, with the coupling constant of $^1J_{C,Rh}$ = 30.7 Hz falling in the expected range for a Rh–CH_2 moiety.[46a] Furthermore, the spectrum exhibits four resonances for the *C*H$_2$ groups of the cod ligand at δ = 30.1, 30.6, 33.1, and 33.7 ppm and two sets of two doublets for the *cis*- (67.4 and 67.6 ppm, $^1J_{C,Rh}$ = 15.0 Hz) and *trans*-coordinated (89.4 and 90.0 ppm, $^1J_{C,Rh}$ = 7.0 Hz) *C*H groups, respectively, which indicate the presence of an asymmetric, chiral complex. Unfortunately, all attempts to reproduce the spectrum or isolate complex **5b** have failed so far. In general, rhodium–alkyl complexes, which are assumed to be intermediates in the migratory insertion process in an olefin hydride complex, are high-energy species.[47] We prepared a solution of

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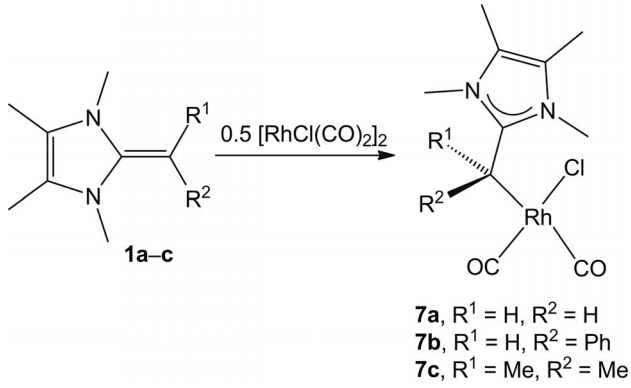
Table 4. ^{13}C NMR spectroscopic resonances [ppm] and coupling constants J [Hz] of the exocyclic α-carbon atoms and *trans*-coordinated CO ligands in complexes **7a**–**c**. Wavenumbers [cm^{-1}] are based on the asymmetric and symmetric stretching frequencies of the CO ligands.

	Rh(C_{exo}–C_{Im}) [$^1J_{C,Rh}$]	*trans*-*CO* [$^1J_{C,Rh}$]	ν(CO)[a]	$\nu(CO)_{av.}$
7a	10.0 [17.1][b]	184.7 [56.5][b]	1969, 2044	2007
7b	33.6 [18.9][c]	185.8 [56.8][c]	1968, 2036	2002
7c	31.7 [20.2][c]	186.8 [54.2][c]	–	–
[RhCl(CO)$_2$(**E**)][34]	–	–	1966, 2040	2003

[a] ATR method. [b] Recorded in CD_2Cl_2. [d] Recorded in [D_8]THF.

1d and [{RhCl(cod)}$_2$] in THF and, after separation of insoluble materials, the yellow solution was cooled to –30 °C. After a couple of days, a color change to brown and precipitation of a dark solid was observed. After several weeks, single crystals in the form of yellow needles were obtained, which were shown by X-ray diffraction analysis to consist of the imidazolium dichlororhodate salt **6b**.[48,49] When **1e** was treated with [{RhCl(cod)}$_2$], we did not observe any coordination of the ligand to metal center. Even after two days, only the starting materials could be identified in solution by NMR spectroscopy.

For the syntheses of the corresponding rhodium–carbonyl complexes **7**, we treated ligands **1a**–**c** with [{RhCl(CO)$_2$}$_2$] in hexane/toluene mixtures (Scheme 4). The addition of **1a** to a solution of [{RhCl(CO)$_2$}$_2$] resulted in precipitation of a dark brown solid. After removal of the solvent, extraction of the residue with THF, and drying under vacuum, the remaining solid was washed with diethyl ether to afford complex **7a** as a yellow-orange solid in low yield (27%). Similarly, large amounts of dark brown and black materials were immediately produced during the reaction of **1c** with [{RhCl(CO)$_2$}$_2$], and we were not able to isolate a pure sample of complex **7c**. Accordingly, we mixed both starting materials in an NMR tube under an inert atmosphere in [D_8]THF and immediately recorded ^1H and ^{13}C NMR spectra, thereby allowing us to characterize complex **7c**. In contrast, when **1b** was added to [{RhCl(CO)$_2$}$_2$], complex **7b** precipitated from the reaction mixture as a yellow solid and could be isolated by filtration in 51% yield. As observed for complexes **4a**–**c**, the ^{13}C NMR spectra of **7a**–**c** display the signals of the exocyclic α-carbon atoms at higher field than the free ligands **1a**–**c** (Table 4). The resonances appear as doublets with $^1J_{C,Rh}$ coupling constants of 17.1–12.2 Hz, which are slightly smaller than those found for **4a**–**c**. The carbonyl resonances for the *trans*-coordinated CO ligands exhibit $^1J_{C,Rh}$ coupling constants (54.2–56.8 Hz) that fall in the range observed for [(NHC)RhCl(CO)$_2$] complexes.[41,42,51,52] The strong donor capacity of ligand **1a** in complexes of the type [(**1a**)M(CO)$_5$] (M = Mo, W) has already been reported by Kuhn et al.,[32] and Fürstner and co-workers prepared a rhodium–carbonyl complex of 2-methylene-1,3-dimethylimidazoline (**E**) to demonstrate the high basicity of such ligands.[35] Unfortunately, we were not able to obtain IR data of complex **7c** because of its instability. Table 3 shows the IR data of **7a** and **7b** in comparison to [RhCl(CO)$_2$(**E**)] and reveals that **1a** is a slightly weaker donor ligand than **1b** and **E**. In general, complexes of the type [(NHC)RhCl(CO)$_2$] exhibit larger IR stretching frequencies of 2088–2069 and 2002–1988 cm^{-1}.[40,52,53]



Scheme 4. Preparation of complexes [(**1**)RhCl(CO)$_2$] (**7**).

Reactivity of 2-Alkylidene-1,3,4,5-tetramethylimidazolines towards $B(C_6F_5)_3$

The reactivity of phosphorus ylides $Ph_3P{=}CH_2$ and $Ph_3P{=}CHPh$ towards the Lewis acid $B(C_6F_5)_3$ was previously studied by Erker et al., but afforded a 1:1 adduct only from the reaction of the borane with methylene triphenylphosphorane. In contrast, a cascade of competing reaction pathways was detected for the benzylidene triphenylphosphorane, and the classical adduct formation was only observed at lower temperatures. The thermodynamic product of this combination was formed by the attack of the phosphorus ylide at the *para* position of one C_6F_5 unit, which was followed by C–F activation and fluoride migration to boron.[54]

It was demonstrated by Kuhn et al. that **1a** forms 1:1 adducts with BH_3 and BF_3.[25] Therefore, we were not surprised to isolate adduct **8a** by the reaction of **1a** and $B(C_6F_5)_3$ in hexane as a white solid in good yield (76%; Scheme 5). The addition of an orange-colored solution of **1b** to a colorless solution of $B(C_6F_5)_3$ resulted in the immediate precipitation of **8b** as an off-white solid, which was collected by filtration in 88% yield. The resonance for the methylene protons in **8a** is observed at δ = 3.16 ppm as a broad quartet ($^2J_{H,B}$ = 5.9 Hz, in CD_2Cl_2), which is shifted to lower field than **1a** and the adducts [(**1a**)BH_3] (δ = 1.87 ppm in $CDCl_3$) and [(**1a**)BF_3] (δ = 1.90 ppm in

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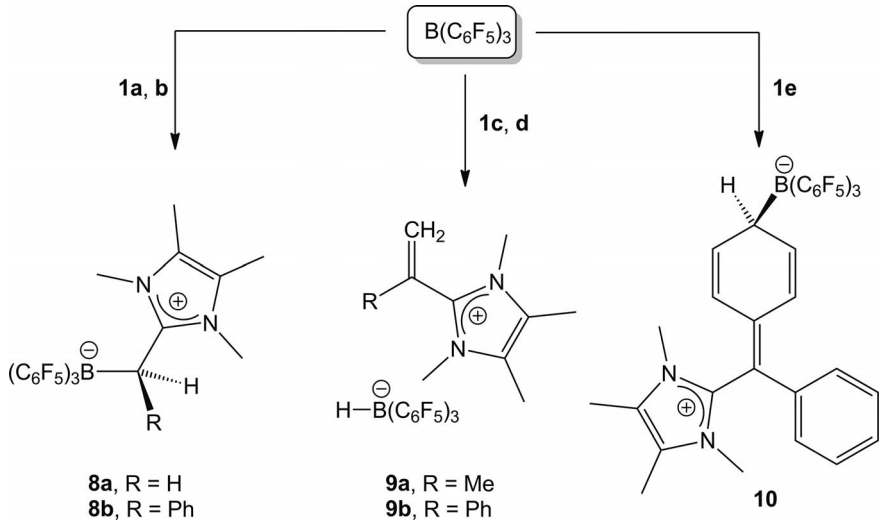

Scheme 5. Reactivity of **1a**–**e** with $B(C_6F_5)_3$.

