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Synthesis and Characterization of Novel Carbene Complexes of Phosphorus(V) Fluorides with Potential Liquid-Crystalline Properties

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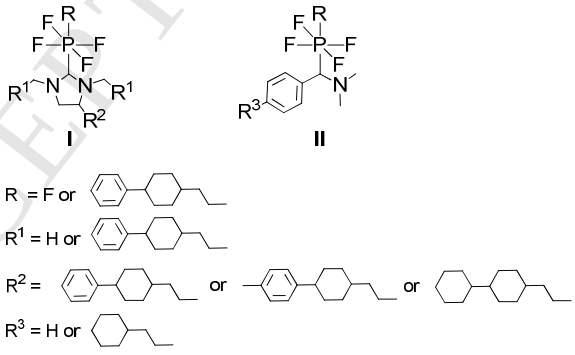
Abstract



A series of novel push-push **I** and push-pull **II** carbene-stabilized complexes of phosphorus(V) fluorides bearing substituents with liquid crystalline properties were synthesized by the oxidative addition of difluoroamines to phosphorus(III) halides. These octahedral complexes were characterized by NMR spectroscopy and X-Ray analysis.

1. Introduction

Over the last five decades, carbenes have played an important role as transient intermediates, however only during the past two decades, the understanding of carbene chemistry has advanced dramatically with the preparation and isolation of the first stable *N*-heterocyclic carbene (NHC).[1] Since then, nucleophilic diaminocarbenes (*push-push* carbenes) and their analogues have emerged as a powerful class of ligands for catalysis which show superior properties in comparison with their phosphine counterparts.[2] Despite the rapid evolution of NHCs as strong σ-donor ligands for transition metals, their application in other areas has experienced substantial advances only during the last 10 years. Especially the increased stability of the M-C_{NHC} bond of NHCs complexes as well as the possibility for structural diversity of NHCs beneficiated for their use in biomedical applications,[3] luminescent components[4] or self-assembled structures.[5] In the latter case, the self-assembly of amphiphilic metal-NHC complexes into birefringent materials provides a suitable approach for preparing metal-containing liquid crystals which are attractive due to the possibility of combining the physico-chemical metal-like properties (*i.e.* color, magnetism, polarizability, spectroscopic properties, redox behavior, *etc.*) with those of the organic framework. These complexes (metallomesogens) can be treated as a new kind of materials with many potential applications in optical and electronic devices.[6]

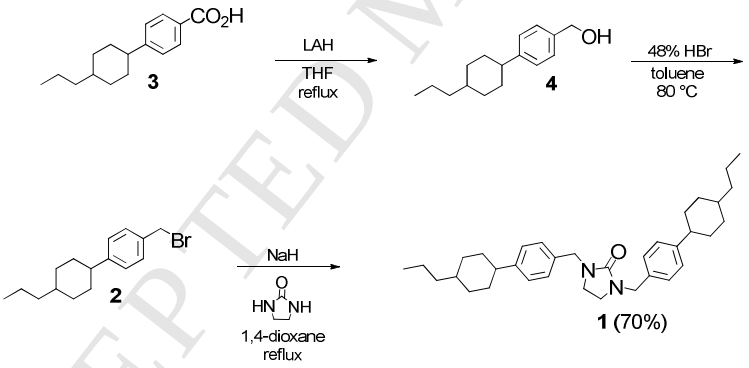
Up to now, only a small number of gold(I),[7] silver(I)[8] and palladium(II)[9] *N*-heterocyclic carbene complexes with various wingtip chain lengths has been proved for liquid-crystalline behavior. Generally, these compounds exhibit increased thermal stability connected with the strong covalent metal bonding to prevent decomposition at the clearing point. Moreover, they possess lower melting temperatures as well as birefringence. It should be however noted, that limited synthetic routes to these molecules and the use of expensive reagents hamper their potential application. Therefore, it is of great interest to design other types of carbene complexes, which are easy to apply, with exceptionally large dipole moments, a prerequisite for applications as liquid crystals. Usually, the dipole moment serve to improve their properties, which in turn could lead to increased brilliance in smarthphone displays or faster circuit time in monitors and flat screens. To fulfill these requirements, a series of carbene complexes of phosphorus(V) fluorides with potential liquid-crystalline properties has been investigated. These liquid crystalline properties could be achieved by the use of different sources of carbene (*push-push* or *push-pull*) as well as by variation of the periphery of carbenes, substituents at nitrogen (the wingtip groups) or at phosphorus. As substituents with liquid-crystalline properties, 4-propyl-1,1'-bi(cyclohexane) and 1-methyl-4-(4-propylcyclohexyl)benzene were used. The carbene ligands were introduced via oxidative addition using difluorobis(dialkylamines) (*push-push* carbenes), as well as difluoroorganyldialkylamines

(*push-pull* carbenes).[10] The latter precursor was reported by our group just recently and only a few examples of main group element compounds coordinated by these carbene ligands are known because aryl(amino)carbene are highly reactive in their free form and the first isolation was achieved not before 2001.[11]

Thus, in this paper we report the preliminary results of these studies as well as structural investigations of novel carbene complexes of phosphorus(V) fluorides with potential liquid-crystalline properties.

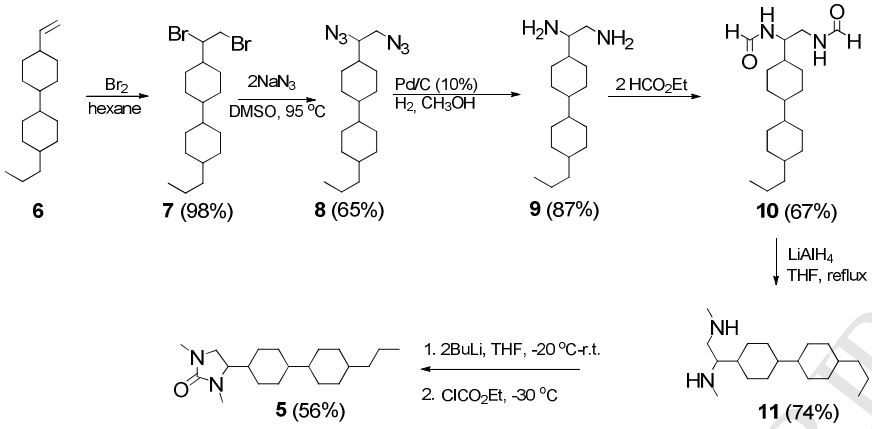
2. Result and Discussion:

In order to gain an access to difluorinated carbene precursors, the synthetic route to various *N*,*N*-disubstituted or 2-substituted-*N*,*N*-dimethyl imidazolidinones was initially investigated. A symmetrical compound **1**, bearing liquid-crystalline wingtip substituents attached to the nitrogen atoms, was successfully obtained *via* dibenzylation of the sodium salt of imidazolidinone using two equivalents of 1-(bromomethyl)-4-(4-propylcyclohexyl)benzene**2** in refluxing 1,4-dioxane (Scheme 1). Consecutively, the appropriate bromo derivative **2** was prepared by reducing the carboxylic acid **3** leading to benzyl alcohol **4**, which was then brominated with 48% of hydrobromic acid to give **2**.



Scheme 1.

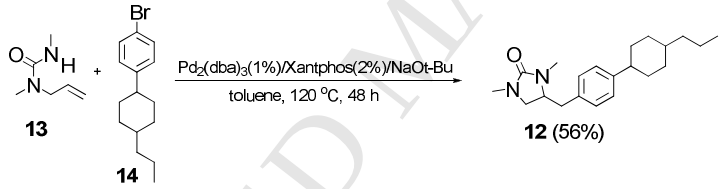
The peripheral liquid-crystalline functions were introduced using two different approaches. The 2-substituted-*N*,*N*-dimethyl imidazolidinone precursor **5** was obtained from the corresponding alkene **6** which was firstly brominated as presented in Scheme 2. This step furnished 1,2-dibromoalkane **7**, which was then substituted with 2 equiv. of sodium azide to give compound **8**, prior to the reduction of azide groups to appropriate 1,2-diamine **9**. Alkylation of the amino groups was then achieved by the reaction of **9** with 2 equiv of chloroformate, followed by reduction of the corresponding formamide **10** with lithium aluminium hydride. Subsequent cyclization of dimethylamine **11** to the desired imidazolidin-2-one **5** was achieved upon deprotonation of **11** with 2 equiv of *n*-butyllithium, followed by addition of ethyl chloroformate (Scheme 2).



