

Phosphorus(V) Complexes with Acyclic Monoaminocarbene Ligands via Oxidative Addition[†]

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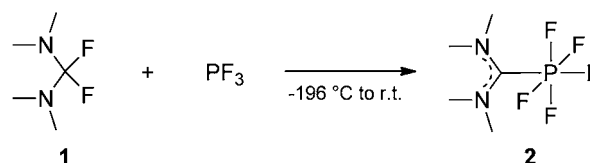
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Supporting Information

ABSTRACT: (Difluoroorganyl)dimethylamines, RCF_2NMe_2 ($\text{R} = \text{H}, \text{Ph}, t\text{Bu}$), can be used as carbene precursors for phosphorus trifluoride in an oxidative addition reaction. By this method, complexes of sterically nondemanding asymmetric and acyclic carbenes were obtained that are otherwise not accessible.

The isolation of “a stable crystalline carbene” by Arduengo and co-workers is considered as a landmark discovery in chemistry.¹ Since then, N-heterocyclic carbenes (NHCs) evolved from a curiosity to an established ligand in modern coordination chemistry.² Moreover, these NHCs took part in the ongoing “renaissance” within main-group-element chemistry.³ Low oxidation states in reactive main-group compounds were stabilized with the help of sterically demanding carbene ligands, eventually allowing the synthesis of main-group compounds in the formal oxidation state of zero on a preparative scale.⁴ The NHCs used in these reactions were readily available imidazolin-2-ylidenes, which are stable in their free form and can be conveniently handled using standard Schlenk techniques, e.g., $\text{C}\{\text{N}(\text{Ar})\text{CH}\}_2$, where $\text{Ar} = 2,6$ -diisopropylphenyl.⁵ Almost all of the recent examples of main-group-element carbene complexes were synthesized by the direct addition of such free uncoordinated carbene-ligand types.⁶ As expected, this procedure is, however, limited to carbene ligands that can be isolated in their free form. Shortly after the initial report of free NHCs, Arduengo and others followed the same synthetic method and successfully synthesized and isolated different imidazoline-based NHC ligands, ranging from free bulky groups at the N and N' positions⁷ to the incorporation of a saturated ring system or an acyclic diaminocarbene,^{8,9} even reaching an air-stable carbene.¹⁰ Despite these extreme examples, some carbenes are too reactive to be isolated in their free form.

However, our group has recently introduced two different methods for the synthesis of carbene complexes of main-group-element compounds: carbene transfer and oxidative addition.¹¹ For the latter method, difluorobis(dialkylamino)methane (**1**) and its cyclic analogue were introduced as precursors that allowed the synthesis of main-group-element complexes with sterically nondemanding carbenes that are otherwise not accessible via the free carbene route (Scheme 1). Although free acyclic diaminocarbenes are known, the derivative with the sterically least demanding groups reported so far is bis-(diisopropylamino)carbene.⁹ The simplest carbene, methylene ($:\text{CH}_2$), however, is a very reactive compound and can only

Scheme 1. **1** as a Carbene Source^a

^aAddition to PF_3 yields the corresponding carbene complex of phosphorus pentafluoride (**2**).

exist as a short-lived intermediate.^{2e} Previously, reactions of Vilsmeier's salt ($[\text{Me}_2\text{NCHCl}]\text{Cl}$) with transition-metal complexes in low oxidation states gave complexes with the (dimethylamino)methylene ligand $:\text{C}(\text{H})(\text{NMe}_2)$.¹² The analogous oxidative addition reaction of this salt toward the respective main-group-element compounds is, however, unknown. Therefore, and in a continuation to our research over new carbene precursors for main-group-element compounds, we decided to test derivatives of **1**, in which one dimethylamino group is replaced by H (**3-H**), Ph (**3-Ph**), and $t\text{Bu}$ (**3-*t*Bu**) as carbene precursors (see Figure 1).

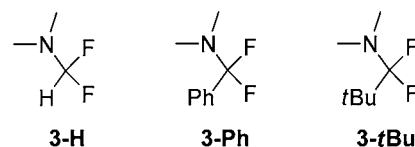


Figure 1. (Difluoroorganyl)dimethylamines (**3-R**) as carbene precursors.

Compound **1** (as well as its imidazoline-based analogue) has been described as a very potent fluorinating agent, caused by negative hyperconjugation of the lone pairs of the two nitrogen atoms into the σ^* orbitals of the C–F bonds.¹³ In contrast to **1**, the $-\text{CF}_2-$ function of compounds **3-R** is only activated by one dimethylamino group, and eventually the carbene carbon atom is stabilized by only one adjacent amine group through the “push–pull” effect. Compounds **3-R** have been reported previously, and an improved synthesis for **3-Ph** and **3-*t*Bu** is given in the Supporting Information [SI; chlorination of $\text{Me}_2\text{N}-\text{C}(\text{O})\text{R}$ with oxalyl chloride and subsequent fluorination with triethylamine trihydrofluoride].¹⁴

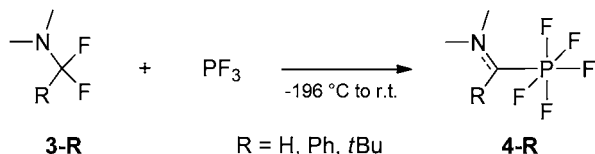
Herein we report the successful use of the asymmetric (difluoroorganyl)dimethylamines **3-R** as carbene precursors.