CD_2Cl_2).[25] The quartet for the benzylidene proton in **8b** is found at δ = 5.84 ppm ($^2J_{H,B}$ = 6.4 Hz, in [D$_6$]acetone). The ^{13}C NMR spectroscopic signals for the methylene and benzylidene carbon atoms in **8a** and **8b** also appear as quartets ($^1J_{C,B}$ = 39.0 and 38.0 Hz) and are shifted to higher field than **1a** and **1b**. The methyl groups at the imidazole ring are diastereotopic in **8b** and result in two sets of two singlets each in the ^{1}H and ^{13}C NMR spectra. Surprisingly, the resonance of one of the *N*-methyl groups is significantly shifted to higher field (δ = 2.17 ppm versus 3.76 ppm).

An explanation for the unusual high-field shift of one *N*-methyl group can be found in the molecular structure of **8b**, which crystallizes as a racemic mixture, of which the *R* enantiomer is shown in Figure 7 (bottom). The carbon atom C7 is located within the shielding region of the π system of the C_6H_5 substituent, with the smallest distance of 2.970 Å between C7 and C9. The observation of two distinctly different *N*-CH_3 NMR spectroscopic resonances indicates hindered rotation around the C1–C8 bonds [1.4997(19) Å] in solution at room temperature on the NMR spectroscopic timescale; likewise, hindered rotation around the B–C8 bond [1.7084(19) Å] is evidenced by significant broadening of the three signals in the ^{19}F NMR spectrum. Both bonds are significantly longer than in **8a** with bond lengths of B–C8 1.6947(19) Å and C1–C8 1.4788(17) Å (Figure 7, top).

When solutions of **1c** or **1d** were added to a solution of $B(C_6F_5)_3$ in hexane or toluene, white or off-white solids were obtained after workup. The ^{13}C NMR spectroscopic data reveal the disappearance of the resonances for the exocyclic α-carbon atoms and the appearance of a CH_2 group in the olefinic region at δ = 129.3 and 132.7 ppm. Likewise, the ^{1}H NMR spectra exhibit two multiplets in the range δ = 5.70–6.76 ppm together with a very broad quartet each between δ = 3.41 and 4.12 ppm with a $^1J_{H,B}$ coupling constant of 92.0 Hz. The corresponding doublet is found at δ = –24.1 ppm in the ^{11}B NMR spectrum, thus confirming the presence of an $[HB(C_5F_5)_3]^-$ ion and the formation of

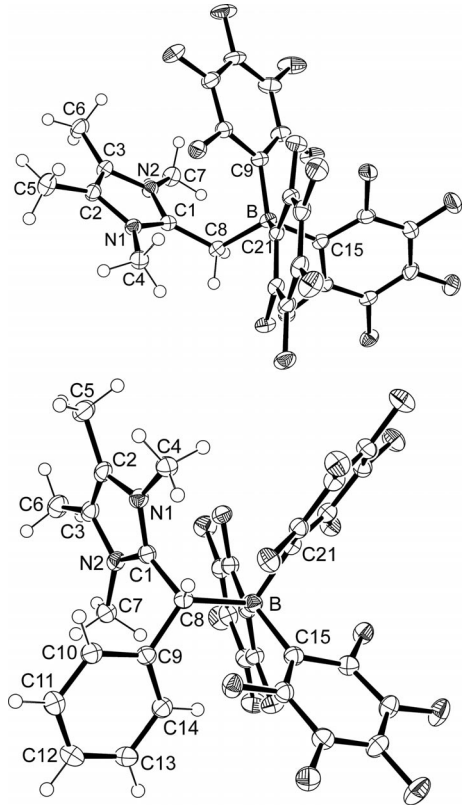

Figure 7. ORTEP drawings of **8a** (top) and **8b** (bottom) with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [°] for **8a**: B–C8 1.6947(19), N1–C1 1.3451(17), N2–C1 1.3467(17), C1–C8 1.4788(17); N1–C1–N2 106.59(11), C1–C8–B 116.62(11). For **8b**: B–C8 1.7084(19), N1–C1 1.3499(18), N2–C1 1.3515(18), C1–C8 1.4997(19), C8–C9 1.5372(18); N1–C1–N2 106.07(12), C1–C8–B 114.68(11), C9–C8–B 119.87(11), C1–C8–C9 107.27(11).

the 2-vinylimidazolium hydridoborates **9a** and **9b**,[55] which were formed by hydride transfer from an exocyclic β-methyl group to the borane Lewis acid. Additionally, the molecular

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structure of **9a** was established by X-ray diffraction analysis (Figure 8), thereby revealing the presence of a tetrahedral borate anion and an imidazolium cation, in which the exocyclic C1–C8 and C8–C10 bonds have single-bond character with bond lengths of 1.478(2) and 1.441(2) Å. In contrast, the C8–C9 distance of 1.363(2) Å indicates a double bond. As described above, the same 2-alkylideneimidazolines **1c** and **1d** decomposed in the presence of $[\{RhCl(cod)\}_2]$ to form unstable rhodium–alkyl complexes **5**. We proposed that this process involves intramolecular hydride transfer through the intermediate zwitterionic rhodium–hydride species **Int** that contains metal-bound 2-vinylimidazolium ions (Scheme 3). The same cations are now made isolable in the salts **9a** and **9b** through intermolecular hydride abstraction by $B(C_6F_5)_3$ and formation of stable ion pairs.

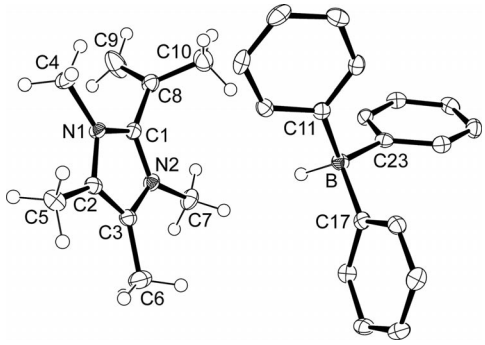

Figure 8. ORTEP drawing of **9a** with thermal displacement parameters drawn at 50% probability. The fluorine atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C8 1.478(2), N1–C1 1.342(2), N2–C1 1.335(2), C8–C9 1.363(2), C8–C10 1.441(2), B–C11 1.648(2), B–C17 1.639(2), B–C23 1.641(2); N2–C1–N1 107.56(12), C9–C8–C10 124.21(15), C10–C8–C1 116.92(14), N2–C1–C8–C9 104.9(2), N1–C1–C8–C10 100.49(19).

A completely different reactivity was observed when a yellow solution of **1e** was added to a solution of $B(C_6F_5)_3$ in benzene. The resulting clear yellow solution was stirred for one hour, and hexane was added to precipitate a yellow solid (95%), which had the chemical composition of a 1:1 adduct of **1e** and $B(C_6F_5)_3$. Storing the crude reaction mixture at room temperature without further stirring afforded pale yellow plates within three days, which were suitable for X-ray diffraction analysis (Figure 9). The molecular structure shows the formation of the adduct **10** by addition of $B(C_6F_5)_3$ to the less sterically hindered *para* position of one phenyl group, which affords a boron–carbon bond of B–C12 1.719(3) Å and a 4-substituted cyclohexa-2,5-dien-1-ylidene moiety. The exocyclic C8–C9 bond length of 1.373(3) Å indicates an elongated double bond, which is slightly twisted according to the torsion angles C1–C8–C9–C10 13.2(3)° and C15–C8–C9–C14 12.5(4)°. The N-heterocycle is oriented in an approximately perpendicular fashion with regard to the olefinic moiety [N1–C1–C8–C9 69.7(3)°, N(2)–C(1)–C(8)–C(15) 71.8(3)°], in agreement with the presence of an imidazolium–borate zwitterion. One C_6F_5 group is located above the cyclohexadiene ring, which creates short intramolecular contacts C11···C33 and C13···C33 of about 3.0 Å and a narrow C33–B–C12 angle of 101.05(17)°.