6 **7** (98%) **8** (65%) **9** (87%) **10** (67%) **11** (74%) **5** (56%)

Scheme 2.

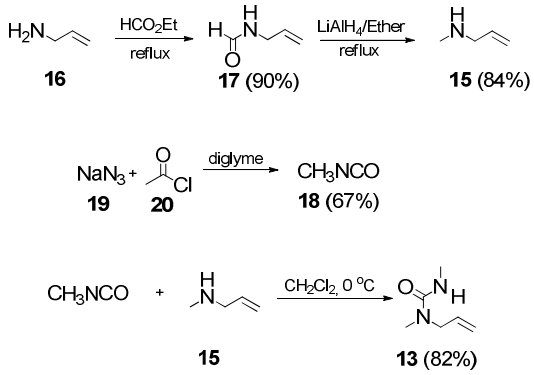
In contrast, the construction of the imidazolidin-2-one ring **12** was successfully accomplished using palladium-catalyzed carboamination of *N*-allylurea **13** with phenyl bromide **14** (Scheme 3).[12] Treatment of **12** with phenyl bromide **14** and NaO*t*-Bu in the presence of 1 mol % of palladium catalyst and 2 mol % of Xanthos afforded the desired product in good yield. It should be however noted, that an attempt to scale up this reaction to more than 1 g of **14** provided lower yield of **12**.



13 **14** **12** (56%)

Scheme 3.

N-Allylurea **13** was readily obtained by the reaction of methyl isocyanate **18** with appropriate *N*-allylamine **15** which was prepared **16** *via* its formylation and subsequent reduction of the formamide **17** using lithium aluminium hydride (Scheme 4). Methyl isocyanate **18** was synthesized by reaction of sodium azide **19** with acetyl chloride **20**, followed by the Curtius rearrangement of *in situ* formed acyl azide to isocyanate in dry diglyme as illustrated at Scheme 4.



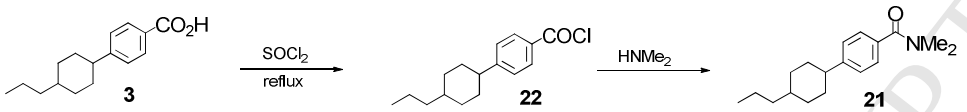
16 **17** (90%) **15** (84%)

19 **20** CH_3NCO **18** (67%)

15 **13** (82%)

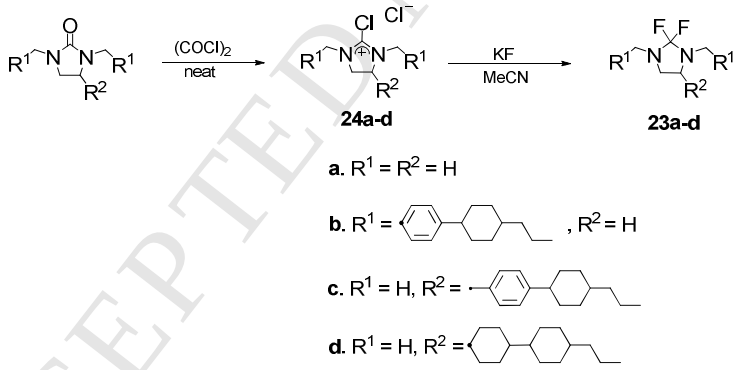
Scheme 4.

The method used to prepare the precursor of aryl(amino)carbene precursor (benzamide) **21** included the preparation of an appropriate acyl chloride **22** from carboxylic acid **3**, followed by the amidation of **22** with *N*,*N*-dimethylamine as presented in Scheme 5.



Scheme 5.

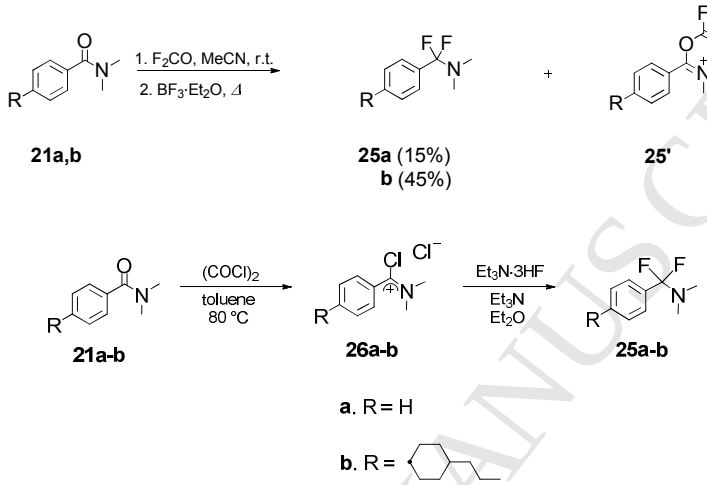
In the next step, appropriate imidazolidinone and benzamides were conveniently transformed to *push-push* carbene precursors - 2,2-difluoro-*N*,*N*-dimethylimidazolidinones **23a-d** and *push-pull* carbene source - 1,1-difluoro-*N*,*N*-dimethyl-phenylmethyldiamines by the known procedure.[13] This method was based on the halogen exchange reaction of appropriate chlorides **24a-d**, prepared from the respective precursors upon heating with oxalyl chloride, with an excess of spray-dried potassium fluoride in refluxing acetonitrile (Scheme 6). After filtration of the inorganic salts (KCl, KF), washing with MeCN or Et_2O, DFI was isolated in a pure form from the reaction mixture by evaporation of the filtrate.



Scheme 6.

Two approaches were applied to the preparation of the corresponding *α*,*α*-difluoroamine. Bearing in mind that various benzamides are able to undergo direct chlorination with using phosgene,[14] we have examined if the similar process for fluorination of amides using difluorophosgene might proceed. For these reasons, we condensed the appropriate amount of carbonyl difluoride onto the solution of amide **21a-b** in dry acetonitrile. Stirring of the resulting mixture at room temperature for 12 hours, subsequent addition of the catalytic amount of Lewis acid ($BF_3 \cdot Et_2O$) and refluxing in acetonitrile led however to the desired difluoroamines **25a-b** in only moderate yield (15% for **25a** and 45% for **25b**, according to ^{19}F NMR). The main product formed during the reaction was

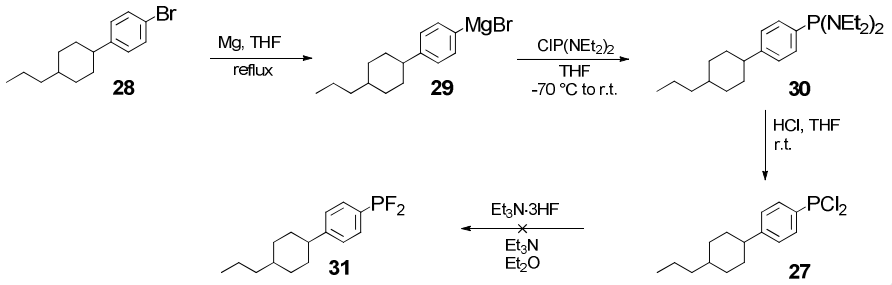
probably the more stable ester **25'** (30%), which might form the conjugated system together with phenyl ring und unreacted carbonyl difluoride as proposed in Scheme 7. Based on these results, we therefore carried out the fluorination *via* a modified procedure to improve the yield.[15] Consequently, benzamide **21a,b** was chlorinated using oxalyl chloride to chlorides **26a,b**, then fluorinated with triethylamine tris(hydrogen fluoride) in the presence of triethylamine to give *α,α*-difluoro(aryl)amines **25a-b** in good yield (Scheme 7).



Scheme 7.