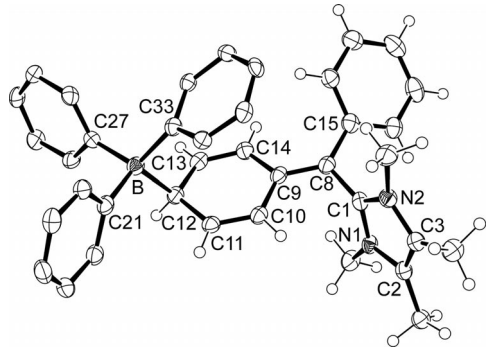

Figure 9. ORTEP drawing of **10** with thermal displacement parameters drawn at 50% probability. The fluorine atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: B–C12 1.719(3), N1–C1 1.346(3), N2–C1 1.344(3), C1–C8 1.469(3), C8–C9 1.373(3), C8–C15 1.485(3), C9–C14 1.452(3), C9–C10 1.458(3), C10–C11 1.340(3), C13–C14 1.345(3), C11–C12 1.478(3), C12–C13 1.479(3); C11–C12–B 110.35(18), C13–C12–B 111.83(18), C9–C8–C1 117.9(2), C9–C8–C15 126.9(2), C33–B–C12 101.05(17), C(1)–C(8)–C(9)–C(10) 13.2(3), C(15)–C(8)–C(9)–C(14) 12.5(4), N1–C1–C8–C9 69.7(3), N(2)–C(1)–C(8)–C(15) 71.8(3).

The CH group in the 4-position of the cyclohexadiene ring gives rise to a broad quartet at δ = 4.98 ppm ($^2J_{H,B}$ = 12.0 Hz) in the ^{1}H NMR spectrum and to a corresponding quartet at δ = 44.7 ppm ($^1J_{C,B}$ = 34.0 Hz) in the ^{13}C NMR spectrum. The signals for the hydrogen atoms in the 3,5-positions are found as very broad doublets at δ = 6.64 and 6.71 ppm because of the close vicinity to the $B(C_6F_5)_3$ substituent; the doublets for the protons in the 2,6-positions differ significantly in their chemical shifts (δ = 5.36 versus 6.53 ppm), which can be ascribed to their distinctly different environments and close proximity to the imidazole or phenyl rings, respectively. The asymmetry of the molecule is also reflected by the observation of four very broad ^{19}F NMR spectroscopic signals in a 4:2:3:6 ratio, which can be assigned to the *ortho*- (δ = –127.7 and –135.7 ppm), *para*- (δ = –162.9 ppm), and *meta*-fluorine atoms (δ = –166.3 ppm).

A similar reactivity was observed by Stephan et al. by reaction of sterically demanding phosphanes with salts that contained the trityl cation $[CPh_3]^+$. Steric hindrance prevents the phosphane from adding to the central carbon atom of the carbenium ion, and nucleophilic attack at the *para* position of a phenyl ring was observed instead.[56] The molecular structure of **10** also shows a close similarity to the structure of the "triphenylmethyl dimer", which exists in equilibrium with Gomberg's triphenylmethyl radical.[57] For a long time, it was falsely assumed that the triphenylmethyl radical dimerizes to hexaphenylethane instead of forming a diphenylmethylenecyclohexadiene structure,[58] and spectroscopic[59] and structural[60] evidence was not provided until 60 years after Gomberg's discovery.

Conclusion

In this contribution, we have demonstrated that 2-alkylidene-substituted 1,3,4,5-tetramethylimidazolines **1a**–**e** ex-

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hibit highly polarized, exocyclic C–C bonds, thus leading to the strongly nucleophilic properties of these compounds. Increasing the steric bulk of the substituents at the α-carbon atom forces the *N*-methyl groups to deviate from a coplanar arrangement with the imidazole rings, with concomitant elongation of the exocyclic C–C bond lengths. As ligands, only **1a** and **1b** are capable of forming isolable Rh^I complexes **4a**–**b** and **7a**–**b**, in which the exocyclic α-carbon atoms are bound to the metal atoms. Ligands **1c** and **1d**, which have methyl groups attached to the exocyclic carbon atoms, do not form stable complexes with the [Rh(cod)Cl] complex fragment, and decomposition was observed instead. The sterically demanding ligand **1e** did not show any tendency to coordinate to [{RhCl(cod)}$_2$]. With $B(C_6F_5)_3$, classical adduct formation was observed for **1a** and **1b**. For the methyl-substituted derivatives **1c** and **1d**, hydride abstraction by the borane from a β-methyl group was observed and the resulting imidazolium hydridoborates **9a** and **9b** can be considered analogues to rhodium–hydride species, which were assumed to be intermediates in the decomposition process of complexes **4c** and **4d**. For steric reasons, classical adduct formation between **1e** and $B(C_6F_5)_3$ is prevented, and instead, electrophilic attack of the borane at the *para* position at one of the phenyl rings in **1e** afforded the zwitterion **10**, which is reminiscent of the dimer of Gomberg's triphenylmethyl radical. Overall, this study reveals the use as well as the limitations, both largely governed by the nature of the substituents present at the alkylidene moiety, of employing 2-alkylideneimidazolines in transition-metal chemistry.

Experimental Section

General Information: All manipulations of air-sensitive materials were performed in an atmosphere of dry argon using Schlenk and vacuum techniques, or in an argon-filled glovebox (MBraun 200B). Solvents were purified by a solvent purification system from MBraun and stored over molecular sieves (4 Å) prior to use. THF for crystallization of rhodium(I) complexes was additionally dried with sodium–potassium alloy. Deuterated solvents were obtained from Sigma Aldrich (all >99 atom-% D) and were degassed, dried, and stored in an argon-filled glovebox over molecular sieves (4 Å). NMR spectra were recorded with Bruker DPX 200, Bruker AV 300, Bruker DPX 400, Bruker AV 400, and Bruker AV II-600 devices. The chemical shifts are expressed in ppm relative to tetramethylsilane (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), and $BF_3{\cdot}Et_2O$ (^{11}B). Coupling constants (*J*) are reported in Hertz [Hz], and spin-coupling patterns are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), sept (septet) and br (broad). Elemental analysis (C, H, N) succeeded by combustion and gas chromatographic analysis with an Elementar varioMICRO. A Bruker Vertex 70 spectrometer was used for recording IR spectra. Compounds **1a**,[25] **3b**,[36] **3c**,[36] [{RhCl(cod)}$_2$],[61] and $B(C_6F_5)_3$[62] were prepared according to literature procedures. Iodides **3a**–**e** were stored in the dark. Diphenylacetaldehyde was purchased from Sigma Aldrich, degassed prior to use, and stored under an atmosphere of argon. Methyl iodide was purchased from Sigma Aldrich, distilled prior to use, and stored under an atmosphere of argon in the absence of light.

2-Benzylidene-1,3,4,5-tetramethylimidazoline (1b): A suspension of the iodide **3b** (150 mg, 0.44 mmol) in THF (25 mL) was treated with KH (35.0 mg, 0.88 mmol) and was stirred at room temperature for 18 h. The solvent was removed under vacuum and the residue was extracted with a mixture of toluene/pentane (1:2, 5 × 5 mL). After filtration through Celite, the solvent was evaporated to yield **1b** (71.0 mg, 75%) as a yellow, crystalline solid, which was stored under an argon atmosphere at –30 °C. An analytically pure sample and crystals suitable for X-ray diffraction analysis were obtained by recrystallization from diethyl ether at –30 °C. ^{1}H NMR (200 MHz, C_6D_6, ambient): δ = 1.40 (s, 6 H, CH_3), 2.62 (s, 6 H, N–CH_3), 4.36 (s, 1 H, C*H*) 6.85–6.93 (m, 1 H, *p*-C_6H_5), 7.17–7.24 (m, 2 H, *o*-C_6H_5), 7.28–7.36 (m, 2 H, *m*-C_6H_5) ppm. ^{13}C NMR (75 MHz, C_6D_6, ambient): δ = 8.7 (s, *C*H$_3$), 32.0 (s, N-*C*H$_3$), 65.4 (s, *C*H), 117.3 (s, *C*-4, *C*-5), 118.2 (s, *p*-C_6H_5), 124.4 (s, *m*-C_6H_5), 128.4 (s, *o*-C_6H_5), 142.6 (s, *i*-C_6H_5), 150.5 (s, *C*-2) ppm. $C_{14}H_{18}N_2$ (214.31): calcd. C 78.46, H 8.47, N 13.07; found C 78.28, H 8.44, N 12.90.

2-Isopropylidene-1,3,4,5-tetramethylimidazoline (1c): Iodide **3c** (610 mg, 2.07 mmol) was suspended in THF (20 mL) and treated with KH (166 mg, 4.14 mmol). The suspension was stirred at room temperature for 18 h. The solvent was removed under vacuum and the residue was extracted with pentane (5 × 5 mL). After filtration through Celite, the solvent was evaporated to yield **1c** (200 mg, 58%) as a colorless, crystalline solid, which was stored under an atmosphere of argon at –30 °C. An analytically pure sample was obtained by recrystallization from pentane at –30 °C. ^{1}H NMR (200 MHz, C_6D_6, ambient): δ = 1.56 (s, 6 H, 4-, 5-CH_3), 1.96 [s, 6 H, C(CH_3)$_2$], 2.69 (s, 6 H, N–CH_3) ppm. ^{13}C NMR (75 MHz, C_6D_6, ambient): δ = 9.8 (s, 4-*C*H$_3$, 5-*C*H$_3$), 21.3 [s, C(*C*H$_3$)$_2$], 36.5 (s, N–*C*H$_3$), 71.4 [s, *C*(CH$_3$)$_2$], 120.4 (s, *C*-4, *C*-5), 153.5 (s, *C*-2) ppm. $C_{10}H_{18}N_2$ (166.27): calcd. C 72.24, H 10.91, N 16.85; found C 72.08, H 11.01, N 16.81.

1,3,4,5-Tetramethyl-2-(1-phenylethylidene)imidazoline (1d): A suspension of iodide **3d** (850 mg, 2.39 mmol) in THF (30 mL) was treated with KH (192 mg, 4.78 mmol) and stirred at room temperature for 18 h. The solvent was removed under vacuum, and the residue was extracted with pentane (5 × 5 mL). After filtration through Celite and concentrating the solvent to a minimum, **1d** (405 mg, 74%) was obtained as a bright yellow, crystalline solid by crystallization at –30 °C. An analytically pure sample and crystals suitable for X-ray diffraction analysis were obtained by recrystallization from pentane at –30 °C. ^{1}H NMR (200 MHz, C_6D_6, ambient): δ = 1.42 (s, 6 H, CH_3), 2.30 (s, 3 H, CCH_3), 2.68 (s, 6 H, N–CH_3), 6.82–6.90 (m, 1 H, *p*-C_6H_5), 7.12–7.17 (m, 2 H, *o*-C_6H_5), 7.31–7.40 (m, 2 H, *m*-C_6H_5) ppm. ^{1}H NMR (400 MHz, [D$_8$]THF, ambient): δ = 1.98 (s, 6 H, CH_3), 2.06 (s, 3 H, CCH_3), 3.01 (s, 6 H, N–CH_3), 6.39 (m, 1 H, *p*-C_6H_5), 6.67 (m, 2 H, *o*-C_6H_5), 6.93 (m, 2 H, *m*-C_6H_5) ppm. ^{13}C NMR (75 MHz, C_6D_6, ambient): δ = 9.0 (s, *C*H$_3$), 19.0 (s, C*C*H$_3$), 34.5 (s, N–*C*H$_3$), 65.2 (s, *C*CH$_3$), 117.1 (s, *p*-C_6H_5), 118.8 (s, *C*-4, *C*-5), 122.1 (s, *m*-C_6H_5), 128.4 (s, *o*-C_6H_5), 145.5 (s, *i*-C_6H_5), 153.7 (s, *C*-2) ppm. ^{13}C NMR (100 MHz, [D$_8$]-THF, ambient): δ = 9.3 (s, *C*H$_3$), 18.7 (s, C*C*H$_3$), 34.7 (s, N-*C*H$_3$), 64.7 (s, *C*CH$_3$), 116.4 (s, *p*-C_6H_5), 119.7 (s, *C*-4, *C*-5), 121.9 (s, *m*-C_6H_5), 128.1 (s, *o*-C_6H_5), 145.9 (s, *i*-C_6H_5), 154.3 (s, *C*-2) ppm. $C_{15}H_{20}N_2$ (228.34): calcd. C 78.90, H 8.83; found C 78.60, H 8.74.

2-Diphenylmethylene-1,3,4,5-tetramethylimidazoline (1e): A suspension of iodide **3e** (716 mg, 1.71 mmol) in diethyl ether (25 mL) was treated with KH (137 mg, 3.42 mmol), and the suspension was stirred for 2 d. The solvent was removed under vacuum, and the residue was suspended in toluene (15 mL) and filtered through Celite. The solvent was reduced under vacuum until a yellow precipitate began to form. Product **1e** was obtained by crystallization at –30 °C as a bright yellow, crystalline solid (275 mg, 55%). Crystals

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suitable for X-ray diffraction analysis were obtained from a saturated solution of **1e** in toluene at –30 °C. ^{1}H NMR (300 MHz, C_6D_6, ambient): δ = 1.35 (s, 6 H, CH_3), 2.67 (s, 6 H, N–CH_3), 6.83–6.89 (m, 2 H, *p*-C$_6H_5$), 7.20–7.25 (m, 4 H, *m*-C$_6H_5$), 7.35–7.38 (m, 4 H, *o*-C$_6H_5$) ppm. ^{13}C NMR (75 MHz, C_6D_6, ambient): δ = 8.3 (s, *C*H$_3$), 33.0 (s, N–*C*H$_3$), 75.3 [s, (C$_6$H$_5$)$_2$*C*], 118.4 (s, *C*-4, *C*-5), 119.1 (s, *p*-C$_6$H$_5$), 126.2 (s, *m*-C$_6$H$_5$), 128.4 (s, *o*-C$_6$H$_5$), 145.5 (s, *i*-C$_6$H$_5$), 151.7 (s, *C*-2) ppm. $C_{20}H_{22}N_2$ (290.41): calcd. C 82.72, H 7.64, N 9.65; found C 82.75, H 7.77, N 9.79.

4,5-Dimethyl-2-(1-phenylethyl)imidazole (2d): A solution of 2,3-butanedione (2.00 mL, 23.0 mmol) in ethanol (30.0 mL) was added to a solution of 2-phenylpropionaldehyde (4.50 mL, 34.2 mmol), aqueous ammonia (30.0 mL, 44.1 mmol), and ethanol (50.0 mL) over a period of 1.5 h. During this time, a white precipitate formed. The reaction mixture was stirred for 18 h at room temperature. After removal of all volatiles, HCl (20.0 mL, 2 M) was added to the residue, and the solution was extracted with Et$_2$O (3 × 50 mL). Solid K_2CO_3 was added to the aqueous layer until a white precipitate separated. The solution was extracted with chloroform (3 × 50 mL), the combined organic layers dried with Na_2SO_4 and the solvent was removed under vacuum. Recrystallization from boiling ethyl acetate afforded **2d** (1.41 g, 31%) as a white solid. ^{1}H NMR (200 MHz, $CDCl_3$, ambient): δ = 1.72 (d, $^3J_{H,H}$ = 7.3 Hz, 3 H, CHCH_3), 2.13 (s, 6 H, CH$_3$), 4.16 (q, $^3J_{H,H}$ = 7.3 Hz, 1 H, C*H*CH$_3$), 7.24–7.41 (m, 5 H, C$_6H_5$) ppm; the resonance for N*H* was not observed. ^{13}C NMR (75 MHz, $CDCl_3$, ambient): δ = 10.7 (s, *C*H$_3$), 20.4 (s, CH*C*H$_3$), 39.5 (s, *C*HCH$_3$), 107.1 (s, *C*-2), 126.8 (s, *p*-C$_6$H$_5$), 127.4 (s, *o*-C$_6$H$_5$), 128.7 (s, *m*-C$_6$H$_5$), 143.6 (s, *i*-C$_6$H$_5$), 148.4 (s, *C*-4, *C*-5) ppm. $C_{13}H_{16}N_2$ (200.28): calcd. C 77.96, H 8.05, N 13.99; found C 78.03, H 8.01, N 13.74.

2-Diphenylmethyl-4,5-dimethylimidazole (2e): A solution of 2,3-butanedione (2.09 mL, 23.5 mmol) in ethanol (20 mL) was added to a solution of diphenylacetaldehyde (5.00 mL, 28.2 mmol) and aqueous ammonia (80.0 mL, 117 mmol) in ethanol (100 mL) over a period of 1 h, and stirring was continued for 16 h. During this time a voluminous white precipitate formed, which was collected by filtration, washed with pentane, and dried under vacuum to yield **2e** (1.70 g, 23%) as a white powder. ^{1}H NMR (200 MHz, $CDCl_3$, ambient): δ = 2.15 (s, 6 H, CH$_3$), 5.62 [s, 1 H, (C$_6$H$_5$)$_2$C*H*], 7.17–7.40 (m, 10 H, C$_6$H$_5$) ppm; the resonance for N*H* was not observed. ^{13}C NMR (75 MHz, CD_3CN, ambient): δ = 10.1 (s, *C*H$_3$), 50.6 [s, (C$_6$H$_5$)$_2$*C*H], 126.0 (s, *C*-2), 126.3 (s, *p*-C$_6$H$_5$), 128.1, 128.3 (s, *o*-C$_6$H$_5$, *m*-C$_6$H$_5$), 141.3 (s, *i*-C$_6$H$_5$), 145.6 (s, *C*-4, *C*-5) ppm. $C_{18}H_{18}N_2$ (262.35): calcd. C 82.41, H 6.92, N 10.68; found C 82.49, H 6.84, N 10.89.