Compounds **23a-d** and **25a-b** were then used as sources of carbene ligands in the oxidative addition to phosphorus(III) halides (fluorides or chlorides) to give carbene-stabilized complexes of substituted and unsubstituted phosphorus(V) fluorides. Noteworthy, difluoroamines are also prone to halide metathesis, therefore the use of easier-to-handle chlorophosphines instead of fluorophosphines is sometimes preferred, like in the case of **27.**[10]

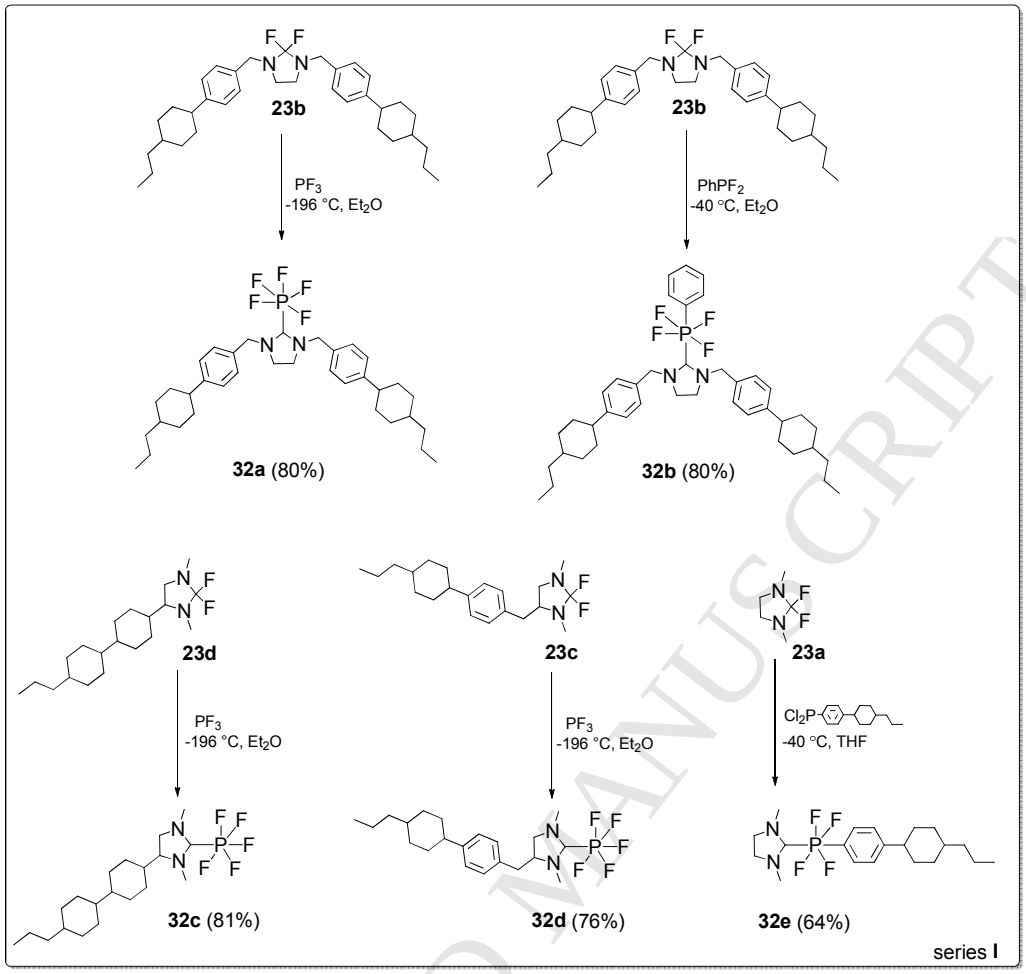
Thus, compound **27** was readily obtained from bromo-*n*PrCP **28** upon treatment with magnesium to give the corresponding Grignard reagent **29** which was then reacted with $ClP(NEt_2)_2$ to furnish **30**. By the substitution of amino groups for chlorine atoms using gaseous anhydrous HCl, the chlorophosphine **27** was formed conveniently. Noteworthy, attempts to prepare difluorophosphine **31** from chlorophosphine **27** were unsuccessful, however, and led to the oxidation of phosphorus. Therefore in this case the chlorophosphine **27** was used as a source of trivalent phosphorus (Scheme 8).

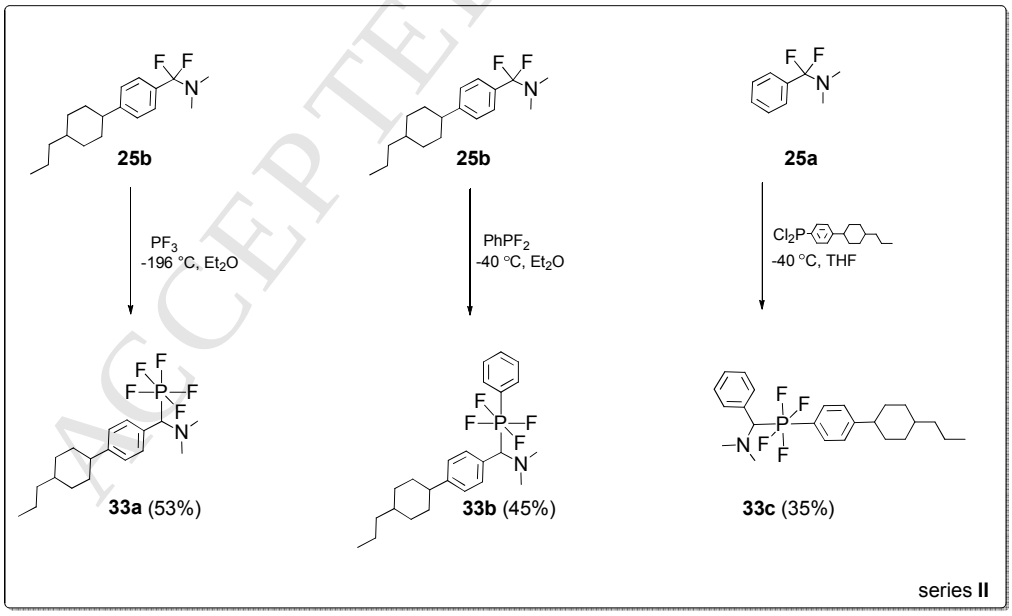


Scheme 8.

As mentioned above, carbene complexes of phosphorus(V) fluorides were obtained by oxidative addition of 2,2-difluorobis(alkylamines) **23a-d** and **25a-b** to phosphorus(III) halides. The complexes series **I** (*push-push* carbene complexes) and **II** (*push-pull* carbene complexes) were thus obtained as presented in Scheme 9.

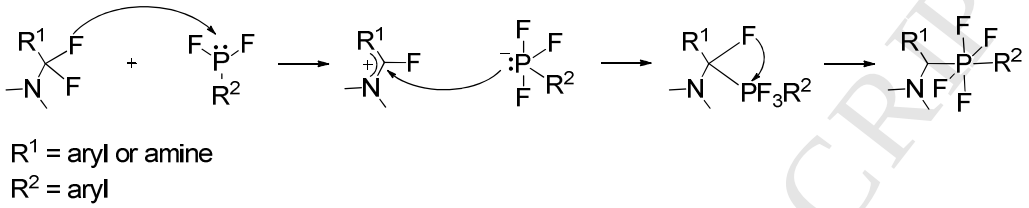
All reactions were carried out under Schlenk conditions in dry diethyl ether or tetrahydrofuran at -196 or -40 °C for 12 h, giving rise to complexes **32a-e** (series **I**) in very good or **33a-c** (series **II**) in moderate yield. In a typical procedure, phosphorus fluoride was condensed onto a frozen mixture (-196) of difluoroamine **23b,c,d; 25b** in anhydrous diethyl ether or appropriate dihalophosphine was added to a cooled (-40 °C) solution of difluoroamine **23a,b; 25a,b** in dry Et_2O or THF to furnish the corresponding adducts: **32a,c,d; 33a** or **32b,e; 33b,c,** respectively (Scheme 9). As observed, the increased reactivity in the series of diaminocarbenes **23a-d** resulted from the donation of the two strong σ-donors (nitrogen lone pairs) and hence enhanced nucleophilicity of the reaction center (higher yields of products) when compared to aryl(amino)carbenes. In the case, when dichlorophosphine **27** was used as a substrate **32e**, **33**c, the chloroamidinium chloride precipitated as a by-product was removed by washing with water. All liquid-crystalline complexes **32a-e** and **33a-c** were obtained as colorless solids, which are stable toward air and moisture. The stability of hexacoordinated phosphorus(V) fluorides in water is known and was reported some time ago by our working group.[16] A general, plausible mechanism toward the formation of these species is presented in Scheme 10. Noteworthy, this process could only be conducted when at least a single electron pair-active substituent is present in the structure of the carbene precursor.