2-(1-Phenylethyl)-1,3,4,5-tetramethylimidazolium Iodide (3d): Imidazole **2d** (750 mg, 3.74 mmol) and $NaHCO_3$ (1.26 g, 14.9 mmol) were suspended in dry acetonitrile (120 mL). Methyl iodide (5.76 mL, 92.0 mmol) was added, and the reaction mixture was heated to reflux for 18 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was extracted with CH_2Cl_2 and filtered through Celite. After removal of the solvent the residue was triturated with Et$_2$O several times until the washings became colorless. Product **3d** was obtained as a pale yellow powder (1.22 g, 92%). ^{1}H NMR (200 MHz, $CDCl_3$, ambient): δ = 1.85 (d, $^3J_{H,H}$ = 7.3 Hz, 3 H, CHCH_3), 2.25 (s, 6 H, CH_3), 3.60 (s, 6 H, N-CH_3), 4.96 (q, $^3J_{H,H}$ = 7.3 Hz, 1 H, C*H*CH$_3$), 7.12–7.40 (m, 5 H, C$_6$H$_5$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, ambient): δ = 9.5 (s, *C*H$_3$), 16.4 (s, CH*C*H$_3$), 33.5 (s, N–*C*H$_3$), 34.2 (s, *C*HCH$_3$), 126.5 (s, *o*-C$_6$H$_5$), 126.5 (s, *C*-4, *C*-5), 127.9 (s, *p*-C$_6$H$_5$), 129.3 (s, *m*-C$_6$H$_5$), 136.2 (s, *i*-C$_6$H$_5$), 146.3 (s, *C*-2) ppm. $C_{15}H_{21}IN_2 \cdot {}^1/_8CH_2Cl_2$ (356.25): calcd. C 49.52, H 5.84, N 7.64; found C 49.49, H 6.00, N 7.88.

2-Diphenylmethyl-4,5-dimethylimidazolium Iodide (3e): Imidazole **2e** (800 mg, 3.05 mmol) and $NaHCO_3$ (1.28 g, 15.2 mmol) were suspended in dry acetonitrile (100 mL). Methyl iodide (4.77 mL, 76.2 mmol) was added, and the reaction mixture was heated to reflux for 18 h. After cooling to room temperature, the solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 and filtered through Celite. After removal of the solvent, the residue was triturated with Et$_2$O several times until the washings became colorless. Product **3e** was obtained as a pale yellow powder (1.08 g, 85%). ^{1}H NMR (200 MHz, $CDCl_3$, ambient): δ = 2.31 (s, 6 H, CH_3), 3.48 (s, 6 H, N–CH_3), 6.53 [s, 1 H, (C$_6$H$_5$)$_2$C*H*], 7.17–7.45 (m, 10 H, C$_6H_5$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, ambient): δ = 9.7 (s, *C*H$_3$), 34.0 (s, N–*C*H$_3$), 127.0 (s, *C*-4, *C*-5), 128.4 (s, *p*-C$_6$H$_5$), 128.8 (s, *o*-C$_6$H$_5$), 129.5 (s, *m*-C$_6$H$_5$), 135.1 (s, *i*-C$_6$H$_5$), 144.1 (s, *C*-2) ppm. $C_{20}H_{23}IN_2$ (418.32): calcd. C 57.42, H 5.54, N 6.70; found C 57.15, H 5.49, N 6.91.

[(1a)RhCl(cod)] (4a): A solution of **1a** (70.0 mg, 0.51 mmol) in hexane (10 mL) was added to a solution of [{RhCl(cod)}$_2$] (125 mg, 0.25 mmol) in hexane/toluene (10 mL, 1:1). The solution was stirred for 15 min. During this time, a yellow solid precipitated from the reaction mixture, and was collected by filtration, washed with pentane until the washings became colorless, and dried under vacuum. Complex **4a** was obtained as a pale yellow powder (175 mg, 90%). Crystals suitable for X-ray diffraction analysis were obtained from a saturated solution of **4a** in THF at –30 °C. ^{1}H NMR (300 MHz, C_6D_6, ambient): δ = 1.26 (s, 6 H, CH_3), 1.38 (br. d, $^2J_{Rh,H}$ = 2.6 Hz, 2 H, CH_2), 1.78–1.96 (m, 4 H, cod–CH_2), 2.33–2.59 (m, 4 H, cod-CH_2), 2.91 (s, 6 H, N–CH_3), 3.52–3.60 (m, 2 H, cod–C*H*), 5.01–5.09 (m, 2 H, cod–C*H*) ppm. ^{1}H NMR (600 MHz, [D$_8$]THF, ambient): δ = 1.29 (d, $^2J_{Rh,H}$ = 2.6 Hz, 2 H, CH_2), 1.66–1.77 (m, 4 H, cod–CH_2), 2.06 (s, 6 H, CH_3), 2.15–2.21, 2.29–2.35 (m, 4 H, cod–CH_2), 3.24–3.28 (m, 2 H, cod–C*H*), 3.42 (s, 6 H, N–CH_3), 4.25–4.29 (m, 2 H, cod–C*H*) ppm. ^{13}C NMR (75 MHz, C_6D_6, ambient): δ = 8.0 (s, *C*H$_3$), 18.8 (d, $^1J_{C,Rh}$ = 21.8 Hz, *C*H$_2$), 30.4 (s, cod–*C*H$_2$), 30.6 (s, N–*C*H$_3$), 33.2 (s, cod–*C*H$_2$), 69.3 (d, $^1J_{C,Rh}$ = 15.1 Hz, cod–*C*H), 87.7 (d, $^1J_{C,Rh}$ = 8.8 Hz, cod–*C*H), 119.8 (s; *C*-4, *C*-5), 162.6 (s, *C*-2) ppm. ^{13}C NMR (150 MHz, [D$_8$]-THF, ambient): δ = 8.4 (s, *C*H$_3$), 14.0 (d, $^1J_{C,Rh}$ = 21.8 Hz, *C*H$_2$), 30.6 (s, cod–*C*H$_2$), 31.2 (s, N–*C*H$_3$), 33.5 (s, cod–*C*H$_2$), 69.3 (d, $^1J_{C,Rh}$ = 15.1 Hz, cod–*C*H), 87.0 (d, $^1J_{C,Rh}$ = 8.8 Hz, cod–*C*H), 121.1 (s, *C*-4, *C*-5), 163.1 (s, *C*-2) ppm. $C_{16}H_{26}ClN_2Rh$ (384.75): calcd. C 49.95, H 6.81, N 7.28; found C 50.21, H 6.72, N 7.10.

[(1b)RhCl(cod)] (4b): A solution of **1b** (80.0 mg, 0.37 mmol) in hexane/toluene (10 mL, 1:1) was added to a solution of [{RhCl(cod)}$_2$] (88.0 mg, 0.18 mmol) in hexane/toluene (10 mL, 1:1), and the solution was stirred for 15 min. During this time, a yellow solid precipitated from the reaction mixture, and was collected by filtration, washed with toluene/hexane (1:1) until the washings became colorless, and dried under vacuum. Complex **4b** was obtained as a pale yellow powder (168 mg, 98%). Crystals suitable for X-ray diffraction analysis were obtained from a saturated solution of **4b** in THF at –30 °C. ^{1}H NMR (400 MHz, [D$_8$]THF, ambient): δ = 1.47–1.70 (m, 4 H, cod–CH_2), 2.16 (s, 6 H, CH_3), 2.17–2.29 (m, 4 H, cod–CH_2), 2.63–2.68 (m, 1 H, cod–C*H*), 3.04–3.09 (m, 1 H, cod–C*H*), 3.47 (d, $^2J_{H,Rh}$ = 2.1 Hz, 1 H, C*H*), 3.90 (s, 6 H, N–CH_3), 4.25–4.34 (m, 2 H, cod–C*H*), 6.75–6.79 (m, 1 H, *p*-C$_6H_5$), 6.83–6.85 (m, 2 H, *o*-C$_6H_5$), 6.98–7.03 (m, 2 H, *m*-C$_6H_5$) ppm. ^{13}C NMR (100 MHz, [D$_8$]THF, ambient): δ = 8.7 (s, *C*H$_3$), 29.8 (s, cod–*C*H$_2$), 30.9 (s, cod–*C*H$_2$), 32.2 (s, cod–*C*H$_2$), 33.2 (d, $^1J_{C,Rh}$ = 21.6 Hz, *C*H), 33.3 (s, N–*C*H$_3$), 33.6 (s, cod–*C*H$_2$), 71.3 (d, $^1J_{C,Rh}$ = 15.7 Hz, cod–*C*H), 71.9 (d, $^1J_{C,Rh}$ = 15.7 Hz, cod–*C*H), 85.6 (d, $^1J_{C,Rh}$ = 8.8 Hz, cod–*C*H), 85.8 (d, $^1J_{C,Rh}$ = 8.8 Hz, cod–*C*H), 123.0 (s, *C*-4, *C*-5), 126.0 (s, *p*-C$_6$H$_5$), 126.6 (s, *m*-C$_6$H$_5$), 128.2 (s, *o*-C$_6$H$_5$),

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147.8 (s, *i*-C_6H_5), 160.1 (s, *C*-2) ppm. $C_{22}H_{30}ClN_2Rh$ (460.85): calcd. C 57.34, H 6.56, N 6.08; found C 57.33, H 6.51, N 6.10.

[(1c)RhCl(cod)] (4c): A solution of **1c** (110 mg, 0.66 mmol) in hexane (10 mL) was added to a solution of [{RhCl(cod)}$_2$] (160 mg, 0.32 mmol) in hexane/toluene (30 mL, 1:1). The solution was stirred for 20 min and the solvent was removed under vacuum. The residue was washed with pentane and dried under vacuum to obtain **4c** as a pale yellow powder (180 mg, 64%). ^{1}H NMR (400 MHz, C_6D_6, ambient): δ = 1.35 (s, 6 H, 4-CH_3, 5-CH_3), 1.56 [s, 6 H, C(CH_3)$_2$], 1.77–1.90 (m, 4 H, cod–CH_2), 2.30–2.40 (m, 2 H, cod–CH_2), 2.42–2.52 (m, 2 H, cod–CH_2), 3.20–3.26 (m, 2 H, cod–C*H*), 3.66 (s, 6 H, N–CH_3), 4.94–5.00 (m, 2 H, cod–C*H*) ppm. ^{1}H NMR (600 MHz, [D$_8$]THF, ambient): δ = 1.39 (s, 6 H, 4-CH_3, 5-CH_3), 1.63–1.74 (m, 4 H, cod–CH_2), 2.08 [s, 6 H, C(CH_3)$_2$], 2.12–2.18 (m, 2 H, cod–CH_2), 2.29–2.36 (m, 2 H, cod–CH_2), 2.99–3.03 (m, 2 H, cod–C*H*), 4.04 (s, 6 H, N–CH_3), 4.27–4.31 (m, 2 H, cod–C*H*) ppm. ^{13}C NMR (150 MHz, C_6D_6, ambient): δ = 8.9 (s, *C*H$_3$), 25.6 [d, $^1J_{C,Rh}$ = 23.9 Hz, *C*(CH$_3$)$_2$], 25.7 [s, C(*C*H$_3$)$_2$], 29.8 (s, cod–*C*H$_2$), 33.0 (s, cod–*C*H$_2$), 33.7 (s, N–*C*H$_3$), 70.4 (d, $^1J_{C,Rh}$ = 16.8 Hz, cod–*C*H), 87.3 (d, $^1J_{C,Rh}$ = 7.8 Hz, cod–*C*H), 121.7 (s, *C*-4, *C*-5), 164.1 (s, *C*-2) ppm. ^{13}C NMR (150 MHz, [D$_8$]THF, ambient): δ = 9.1 (s, *C*H$_3$), 25.6 (br. s, *C*H$_3$), 25.9 [d, $^1J_{C,Rh}$ = 23.9 Hz, *C*(CH$_3$)$_2$], 30.0 (s, cod-*C*H$_2$), 33.2 (s, cod–*C*H$_2$), 34.2 (s, N–*C*H$_3$), 70.4 (d, $^1J_{C,Rh}$ = 16.6 Hz, cod–*C*H), 87.1 (d, $^1J_{C,Rh}$ = 8.1 Hz, cod–*C*H), 122.7 (s, *C*-4, *C*-5), 164.9 (br. d, $^1J_{C,Rh}$ = 2.0 Hz, *C*-2) ppm. $C_{18}H_{30}ClN_2Rh$ (412.81): calcd. C 52.37, H 7.33, N 6.79; found C 52.15, H 7.16, N 6.61.

[(1a)RhCl(CO)$_2$] (7a): A solution of **1a** (77.0 mg, 0.55 mmol) in hexane (5 mL) was added to a solution of [{RhCl(CO)$_2$}$_2$] (102 mg, 0.26 mmol) in hexane/toluene (5 mL, 1:1), which led to the precipitation of a dark brown solid. The solution was stirred for 20 min, and the solvent was removed under vacuum. The residue was suspended in THF, filtered, and the solvent was evaporated to yield a dark brown solid, which was washed with diethyl ether and dried under vacuum. Complex **7a** was obtained as an orange solid (51.0 mg, 27%). ^{1}H NMR (200 MHz, C_6D_6, ambient): δ = 1.24 (s, 6 H, CH_3), 2.10 (br. d, $^2J_{H,Rh}$ = 2.01 Hz, 2 H, CH_2) 2.83 (s, 6 H, N–CH_3) ppm. ^{1}H NMR (400 MHz, CD_2Cl_2, ambient): δ = 2.11 (s, 6 H, CH_3), 2.12 (br. m, 2 H, CH_2), 2.47 (s, 6 H, N–CH_3) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2, ambient): δ = 8.8 (s, *C*H$_3$), 10.0 (d, $^1J_{C,Rh}$ = 17.1 Hz, *C*H$_2$), 31.7 (s, N–*C*H$_3$), 121.9 (s, *C*-4, *C*-5), 159.0 (s, *C*-2), 184.7 (d, $^1J_{C,Rh}$ = 56.4 Hz, *C*O), 186.6 (d, $^1J_{C,Rh}$ = 77.7 Hz, *C*O) ppm. IR (ATR): $\tilde{\nu}$ = 1969, 2044 cm^{-1} (s, CO). $C_{10}H_{14}ClN_2O_2Rh$ (332.59): calcd. C 36.11, H 4.24, N 8.42; found C 35.99, H 4.35, N 8.39.

[(1b)RhCl(CO)$_2$] (7b): A solution of **1b** (110 mg, 0.51 mmol) in toluene (5 mL) was added to a solution of [{RhCl(CO)$_2$}$_2$] (99.5 mg, 0.25 mmol) in hexane/toluene (5 mL, 1:1), and the reaction mixture was stirred for 2 h. During this time a yellow solid precipitated, which was collected by filtration and washed with hexane. The crude product was recrystallized from a mixture of dichloromethane/diethyl ether/pentane at –30 °C and **7b** was obtained as a yellow solid (106 mg, 51%). ^{1}H NMR (300 MHz, [D$_8$]THF, ambient): δ = 2.21 (s, 6 H, CH_3), 3.70 (s, 6 H, NCH_3), 4.47 (br. m, 1 H, C*H*), 6.87–6.92 (m, 1 H, *p*-C_6H_5), 7.01–7.12 (m, 4 H, *m*-, *o*-C_6H_5) ppm. ^{13}C NMR (75 MHz, [D$_8$]THF, ambient): δ = 8.6 (s, *C*H$_3$), 33.4 (s, N–*C*H$_3$), 33.6 (d, $^1J_{C,Rh}$ = 18.9 Hz, *C*H), 124.0 (s, *p*-C_6H_5), 124.1 (s, *C*-4, *C*-5), 127.3 (br. s, *m*-C_6H_5), 128.6 (br. s, *o*-C_6H_5), 148.3 (s, *i*-C_6H_5), 155.7 (br. s, *C*-2), 185.8 (d, $^1J_{C,Rh}$ = 56.8 Hz, *C*O), 187.4 (d, $^1J_{C,Rh}$ = 79.0 Hz, *C*O) ppm. IR (ATR): $\tilde{\nu}$ = 1968, 2036 cm^{-1} (m, CO). $C_{16}H_{18}ClN_2O_2Rh$ (408.69): calcd. C 47.02, H 4.44, N 6.85; found C 47.15, H 4.64, N 6.73.