Scheme 9.

Thus, in the first step a fluoride is transferred from the difluoride to phosphorus fluoride to give a phosphoranide and monofluorinated species. In the second step, the carbon atom at the 2 position of monofluoride cation undergoes nucleophilic attack by the phosphoranide to give a carbon-phosphorus bond. In the latter step, the redox-rearrangement takes place, where the electron poor and highly acidic phosphorus(III) abstracts the second fluoride and is oxidized to give phosphorus (V), whereas carbon(IV) is reduced to the carbene atom.[10]



Scheme 10.

All products were characterized by ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectroscopy and high resolution mass spectrometry. The most distinguished features could be observed in ^{19}F and ^{31}P NMR spectra. Selected chemical shifts and coupling constants were presented in Table 1.

Table 1. Selected chemical shifts [ppm] and coupling constants [Hz] of carbene complexes

	32a	**32b**	**32c**	**32d**	**32e**	**33a**	**33b**	**33c**
				δ [ppm], J [Hz]				
^{19}F	*-53.4* (dd) J_{FP} 798 J_{FF} 53.5 *-75.2* (dquint) J_{FP} 769 J_{FF} 53.4	*-42.2* (d) J_{FP} 871	*-56.6* (dd) J_{FP} 759 J_{FF} 51.0 *-74.7* (dquint) J_{FP} 758 J_{FF} 51.0	*-56.8* (dd) J_{FP} 796 J_{FF} 50.6 *-74.6* (dquint) J_{FP} 796 J_{FF} 50.6	*-45.0* (d) J_{FP} 865	*-59.4* (dd) J_{FP} 815 J_{FF} 50. *-73.3* (dquint) J_{FP} 751 J_{FF} 33.2	*-47.9* (d) J_{FP} 887	*-47.0* (d) J_{FP} 887
^{31}P	*-153.3* (dquint) J_{PF} 800 J_{PF} 770	*-138.9* quint J_{PF} 800	*-150.3* (dquint) J_{PF} 797 J_{PF} 760	*-150.4* (dquint) J_{PF} 796 J_{PF} 758	*-139.1* (quint) J_{PF} 865	*-149.8* (dquint) J_{PF} 815 J_{PF} 744	*-140.8* (quint) J_{PF} 886	*-139.1* (quint) J_{PF} 887

For the diaminocarbene adducts **32a, c, d**, two magnetic environments for the fluorine centers could be distinguished. These two fluorine signals (doublet of doublets and doublet of quintets) occur in a 1:4 ratio and correspond to the axial (opposite to the carbene) and equatorial (adjacent to the carbene) fluorine sites. Moreover, the larger F-P coupling constants to the equatorial fluorine substituents than to axial is observed what could be explained by higher *s*-character of orbitals used by phosphorus to make its equatorial bonds. The ^{31}P NMR spectra of **32a, c, d** show a doublet of

quintets at about -150 ppm, which clearly indicates the presence of a hexacoordinated phosphorus center. For the PF_4Ph adducts **32b, e**, the ^{19}F resonance appears as a doublet at about -42.2 and -45.0 ppm, suggesting four equatorial fluorine sites whereas ^{31}P NMR spectrum shows a quintet at -138 and -139 ppm, respectively. Examining the data given for aryl(amino)carbene complexes **33a-c**, the similar coupling pattern in ^{19}F as well as ^{31}P NMR is observed for PF_5 (**33a**) and PF_4Ph (**33b, c**) complexes when compared to the previously described diaminocarbene adducts. However for the products derived from the *push-push N*-heterocyclic carbene source, the phosphorus resonance occurs at slightly higher field than for the adduct derived from *push-pull* carbene precursor indicating, as expected, greater relative electron donating ability of the diaminocarbene. Moreover, analysis of the ^{13}C NMR chemical shifts of the carbene centers suggests a strong phosphorus bond to carbene carbon nuclei. Examining the resonance of the corresponding free carbenes, these signals fall approximately 60 ppm upfield for diaminocarbene complexes and 110 ppm for aryl(amino)adducts.[11,17]

As reported above, adducts derived from oxidative addition of difluoroamines to phosphorus(III) fluorides (chlorides) were stable compounds and compound **32e** could conveniently be recrystallized to produce suitable crystals for X-Ray analysis. Single crystal of **32e** was thus obtained by slow diffusion of diethyl ether into a solution of the adduct in acetonitrile. Compound **32e** crystallizes in the triclinic space group *P-1* and its X-Ray crystal structure is illustrated in Figure 1. Selected structural parameters of **32e** are given in Table 2.

Table 2. Selected bond lengths [pm] and angles [°C] for **32e**

	32e
$C_{carbene}$-P	190.7(5)
P-C_{aryl}	181.9(5)
av $C_{carbene}$-N	133.4(6)
av P-F	162.8(3)
$C_{carbene}$-P-C_{aryl}	179.3(2) °
NHC/phenyl	87.3 °

The structure of **32e** shows the expected octahedral geometry at the phosphorus atom, with almost linear C-P-C bond (179.3°). The four equatorial fluorine atoms form a plane with a slight up-down altering arrangement of the fluorines. Moreover, similarly to the Arduengo carbene adduct,[17] the NHC and the phenyl ring are twisted by 87.3° to perpendicular configuration (Figure 1), what could be explained by the packing effects of the crystal lattice (Figure 2). As observed, the crystal consists

of parallel layers of head-to-tail ‘dimers’, where imidazole and phenyl rings are in every layer parallel to each other.

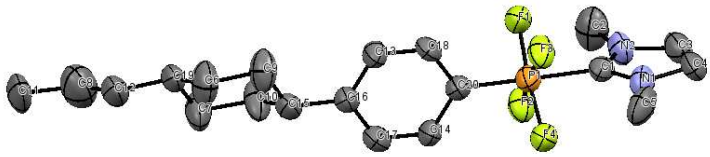


Figure 1.

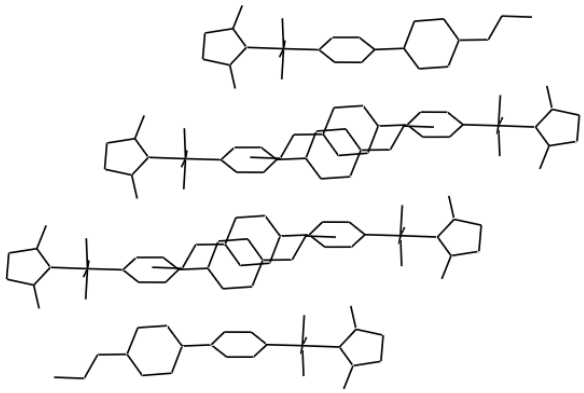


Figure 2.

The carbene-phosphorus bond distance in **32e** is rather long (190.7 pm), but very similar to the corresponding NHC carbene adducts described in the literature.[10,17,18] The C-P bond length of the *ipso*-carbon of the phenyl substituent resembles a normal P-C single bond whereas the C-N bond distance is typical for NHC complexes but longer as for other *push-pull* complex.[11]

3. Conclusions

A series of novel *push-push* and *push-pull* carbene complexes of phosphorus(V) fluorides bearing liquid-crystalline substituents has been prepared and characterized by NMR spectroscopy. Compound **32e** was additionally characterized by X-Ray. Moreover, for the first time 1,1-difluoro-*N,N*-dimethyl-1-phenylmethanamine was used in the oxidative addition to phosphorus(III) halides as a source of aryl(amino)carbene. Further studies including the properties and application of novel carbene complexes as liquid-crystalline molecules will be reported in due course.