[(1c)RhCl(CO)$_2$] (7c): An NMR tube was charged with [{RhCl(CO)$_2$}$_2$] (40.0 mg, 0.10 mmol), **1c** (34.0 mg, 0.20 mmol), and [D$_8$]THF (0.7 mL), and was sealed under an atmosphere of argon. The sample was inserted into the NMR spectrometer immediately. After a short time, the precipitation of dark materials and the formation of a rhodium mirror were observed. ^{1}H NMR (600 MHz, [D$_8$]THF, ambient): δ = 1.90 (s, 3 H, CH_3), 1.90 (s, 3 H, CH_3), 2.12 [s, 6 H, C(CH_3)$_2$], 3.94 (s, 6 H, N–CH_3) ppm. ^{13}C NMR (150 MHz, [D$_8$]THF, ambient): δ = 9.0 (s, *C*H$_3$), 30.1 (s, *C*H$_3$), 31.7 [d, $^1J_{C,Rh}$ = 20.2 Hz, *C*(CH$_3$)$_2$], 34.6 (s, N–*C*H$_3$), 123.7 (s, *C*-4, *C*-5), 161.4 (s, *C*-2), 186.8 (d, $^1J_{C,Rh}$ = 54.2 Hz, *C*O), 188.6 (d, $^1J_{C,Rh}$ = 83.4 Hz, *C*O) ppm.

[(1a)B(C_6F_5)$_3$] (8a): A solution of **1a** (40.6 mg, 0.29 mmol) in hexane (5 mL) was added to a solution of B(C_6F_5)$_3$ (150 mg, 0.29 mmol) in hexane (15 mL), which resulted in the immediate precipitation of a white solid, and the reaction mixture was stirred for 10 min. The solid was filtered off, washed with pentane (3 × 5 mL), and dried under vacuum to yield compound **7a** as a white powder (144 mg, 76%). Crystals suitable for X-ray diffraction analysis were obtained from slow diffusion of pentane into a saturated solution of **8a** in CH_2Cl_2 at –30 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, ambient): δ = 2.04 (s, 6 H, CH_3), 3.02 (s, 6 H, N–CH_3), 3.16 (br. q, $^2J_{H,B}$ = 5.9 Hz, 2 H, BCH_2) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone, ambient): δ = 8.3 (s, *C*H$_3$), 19.8 (br. q, $^1J_{C,B}$ = 39.0 Hz, B*C*H$_2$), 31.2 (s, N–*C*H$_3$), 124.5 (s, *C*-4, *C*-5), 135.8–138.3 (dm, $^1J_{C,F}$ = 147.3 Hz, *m*-C_6F_5), 137.7–140.2 (dm, $^1J_{C,F}$ = 147.3 Hz, *p*-C_6F_5), 147.5–149.9 (dm, $^1J_{C,F}$ = 139.2 Hz, *o*-C_6F_5), 152.5 (s, *C*-2) ppm. ^{19}F NMR (200 MHz, CD_2Cl_2, ambient): δ = –165.6 (br. t, $^3J_{F,F}$ = 19.6 Hz, 6 F, *m*-C_6F_5), –161.0 (t, $^3J_{F,F}$ = 20.0 Hz, 3 F, *p*-C_6F_5), –132.3 (d, $^3J_{F,F}$ = 21.1 Hz, 6 F, *o*-C_6F_5) ppm. ^{11}B NMR (96 MHz, CD_2Cl_2, ambient): δ = –13.7 (s) ppm. $C_{26}H_{14}BF_{15}N_2$·1/6C_5H_{12} [650.2 + (72.1/6)]: C 48.67, H 2.44, N 4.23; found C 48.54, H 2.45, N 4.35.

[(1b)B(C_6F_5)$_3$] (8b): A solution of **1b** (63.0 mg, 0.29 mmol) in hexane/toluene (5 mL, 2:1) was added to a solution of B(C_6F_5)$_3$ (150 mg, 0.29 mmol) in hexane (15 mL), which resulted in the immediate precipitation of a light yellow solid. The reaction mixture was stirred for 15 min. The solid was removed by filtration, washed with toluene and pentane, and dried under vacuum to yield compound **8b** as an off-white powder (187 mg, 88%). Crystals suitable for X-ray diffraction analysis were obtained from slow diffusion of pentane into a saturated solution of **8b** in CH_2Cl_2 at –30 °C. ^{1}H NMR (600 MHz; [D$_6$]acetone, ambient): δ = 2.07 (s, 3 H, CH_3), 2.17 (s, 3 H, N–CH_3), 2.28 (s, 3 H, CH_3), 3.76 (s, 3 H, N–CH_3), 5.84 (br. q, $^2J_{H,B}$ = 6.4 Hz, 1 H, BC*H*), 7.14 (m, 1 H, *p*-C_6H_5), 7.20 (m, 2 H, *m*-C_6H_5), 7.34 (br. d, $^3J_{H,H}$ = 7.4 Hz, 2 H, *o*-C_6H_5) ppm. ^{13}C NMR (150 MHz, [D$_6$]acetone, ambient): δ = 8.5, 9.0 (s, *C*H$_3$), 32.3, 32.8 (s, N–*C*H$_3$), 38.0 (q, $^1J_{C,B}$ = 38.0 Hz, B*C*H), 126.0, 126.2 (s, *C*-4, *C*-5), 126.6 (s, *p*-C_6H_5), 129.1 (s, *m*-C_6H_5), 130.5 (s, *o*-C_6H_5), 137.5 (dm, $^1J_{C,F}$ = 246 Hz, *m*-C_6F_5), 139.5 (dm, $^1J_{C,F}$ = 246 Hz, *p*-C_6F_5), 143.8 (s, *i*-C_6H_5), 149.2 (dm, $^1J_{C,F}$ = 238 Hz, *o*-C_6F_5), 153.7 (s, *C*-2) ppm. ^{19}F NMR (400 MHz, [D$_6$]acetone, ambient): δ = –165.7 (br. s, 6 F, *m*-C_6F_5), –161.0 (br. m, 3 F, *p*-C_6F_5), –128.3 (br. s, 6 F, *o*-C_6F_5) ppm. ^{11}B NMR (96 MHz, [D$_6$]acetone, ambient): δ = –11.3 (s) ppm. $C_{32}H_{18}BF_{15}N$ (712.28): calcd. C 52.92, H 2.50, N 3.86; found C 53.09, H 2.80, N 3.75.

[(CH_2=CH$_3$)C(Im^{Me})][HB(C_6F_5)$_3$] (9a): A solution of **1c** (48.5 mg, 0.29 mmol) in hexane (5 mL) was added dropwise to a solution of B(C_6F_5)$_3$ (150 mg, 0.29 mmol) in hexane (10 mL), which led to the instantaneous precipitation of a white solid. After 15 min, the precipitate was collected, washed with hexane, and dried under vacuum to afforded **9a** as a white powder (171 mg, 86%). Crystals

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suitable for X-ray diffraction analysis were obtained from slow diffusion of pentane into a saturated solution of **9a** in CH_2Cl_2 at –30 °C. ^{1}H NMR (300 MHz, [D$_6$]acetone, ambient): δ = 2.18 (dd, $^4J_{H,H}$ = 1.0, 1.7 Hz, 3 H, CH_3), 2.35 (s, 6 H, CH_3), 3.79 (s, 6 H, N–CH_3), 3.41–4.11 (br. q, $^1J_{H,B}$ = 92.0 Hz, 1 H, B–*H*), 5.69, 6.09 (m, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone, ambient): δ = 8.4 (s, *C*H$_3$), 21.2 (s, *C*H$_3$), 32.9 (s, N-*C*H$_3$), 127.5 (s, *C*-4, *C*-5), 129.1 (s, *C*H$_2$), 129.3 (s, CH$_2$=*C*), 137.2 (dm, $^1J_{C,F}$ = 245 Hz, *m*-*C*$_6$F$_5$), 138.4 (dm, $^1J_{C,F}$ = 245 Hz, *p*-*C*$_6$F$_5$), 145.2 (s, *C*-2), 149.0 (dm, $^1J_{C,F}$ = 235 Hz, *o*-*C*$_6$F$_5$) ppm. ^{19}F NMR (200 MHz, [D$_6$]-acetone, ambient): δ = –167.6 (m, 6 F, *m*-C$_6$*F*$_5$), –164.8 (t, $^3J_{F,F}$ = 19.8 Hz, 3 F, *p*-C$_6$*F*$_5$), –132.8 (d, $^3J_{F,F}$ = 21.6 Hz, 6 F, *o*-C$_6$*F*$_5$) ppm. ^{11}B NMR (96 MHz, [D$_6$]acetone, ambient): δ = –24.1 (d, $^1J_{B,H}$ = 92.0 Hz) ppm. $C_{28}H_{18}BF_{15}N_2$ (678.24): calcd. C 49.58, H 2.67, N 4.13; found C 49.97, H 2.89, N 4.20.