4. Experimental Part

All reactions were carried out under an atmosphere of dry argon. THF was freshly distilled from sodium benzophenone ketyl. Reagents obtained from commercial sources (1.3-dimethylimidazolidinone, *N,N*-dimethylbenzamide, phosphorus trifluoride), were used without further purification. All other reagents were distilled or recrystallized, if necessary. DFI was obtained according to the known procedure.[13] Phenyldifluorophosphine was prepared by the method of Riesel *et al*.[19] Column chromatography was performed using Merck silica gel 60 (230–400 mesh ASTM) and TLCs using Merck silica gel 60 F254.Visualization was achieved by UV light or by spraying with $Ce(SO_4)_2$ solution in 5% H_2SO_4. ^1H (400 MHz), ^{13}C (100 MHz), ^{19}F (376 MHz) and ^{31}P NMR (161 MHz) spectra were measured on a JEOL ECX 400 MHz spectrometer at room temperature using 5 mm tubes. TMS was the internal standard in ^1H NMR, $CFCl_3$ was used as a reference for ^{19}F NMR and 85% H_3PO_4 in ^{31}P NMR. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. ^{31}P NMR spectra were broadband decoupled from hydrogen nuclei. High resolution mass spectra were recorded on a MicroTOF-Q fitted with an ESI source. Elemental analysis was performed by the 'Microanalytical Laboratory Beller-Matthies' in Göttingen. Melting points were determined with an Electrothermal IA9100 Digital Melting Point Apparatus and are uncorrected.

[4-(4-Propylcyclohexyl)phenyl]methanol **(4)**

Lithium aluminium hydride (3.1 g, 2 equiv.) was added to a solution of carboxylic acid **3** (10 g, 1 equiv.) in dry THF and the mixture was refluxed for 10 h. The reaction was quenched with water (10 mL), 15% NaOH (10 mL) and water (30 mL), stirred for 1 hour and then filtered. The filtrate was dried over Na_2SO_4, evaporated under reduced pressure to give pure [4-(4-propylcyclohexyl)phenyl]methanol **4** as a white solid.

Yield: 93%; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.9 (t, J = 7.3 Hz, 3H), 1.1 (m, 2H), 1.3 (m, 8H, C*H*, O*H*), 1.9 (m, 2H), 2.6 (tt, J = 12.2, 3.2 Hz, 1H), 4.7 (s, 2H), 7.2 (d, J = 7.0 Hz, 2H), 7.3 (d, J = 7.0 Hz, 2H)

1-(Bromomethyl)-4-(4-propylcyclohexyl)benzene **(2)**

Toluene (100 mL) and 48% hydrobromic acid (20 mL) were mixed together with benzyl alcohol **4** (15 g, 65 mmol) and the mixture was stirred at 80°C for 14 hr. After partitioning, the organic layer was successively washed with water (50 ml), saturated aqueous sodium hydrogen carbonate (50 ml), water (50 ml) and saturated brine and dried over magnesium sulfate. After filtration and solvent evaporation, the residue was dried *in vacuo* to give **2** as a pale-yellow oil.

Yield: 84%; ^1H NMR (400 MHz, $CDCl_3$) δ: 0.9 (t, J = 7.3 Hz, 3H), 1.1 (m, 2H), 1.3 (m, 7H), 1.9 (m, 2H), 2.5 (tt, J = 12.2, 3.2 Hz, 1H), 4.5 (s, 2H), 7.2 (d, J = 7.0 Hz, 2H), 7.3 (d, J = 7.0 Hz, 2H)

1,3-Bis[4-(4-propylcyclohexyl)benzyl]imidazolidin-2-one **(1)**

A mixture of cyclic urea (1.5 g, 17 mmol), NaH (0.8 g, 34 mmol) and dioxane (100 mL) was refluxed for 1.5 h. The suspension was cooled to 20°C and then bromide **2** (10 g, 34 mmol) was added. The mixture was refluxed for 5 hrs, cooled to r.t. and filtered. The solvent was evaporated from the filtrate, to afford a white solid **1** which was purified by recrystallization from dichloromethane-pentane.

Yield: 70%; mp 180-190°C. ^{1}H NMR (399.8 MHz, $CDCl_3$) δ: 0.9 (t, J = 7.3 Hz), 1.0 (m, 4H), 1.3 (m, 14H), 1.9 (m, 8H), 2.4 (m, 2H), 3.2 (s, 4H), 4.4 (s, 4H), 7.16 (d, J = 8.2 Hz, 4H), 7.19 (d, J = 8.2 Hz, 4H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ: 14.5, 20.1, 33.7, 34.4, 37.1, 39.8, 44.4, 48.3, 127.1, 128.3, 134.8, 147.2, 161.2 (*C*=O)

4-(1,2-Dibromoethyl)-4'-propylbi(cyclohexane) **(7)**

To a solution of **6** (0.2 mol) in hexane (30 mL), 1 equiv. of bromine was added slowly at ambient temperature, and then the reaction mixture was stirred for 3 hrs. Hexane was removed *in vacuo* and the dibromide **7** was obtained as yellow crystals which were used in the next step without further purification.

Yield: 98%; mp. 51-53 ºC; ^{1}H NMR (399.8 MHz, $CDCl_3$): δ 0.86 (t, J = 6.8 Hz, 3H, CH_3), 0.90-1.44 (m, 14H), 1.62-1.86 (m, 10H), 3.74 (A-part ABX, J = 10.4, 9.6 Hz, 1H), 3.81 (B-part ABX, J = 10.4, 5.6 Hz, 1H), 4.16 (m, 1H).

4-(1,2-Diazidoethyl)-4'-propylbi(cyclohexane) **(8)**

A mixture of **7** (0.2 mol) and NaN_3 (2 mol) in DMSO (30 mL) was stirred at 95 ^{o}C for 10 h. Than the mixture was diluted with 150 mL of water and extracted with hexane (5×20 mL). The organic layers were combined, washed with brine and dried over $NaSO_4$. The solvent was removed and the residue was purified by column chromatography eluting with *n*-hexane, giving pure **8** as an yellow oil.

Yield: 65%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, J = 6.8 Hz, 3H, CH_3), 0.79-1.20 (m, 13H), 1.22-1.34 (m, 2H), 1.45 (m, 1H), 1.62-1.86 (m, 8H), 3.25 (m, 1H), 3.34 (A-part ABX, J = 12.8, 7.8 Hz, 1H), 3.44 (B-part ABX, J = 12.8, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 20.1, 28.9, 29.4, 29.5, 29.9, 30.1, 33.6, 37.7, 39.9, 40.4, 43.0, 43.3, 53.3, 67.7.

1-[4'-Propylbi(cyclohexan)-4-yl]ethane-1,2-diamine **(9)**

A mixture of **8** (0.2 mol) and 0.05 equiv. of Pd (10% on C) in EtOH (30 mL) was stirred overnight under H_2 atmosphere at room temperature. The Pd/C was filtered off and EtOH was removed giving pure **9** as an yellow oil.

Yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.79-2.0 (m, 31H), 2.44 (m, 2H), 2.77 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 20.1, 28.7, 29.9, 30.0, 30.1, 33.7, 37.7, 39.9, 42.3, 43.4, 46.1, 58.7.

N,N'-1-[4'-Propylbi(cyclohexan)-4-yl)ethane-1,2-diyl]diformamide **(10)**

A mixture of **9** (0.02 mol), 10 equiv. of ethyl formate in 20 mL of $CHCl_3$ was refluxed for 24 hrs. All volatiles were removed at reduced pressure and the residue was crystallized from acetone giving a crystalline product containing ~80% of the desired **10** (according to NMR). This mixture was used in the next step without further purification.

Yield: 67%; ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.80 (t, J = 6.8 Hz, 3H, CH_3), 0.77-1.00 (m, 10H), 1.08 (m, 2H), 1.23 (m, 2H), 1.65 (m, 10H), 2.98 (m, 1H), 3.27 (m, 1H), 3.66 (m, 1H), 7.70-8.05 (m, 4H, NH, C(O)H).

N,N-Dimethyl-1-[4'-propylbi(cyclohexan)-4-yl]ethane-1,2-diamine **(11)**

To a suspension of $LiAlH_4$ (0.035mol) in 50 mL of dry THF, diformamide **10** (0.02 mol) was added portionwise under stirring and cooling with an ice bath. The reaction mixture was refluxed for 15 h. Than 5 mL of water was dropwise added. All precipitates were filtered off and washed with diethyl ether. The organic layers were extracted with water (5×10 mL), dried over NaOH. The solvent was removed giving **11** as an yellow oil, which was used in the next step without purification.

Yield: 74%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, J = 6.8 Hz, 3H, CH_3), 0.79-1.20 (m, 10H), 1.11 (m, 2H), 1.28 (m, 2H), 1.42 (bs, 2H, NH), 1.61-1.80 (m, 10H), 2.25 (m, 1H), 2.39 (A-part ABX, J = 12.0 Hz, 8.4 Hz, 1H), 2.38 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.59 (B-part ABX, J = 12.0 Hz, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 20.1, 25.7, 28.7, 30.0, 30.2, 33.7, 34.8, 36.9, 37.7, 39.3, 39.9, 43.5, 43.6, 52.5, 64.2, 68.1.

1,3-Dimethyl-4-[4'-propylbi(cyclohexan)-4-yl]imidazolidin-2-one **(5)**

To a stirred solution of **11** (24 mmol) in 100 mL of THF, two equiv. of 2.5M *n*-BuLi in hexanes were dropwise added. The reaction mixture was stirred at ambient temperature for 2 hrs. Then the reaction mixture was cooled to -30 ºC and one equiv. of ethyl chloroformate (2.61 g, 24 mmol) dissolved in 10 mL of THF was dropwise added upon stirring. The resulting solution was stirred at room temperature overnight and filtered through a glass frit. The solution was washed with brine, and dried over $NaSO_4$. The solvent was removed, and the residue was purified by chromatography (eluent: $CHCl_3$/AcOEt = 10/1), giving pure **5** as white crystals.

Yield: 56%; mp 69-80 ºC ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, J = 6.8 Hz, 3H, CH_3), 0.79-1.08 (m, 10H), 1.12 (m, 2H), 1.29 (m, 2H), 1.51-1.82 (m, 10H), 2.73 (s, 3H, CH_3), 2.75 (s, 3H, CH_3), 2.97 (A-part ABX, J = 8.7, 7.8 Hz, 1H), 3.19 (B-part ABX, J = 8.7, 7.0 Hz, 1H), 3.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 20.1, 25.6, 28.8, 29.4, 29.9, 30.1, 31.3, 33.6, 37.7, 38.5, 39.9, 43.4, 43.6, 47.0, 59.7, 161.8.

1-Allyl-1,3-dimethylurea **(13)**

An oven- or flame-dried round bottom flask equipped with a stirbar was cooled under a stream of nitrogen and charged with *N*-allylamine **15** (0.02 mol), the appropriate isocyanate (0.022 mol), and CH_2Cl_2 (20 mL). The reaction was stirred at room temperature until the starting amine was

completely consumed as monitored by TLC analysis. The reaction mixture was then concentrated *in vacuo* and the crude product was purified by column chromatography on silica gel giving **13** as an yellow oil (eluent: CH_2Cl_2).

Yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.84 (s, 3H, CH_3), 2.78 (d, *J* = 6.0 Hz, 3H, CH_3), 3.85 (dm, *J* = 6.5 Hz, 2H, CH_2), 4.39 (bs, 1H, NH), 5.12 (m, 1H), 5.15 (s, 1H), 5.76 (m, 1H).

1,3-Dimethyl-4-[4-(4-propylcyclohexyl)benzyl]imidazolidin-2-one **(12)**

An oven- or flame-dried Schlenk tube equipped with a stirbar was cooled under a stream of nitrogen and charged with $Pd_2(dba)_3$ (1 mol % complex, 2 mol % Pd), Xantphos (2 mol %), NaOtBu (1.2 equiv), *N*-allylurea **13** (1.0 equiv), and the aryl bromide **14** (1.2 equiv). The tube was purged with nitrogen and toluene (4ml/mmol of urea) was then added. The urea was added at the same time as toluene. The Schlenk tube was then heated to 110 °C with stirring until total consumption of the starting materials as judged by GC of the reaction mixture. The mixture was then cooled to r.t., saturated aqueous NH_4Cl (4–6 mL/mmol substrate) was added, and the mixture was extracted with methylene chloride (3×7 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by chromatography on silica gel (eluent: CH_2Cl_2) to give **12** as an yellow oil.

Yield: 56%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.3 Hz, 3H, CH_3), 1.02 (m, 2H), 1.16-1.48 (m, 7H), 1.8-1.9 (m, 4H), 2.43 (tt, *J* = 11.9, 3.2 Hz, 1H), 2.55 (dd, *J* = 13.7, 9.2 Hz, 1H), 2.71 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 2.91 (dd, *J* = 8.7, 7.8 Hz, 1H), 3.08 (dd, *J* = 15.6, 4.6 Hz, 1H), 3.17 (t, *J* = 8.7 Hz, 1H), 3.57 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 20.1, 29.8, 31.3, 33.6, 34.4, 37.1, 38.4, 39.8, 44.3, 50.8, 57.2, 127.2, 129.1, 134.1, 146.5, 161.8.

General procedure for the synthesis of chloroamidinium chlorides (**24a-d)**: *N,N´*-Disubstituted cyclic urea (6 mmol) was dissolved in toluene (50 mL) and oxalyl chloride (7.6 g, 5.2 mL, 60 mmol) was added. The resulting mixture was stirred at 80 °C for 12 hrs. The white precipitate was then filtered off under an inert atmosphere, washed with anhydrous Et_2O and dried *in vacuo* to give the pure chloride as a white solid.

2-Chloro-1,3-bis[4-(4-propylcyclohexyl)benzyl]-4,5-dihydro-1H-imidazol-3-ium chloride **(24b)**

Yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.9 (t, *J* = 7.3 Hz), 1.0 (m, 4H), 1.3 (m, 14H), 1.9 (m, 8H), 2.4 (m, 2H), 3.4 (s, 4H), 4.9 (s, 4H), 7.18 (d, *J* = 8.2 Hz, 4H), 7.22 (d, *J* = 8.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 14.5, 20.1, 33.6, 34.4, 37.1, 39.8, 44.3, 47.7, 53.2, 127.5, 128.7, 131.7, 148.4, C^2 not observed.

2-Chloro-1,3-dimethyl-4-[4-(4-propylcyclohexyl)benzyl]-4,5-dihydro-1H-imidazol-3-ium chloride (**24c)**

Yield: 89%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (t, *J* = 7.3 Hz, 3H, CH_3), 0.80-1.18 (m, 13H), 1.29 (m, 2H), 1.49 (m, 1H), 1.61-1.90 (m, 8H), 3.27 (s, 3H), 3.30 (s, 3H), 3.69 (m, 1H), 4.55 (m, 1H), 4.69 (m, 1H).