[(CH$_2$=Ph)C(Im^{Me})][HB(C$_6$F$_5$)$_3$] (9b): A solution of **1d** (67.0 mg, 0.29 mmol) in toluene (5 mL) was added dropwise to a solution of B(C$_6$F$_5$)$_3$ (150 mg, 0.29 mmol) in toluene (10 mL). The resulting pale yellow solution was stirred for 30 min. Pentane (10 mL) was slowly added, and the resulting precipitate was collected by filtration, washed with pentane until the washings became colorless, and dried under vacuum to obtain **9b** as an off-white powder (196 mg, 90%). ^{1}H NMR (300 MHz, [D$_6$]acetone, ambient): δ = 2.42 (s, 6 H, CH_3), 3.72 (s, 6 H, N–CH_3), 3.43–4.12 (br. q, $^1J_{H,B}$ = 92.0 Hz, 1 H, B–*H*), 6.02, 6.74 (br. m, 2 H, CH_2), 7.37–7.46 (m, 5 H, C$_6$*H*$_5$) ppm. ^{13}C NMR (100 MHz, [D$_6$]acetone, ambient): δ = 8.6 (s, *C*H$_3$), 33.2 (s, N–*C*H$_3$), 126.7 (s, *p*-*C*$_6$H$_5$), 127.2 (s, *C*H$_2$), 128.3 (s, *C*-4, *C*-5), 130.3 (s, *m*-*C*$_6$H$_5$), 130.7 (s, *o*-*C*$_6$H$_5$), 132.7 (s, C=*C*H$_2$), 135.7 (s, *i*-*C*$_6$H$_5$), 137.2 (dm, $^1J_{C,F}$ = 250 Hz, *m*-*C*$_6$F$_5$), 138.4 (dm, $^1J_{C,F}$ = 242 Hz, *p*-*C*$_6$F$_5$), 143.6 (s, *C*-2), 149.1 (dm, $^1J_{C,F}$ = 236 Hz, *o*-*C*$_6$F$_5$) ppm. ^{19}F NMR (200 MHz, [D$_6$]acetone, ambient): δ = –167.5 (m, 6 F, *m*-C$_6$*F*$_5$), –164.7 (t, $^3J_{F,F}$ = 19.6 Hz, 3 F, *p*-C$_6$*F*$_5$), –132.8 (d, $^3J_{F,F}$ = 23.0 Hz, 6 F, *o*-C$_6$*F*$_5$) ppm. ^{11}B NMR (96 MHz, [D$_6$]acetone, ambient): δ = –24.1 (d, $^1J_{B,H}$ = 92.0 Hz) ppm. $C_{33}H_{20}BF_{15}N_2$ (740.31): calcd. C 53.54, H 2.72, N 3.78; found C 53.82, H 2.87, N 3.89.

[(C$_6$F$_5$)$_3$B(C$_6$H$_5$)CPh(Im^{Me})] (10): A solution of **1e** (80.0 mg, 0.275 mmol) in benzene (3 mL) was added to a solution of B(C$_6$F$_5$)$_3$ (141 mg, 0.275 mmol) in benzene (2 mL). The yellow solution was stirred for 1 h. Hexane (10 mL) was added to precipitate the product **10** as a pale yellow solid (209 mg, 95%). Crystals suitable for X-ray diffraction analysis were obtained by leaving the crude reaction mixture to stand at room temperature for 3 d. ^{1}H NMR (600 MHz, CD_2Cl_2, ambient): δ = 2.21 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 3.15 (s, 3 H, N–CH_3), 3.45 (s, 3 H, N–CH_3), 4.98 (br. q, $^3J_{H,B}$ = 12.0 Hz, 1 H, 4-C$_6$*H*$_5$), 5.36 (br. d, $^3J_{H,H}$ = 9.8 Hz, 1 H, 2-C$_6$*H*$_5$), 6.53 (br. d, $^3J_{H,H}$ = 10.0 Hz, 1 H, 2′-C$_6$*H*$_5$), 6.64 (br. d, $^3J_{H,H}$ = 9.5 Hz, 1 H, 3-C$_6$*H*$_5$), 6.71 (br. d, $^3J_{H,H}$ = 9.5 Hz, 1 H, 3-C$_6$*H*$_5$), 6.83–6.84 (m, 2 H, *o*-C$_6$*H*$_5$), 7.21–7.24 (m, 1 H, *p*-C$_6$*H*$_5$), 7.29–7.32 (m, 2 H, *m*-C$_6$*H*$_5$) ppm. ^{13}C NMR (150 MHz, CD_2Cl_2, ambient): δ = 9.0 (s, *C*H$_3$), 9.1 (s, *C*H$_3$), 31.8 (s, N-CH_3), 32.6 (s, N–CH_3), 44.7 (br. q, $^1J_{C,B}$ = 34.0 Hz, 4-*C*$_6$H$_5$), 103.5 (s, C$_6$H$_5$=*C*), 120.1, 120.4 (s, 2,2′-C$_6$*H*$_5$), 126.5, 126.6 (s, *C*-4, *C*-5), 127.8 (s, *p*-*C*$_6$H$_5$), 128.8 (s, *o*-*C*$_6$H$_5$), 129.4 (s, *m*-*C*$_6$H$_5$), 126.2 (s, *i*-*C*$_6$H$_5$), 136.0–139.1 (br. m, C$_6$*F*$_5$), 143.4 (s, 1-C$_6$*H*$_5$), 146.2 (s, *C*-2), 147.6–149.1 (br. m, C$_6$*F*$_5$), 149.4, 150.1 (s, 3,3′-C$_6$*H*$_5$) ppm. ^{19}F NMR (200 MHz, CD_2Cl_2, ambient): δ = –166.3 (br. m, 6 F, *m*-C$_6$*F*$_5$), –162.9 (br. m, 3 F, *p*-C$_6$*F*$_5$), –135.7 to –133.5 (br. m, 2 F, *o*-C$_6$*F*$_5$), –127.7 (br. m, 4 F, *o*-C$_6$*F*$_5$) ppm. ^{11}B NMR (96 MHz, CD_2Cl_2, ambient): δ = –10.8 (s) ppm. $C_{38}H_{22}BF_{15}N_2$ (802.39): calcd. C 56.88, H 2.76, N 3.49; found C 56.97, H 2.98, N 3.65.

Single-Crystal X-ray Structure Determinations: Crystal data are summarized in the Supporting Material. For data collection, crystals were mounted in inert oil and transferred to the cold gas stream of various Oxford Diffraction diffractometers. Data were recorded using monochromated Mo-K_α or mirror-focused Cu-K_α radiation. Absorption corrections were performed on the basis of multi-scans. For structure refinement, the structures were refined anisotropically on F^2 using the program system SHELXL-97.[63] Hydrogen atoms were included using a riding model or as rigid idealized methyl groups allowed to rotate but not tip. *Exceptions and special features:* Hydrogen atoms of coordinated double bonds were refined freely using C–H distance restraints. The methine hydrogen of **10** was also refined freely. For compound **4a**, the intensity data were weak, thus leading to a high R_{int} and a low GOF value. Compound **5a** crystallizes as a toluene solvate; the toluene molecule is well-ordered. For compound **9a**, the double bond C8=C9 is somewhat too long and the single bond C8–C10 is somewhat too short. An obvious explanation would be some disorder, whereby the double and single bonds exchange positions in the minor disorder component. However, all attempts to refine such a disorder were unsuccessful; the apparent occupation factor of the minor component lay in the range 0.1–0.2. Bond lengths in this moiety should be interpreted with caution.

CCDC-915264 (for **1b**), -915265 (for **1d**), -915266 (for **1e**), -915267 (for **4a**), -915268 (for **4b**), -915269 (for **5a**), -915270 (for **6a**), -915271 (for **6b**), -915272 (for **8a**), -915273 (for **8b**), -915274 (for **9a**) and -915275 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Details of the single-crystal X-ray structure determinations and presentations of the crystal structures of **6a** and **6b**. ^{1}H and ^{13}C NMR spectra of compounds **1b**–**1e**; ^{13}C NMR spectrum of compound **5b**.

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