2-Chloro-1,3-dimethyl-4-[4'-propyl-1,1'-bi(cyclohexyl)-4-yl]-4,5-dihydro-1H-imidazol-3-ium chloride (**24d)**

Yield: 79%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.3 Hz, 3H, CH_3), 1.03 (m, 2H), 1.16-1.48 (m, 7H), 1.80-1.90 (m, 4H), 2.43 (tm, *J* = 8.7 Hz, 1H), 3.05 (A-part ABX, *J* = 14.2, 7.8 Hz, 1H), 3.15 (B-part ABX, *J* = 14.2, 5.0 Hz, 1H), 3.15 (s, 3H, CH_3), 3.30 (s, 3H, CH_3), 3.77 (dd, *J* = 11.0 6.9 Hz, 1H), 4.40 (t, *J* = 11.5 Hz, 1H), 4.93 (m, Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H);

N-{Chloro[4-(4-propylcyclohexyl)phenyl]methylene}-N-methylmethanaminium chloride (**26b)**

Yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.9 (t, *J* = 7.3 Hz, 3H), 1.1 (m, 2H), 1.3 (m, 8H, C*H*), 1.9 (m, 2H), 2.5 (t, *J* = 12.4 Hz, 1H), 3.3 (s, 6H), 7.2 (d, *J* = 8.2 Hz, 2H), 7.3 (d, *J* = 8.2 Hz, 2H)

General procedure for the synthesis of difluorides (**23b-d)**:

To a solution of imidazolium chloride **24b-d** (3.5 mmol) in anhydrous acetonitrile 60 mL, (10 equiv.) of spray dried potassium fluoride were added. The reaction mixture was heated with stirring at 85 ºC under argon for 12 hours. After cooling to room temperature, insoluble solids (KCl, KF) were filtered off under an inert atmosphere. The solids were washed three times with anhydrous Et_2O. The filtrate was concentrated *in vacuo* to give pure difluoride.

2,2-Difluoro-1,3-bis[4-(4-propylcyclohexyl)benzyl]imidazolidine (**23b)**

Yield: 76%; white hygroscopic solid; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.9 (t, *J* = 7.3 Hz), 1.0 (m, 4H), 1.3 (m, 14H), 1.9 (m, 8H), 2.4 (m, 2H), 2.9 (s, 4H), 4.1 (s, 4H), 7.16 (d, *J* = 8.2 Hz, 4H), 7.19 (d, *J* = 8.2 Hz, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) *δ*: -67.3 (s, 2F).

2,2-Difluoro-1,3-dimethyl-4-[4-(4-propylcyclohexyl)benzyl]imidazolidine (**23c)**

Yield: 86%; colorless oil; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -73 (bs)

2,2-Difluoro-1,3-dimethyl-4-[4'-propyl-1,1'-bi(cyclohexyl)-4-yl]imidazolidine (**23d)**

Yield: 83%; colorless oil; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -73 (bs)

General procedure for the synthesis of difluorides (**25a,b)**:

A solution of benzamide **21a** or **b** (67 mmol) in dichloromethane (60 mL) was placed into a 2-neck 250 mL flask equipped with a reflux condenser. Oxalyl chloride (74 mmol) was slowly added and the reaction mixture was refluxed for 1 h. After reaching room temperature, triethylamine trihydrofluoride (50 mmol) was added, followed by dropwise addition of triethylamine (100 mmol). The reaction mixture was diluted with 40 mL of dichloromethane and stirred for 3 hrs. Compounds **25a** or **b** were obtained by fractional distillation of the reaction mixture under reduced pressure.

1,1-Difluoro-N,N-dimethyl-1-phenylmethanamine (**25a)**

Yield: 83%; colorless liquid; bp 50-51 °C/0.001 Bar; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.5 (s, 6H, CH_3), 7.4-7.6 (m, 5H, Ph); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -85.7 (s, 2F).

1,1-Difluoro-N,N-dimethyl-1-[4-(4-propylcyclohexyl)phenyl]methanamine **(25b)**

Yield: 90%; colorless liquid; bp 100-102 °C/0.001 Bar; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -67.5 (s, 2F)

N,N,N',N'-Tetraethyl-1-[4-(4-propylcyclohexyl)phenyl]phosphinediamine (**30)**

A solution of **28** (10g, 36 mmol) in dry THF (40 mL) was slowly added into a 250 mL 2-neck flask equipped wit a reflux condenser, to a suspension of magnesium turnings (0.87 g, 36 mmol) in THF (20 mL). The reaction mixture was refluxed for 1h and then cooled to -20 °C. A solution of $ClP(NEt_2)_2$ (7.6 g, 36 mmol) in THF (15 mL) was slowly added. The reaction mixture was stirred for 16 h, during which it was allowed to reach room temperature. After removing of all volatiles under reduced pressure, the residue was dissolved in Et_2O (100 mL) and filtered through a celite to give a pale yellow solution of **30**.

^{31}P NMR (161 MHz, Et_2O): δ 98.1 (s)

Dichloro[4-(4-propylcyclohexyl)phenyl]phosphine **(27)**

Dry gaseous HCl was passed through a solution of **30** (11g, 36 mmol) in Et_2O (100 mL) at r.t. until the reaction was completed (monitoring by ^{31}P NMR). The reaction mixture was then passe through a P4 glass frit and all volatile components were removed under reduced pressure. The residue was washed with small amount of Et_2O. Drying *in vacuo* gave **27** as a pale yellow solid.

Yield: 88%; ^{31}P NMR (161 MHz, Et_2O): δ 162.6 (s)

General procedure for the synthesis of PF_5 carbene complexes **(32a,c,d)** *and* **(33a)**: Onto a frozen solution (-196 °C) of an appropriate difluoride **23b,c,d ; 25b** (5 mmol) in dry diethyl ether (20 mL), an equimolar amount of phosphorus trifluoride was condensed using a vacuum line. The resulting mixture was then left with stirring overnight and concentrated *in vacuo*. The precipitate was filtered off, washed with cold ether, ethanol and hexane to give the corresponding adduct which was additionally recrystallized from acetonitrile.

1,3-Bis[4-(4-propylcyclohexyl)benzyl]imidazolin-2-ylidene – phosphorus(V) pentafluoride adduct **(32a)**

Yield: 80%; white crystals; mp 235-245°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.9 (t, J = 7.3 Hz), 1.0 (m, 4H), 1.3 (m, 14H), 1.9 (d, J = 11.0 Hz, 8H), 2.5 (m, 2H), 3.4 (s, 4H), 4.9 (s, 4H), 7.18 (d, J = 8.2 Hz, 4H), 7.23 (d, J = 8.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 20.1, 33.6, 34.4, 37.1, 39.8, 44.3, 48.2, 52.5, 127.9, 128.7, 149.3, 155.0, C^2 not observed; ^{19}F NMR (376 MHz, $CDCl_3$): δ -75.2 (dquint, J_{FP} = 768.7 Hz, J_{FF} = 53.4 Hz, PF_4F), -53.4 (dd, J_{PF} = 797.6 Hz, J_{FF} = 53.5 Hz, PF_4F); ^{31}P NMR (161 MHz, $CDCl_3$): δ -153.3 (dquint, J_{PF} = 800.4 Hz, J_{PF} = 770.4 Hz, PF_4F); HRMS (ESI, positive): Calcd for $C_{36}H_{55}F_5N_2PNa$ 664.3920 $[M+Na]^+$, found: 664.3914.

1,3-Dimethyl-4-{4'-propyl-[1,1'-bi(cyclohexan)]-4-yl}imidazolin-2-ylidene - phosphorus(V) pentafluoride adduct (**32c)**

Yield: 76%; white crystals; mp 180-182 °C; ^{1}H NMR (400 MHz, Acetone-d_6): δ 0.84 (t, *J* = 7.3 Hz, 3H, CH_3), 0.91-1.18 (m, 13H), 1.29 (m, 2H), 1.43 (m, 1H), 1.57 (m, 1H), 1.65-1.85 (m, 7H), 3.20 (s, 6H), 3.64 (m, 1H), 3.89 (m, 1H), 4.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 19.7, 26.1, 29.3, 29.9, 30.8, 31.5, 31.9, 34.5, 37.7, 38.2, 40.5, 41.4, 43.1, 53.5 (d, J_{CP} = 11.0 Hz), 61.2 (d, J_{CP} = 10.3 Hz); ^{31}P NMR (162 MHz, Acetone-d_6): δ -150.27 (quint,d, *J* = 796.6, 760.1 Hz); ^{19}F NMR (376 MHz, Acetone-d_6): δ -56.6 (dd, J_{FP} = 758.6 Hz, J_{FF} = 50.6 Hz, 4F), -74.7 (dquint, J_{FP} = 758.2 Hz, J_{FF} = 50.6 Hz, 1F); Anal. Calc. for $C_{20}H_{36}F_5N_2P$: C, 55.80%; H, 8.43%; N, 6.51%. Found: C, 55.91%; H, 8.36%; N(6.41%).

1,3-Dimethyl-4-[4'-(4-propylcyclohexyl)benzyl]imidazolin-2-ylidene - phosphorus(V) pentafluoride adduct **(32d)**

Yield: white crystals; mp 192-195 °C; ^{1}H NMR (400 MHz, Acetone-d_6): δ 0.88 (t, *J* = 7.3 Hz, 3H, CH_3), 1.07 (m, 2H), 1.00-1.11 (m, 2H), 1.15-1.23 (m, 2H), 1.31 (m, 3H), 1.47 (m, 2H), 1.83 (m, 4H), 2.45 (tm, *J* = 12.4 Hz, 1H), 2.82 (dd, *J* = 13.7 Hz, 8.7 Hz, 1H), 3.07 (s, 3H, CH_3), 3.21 (dd, *J* = 13.7 Hz, 4.1 Hz, 1H), 3.33 (s, 3H, CH_3), 3.55 (dd, *J* = 11.9 Hz, 6.4 Hz, 1H), 3.85 (t, *J* = 11.5 Hz, 1H), 4.33 (m, Hz, 1H), 7.12-7.25 (m, 4H); ^{13}C NMR (101 MHz, Acetone-d_6): δ 13.8, 19.8, 33.5, 34.3, 34.3, 36.6, 36.9, 39.7, 44.2, 55.7 (d, J_{CP} = 10.6 Hz), 63.4 (d, J_{CP} = 9.7 Hz), 127.1, 129.5, 133.0, 146.6; ^{31}P NMR (162 MHz, Acetone-d_6): δ -150.47 (quint,d, *J* = 796.5, 758.8 Hz); ^{19}F NMR (376 MHz, Acetone-d_6): δ -56.8 (dd, J_{FP} = 796.2 Hz, J_{FF} = 50.6 Hz, 4F), -74.6 (dquint, J_{FP} = 796.2 Hz, J_{FF} = 50.6 Hz, 1F); Anal. Calc. for $C_{21}H_{32}F_5N_2P$: C, 57.53%; H, 7.36%; N, 6.39%. Found: C, 57.45%; H, 7.28%; N, 6.32%.

Dimethylamino[4-(4-propylcyclohexyl)phenyl]methylidene - phosphorus(V) pentafluoride adduct **(33a)**

Yield: 53 %; white solid, mp 170–172°C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 0.88 (t, *J* = 7.3 Hz, 3H, CH_3), 1.04 (m, 2H), 1.19-1.49 (m, 7H), 1.8-1.9 (m, 4H), 2.53 (tt, *J* = 11.9, 3.2 Hz, 1H), 3.1 (s, 3H, CH_3), 3.9 (s, 3H, CH_3), 7.1 (d, *J* = 7.8 Hz, 2H), 7.3 (d, *J* = 8.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): *δ* -59.4 (dd, J_{FP} 814.9 Hz, J_{FF} 49.1 Hz); -73.3 (dquint, J_{FP} 751.4 Hz, J_{FF} 33.2 Hz). ^{31}P NMR (161 MHz, $CDCl_3$): *δ* -149.8 (dquint, J_{PF} 815.4 Hz, J_{PF} 744.2 Hz); HRMS (ESI, positive): Calcd for $C_{18}H_{28}F_5NPNa$ 407.1777 $[M+Na]^+$, found: 407.1772.

General procedure for the synthesis of PF_4Ph carbene complexes **(32b, 33b):**

Phenyldifluorophosphine (3.4 mmol) was added to a solution of difluoride (3.2 mmol) in 30 mL of anhydrous Et_2O or THF at -40°C. After warming to room temperature the solid formed was collected by filtration yielding **32b** or **33b**.

1,3-Bis[4-(4-propylcyclohexyl)benzyl]imidazolin-2-ylidene – tetrafluoro(phenyl)phosphorane adduct **(32b)**

Yield: 80%; white solid, mp 133–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (t, J = 7.3 Hz, 6H, CH_3), 1.04 (m, 4H), 1.18-1.48 (m, 14H), 1.8 (m, 8H), 2.4 (tt, J = 11.9 Hz, 3.2 Hz, 2H), 3.4 (s, 2H), 3.5 (s, 2H), 7.14-7.1 (m, 11H), 7.7 (d, J = 7. Hz, 1H), 7.8 (d, J = 6.8 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -42.2 (d, J_{FP} 871.4 Hz); ^{31}P NMR (161 MHz, $CDCl_3$): δ -138.9 (quint, J_{PF} 800.4 Hz); HRMS (ESI, positive): Calcd for $C_{42}H_{60}F_4N_2PNa$ 722.4327 $[M+Na]^+$, found: 722.4321.

Dimethylamino[4-(4-propylcyclohexyl)phenyl]methylidene - tetrafluoro(phenyl)phosphorane adduct (**33b)**

Yield: 45 %; white crystals; m.p. 164–167 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, J = 7.3 Hz, 3H, CH_3), 1.04 (m, 2H), 1.18-1.48 (m, 7H), 1.8 (m, 4H), 2.4 (tt, J = 11.9, 3.2 Hz, 1H), 3.1 (s, 3H, CH_3), 3.9 (s, 3H, CH_3), 7.15-7.28 (m, 7H), 7.64 (d, J = 7.6 Hz, 1H), 7.69 (d, J = 6.8 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ: -47.9 (d, J_{FP} = 887.2 Hz); ^{31}P NMR (161 MHz, $CDCl_3$): δ -140.8 (quint, J_{PF} 886.4 Hz); HRMS (ESI, positive): Calcd for $C_{24}H_{33}F_4NPNa$ 465.2184 $[M+Na]^+$, found: 465.2178.

General procedure for the synthesis of carbene complexes using dichlorophosphines (**32e, 33c)**

A solution of 27 (17 mmol) in dry THF (70 mL) was placed into a 2-neck 250 mL flask equipped with a septum. At -40 °C a solution of difluoride **23a; 25a** (49 mmol) in THF (15 mL) was slowly added through the septum. During a period of 18 hrs the reaction was allowed to reach r.t. All volatiles were then removed under reduced pressure and the residue was treated with cold water (100 mL) and stirred for an additional 1 h. The aqueous solution was decanted and the insoluble residue was washed with addition portion of water, followed by ethanol and diethyl ether. Drying *in vacuo* gave the desired product **32e** or **33c**. Compound **32e** was additionally crystallized by slow diffusion of diethyl ether into a solution of **32e** in acetonitrile.

1,3-Dimethylimidazolin-2-ylidene - tetrafluoro[4-(4-propylcyclohexyl)phenyl]phosphorane adduct **(32e)**

Yield: 64%; white crystals; mp 165-166 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.9-1.0 (m, 3H), 0.9-1.1 (m, 2H), 1.1-1.2 (m, 2H), 1.3-1.4 (m, 2H), 1.4-1.5 (m, 2H), 1.8-1.9 (m, 4H), 2.4-2.5 (m, 1H), 3.3 (s, 6H), 3.7 (s, 4H), 7.1-7.2 (m, 2H), 7.6-7.7 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -45.0 (d, J_{FP} = 865 Hz); ^{31}P NMR (161 MHz, $CDCl_3$): δ -139.1 (quint, J_{PF} 885 = Hz).

(Dimethylamino)(phenyl)methylidene – tetrafluoro[4-(4-propylcyclohexyl)phenyl]phosphorane **(33c)**

Yield: 64%; white crystals; mp 110-111 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.8-0.9 (m, 3H), 0.9-1.1 (m, 2H), 1.1-1.5 (m, 6H), 1.8-1.9 (m, 4H), 2.3-2.5 (m, 1H), 3.1 (s, 3H), 4.0 (s, 3H), 7.0-7.1

(m, 2H), 7.2-7.3 (m, 2H), 7.4-7.5 (m, 3H), 7.5-7.6 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -47.1 (d, J_{FP} = 886 Hz); ^{31}P NMR (161 MHz, $CDCl_3$): δ -140.1 (quint, J_{PF} 887 = Hz).

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