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The addition of **3-R** to PF₃ in diethyl ether at -196 °C and slowly allowing the reaction mixture to reach room temperature gave the corresponding carbene complexes of phosphorus pentafluoride **4-R** as colorless solids (Scheme 2).

Scheme 2. Synthesis of Complexes with Asymmetric Carbene Ligands and Phosphorus Pentafluoride



Compared to the *quasi*-quantitative reactions following Scheme 1, the oxidative addition products **4-R** were obtained in considerably lower yields: 55% for **4-H**, 14% for **4-Ph**, and 6% for **4-*t*Bu**. Whereas **4-H** and **4-Ph** were fully characterized by multinuclear NMR spectroscopy and high-resolution mass spectrometry, the low yield of **4-*t*Bu** allowed partial characterization only. Contrary to the previously reported compound **2**, which was found to be stable toward and insoluble in water, **3-R** showed decomposition (monitored by ³¹P NMR) and had to be washed with cold ethanol instead. All three products were each recrystallized by slow diffusion of diethyl ether into a saturated acetonitrile solution of the respective material, leading to crystals suitable for single-crystal X-ray diffraction. Compound **4-H** crystallized in the monoclinic space group *P*₂/*c* and both **4-Ph** and **4-*t*Bu** in the orthorhombic space group *Pnma*.

The crystal structures showed that, in all compounds, the phosphorus is in the expected octahedral environment (Figure 2). The C–P bond length varied significantly between the three title compounds; the shortest was found in **4-H** [186.27(12) pm], followed by **4-Ph** [191.32(15) pm] and **4-*t*Bu** [193.71(15) pm]. In comparison, the corresponding bond length of the acyclic diaminocarbene adduct **2** is 192.49(12) pm, more than 6 pm longer compared to the shortest one in **4-H**. The variation in the C1–P1 bond length as well as the N1–C1–P1 angle (see Table 1) might be attributed to steric rather than electronic effects. Diaminocarbenes are exceptionally stable carbenes. On the one hand, the lone pairs of the two adjacent nitrogen atoms donate electron density into the empty p orbital of the carbene via the formation of a three center/4π mesomeric system. On the other hand, the two electronegative

Table 1. Selected Bond Lengths (pm) and Angles (deg) for Compounds **4-R and, for Comparison, **2**, the Acyclic Diaminocarbene Complex of PF₅ (Average Values for the Two Independent Molecules of **4-H**)**

	4-H	4-Ph	4-<i>t</i>Bu	2
C1–P1	186.27(12)	191.32(15)	193.71(15)	192.49(12)
C1–N1	127.50(15)	129.49(19)	130.46(19)	133.67(16)
C1–R	93(2)	149.70(19)	155.7(2)	
P1–F1	159.27(9)	159.72(10)	160.39(11)	161.04(8)
av P1–F _{cis}	161.20(10)	161.60(7)	161.01(8)	161.03(9)
C1–P1–F1	176.26(5)	178.36(6)	179.01(7)	179.74(5)
N1–C1–P1	131.00(9)	126.02(11)	120.08(12)	121.52(9)

nitrogen atoms pull σ electron density from the carbene carbon atom, stabilizing therefore further the singlet ground state by lowering the energy of the carbene's σ orbital.¹⁵ In the case of **4-R**, the carbene carbon atom is stabilized by only one amino function, leading to a significant shortening in the N1–C1 bond length compared to the average C–N bond length in **2** [133.67(16) pm]. The related bond length in **4-H** was found to be 127.50(15) pm, that in **4-Ph** 129.49(19) pm, and that in **4-*t*Bu** 130.46(19) pm. For compound **4-H**, the bond length lies in the typical region of imines and can already be attributed to a double bond.¹⁶ Finally, the *cis* and *trans* P–F bond lengths differ only slightly between the different compounds (including **2**; see Table 1).

The respective chemical shifts in the ³¹P and ¹⁹F NMR spectra for the three complexes are very similar, giving therefore no conclusive statements in relation to the donor strength of the carbene ligand. All shift values and coupling constants are given in the SI.

The mechanism of the oxidative addition reaction of the symmetric precursor (**1**) and PF₃ was proposed earlier and involves a fluoroamidinium cation, which undergoes nucleophilic attack by a phosphoranide.^{11b} The situation for the asymmetric precursors **3-R** is supposed to follow the same scheme. However, the fluoroiminium cation formed during this process is a stronger electrophile, which may cause unwanted side reactions. For **3-Ph** and **3-*t*Bu**, steric hindrance is likely to explain the low yields. All products are sensitive (unlike their diaminocarbene counterparts) and tend to show decomposition if kept in the reaction mixture. The pure compounds are stable under a nitrogen atmosphere at room temperature for at least several weeks.

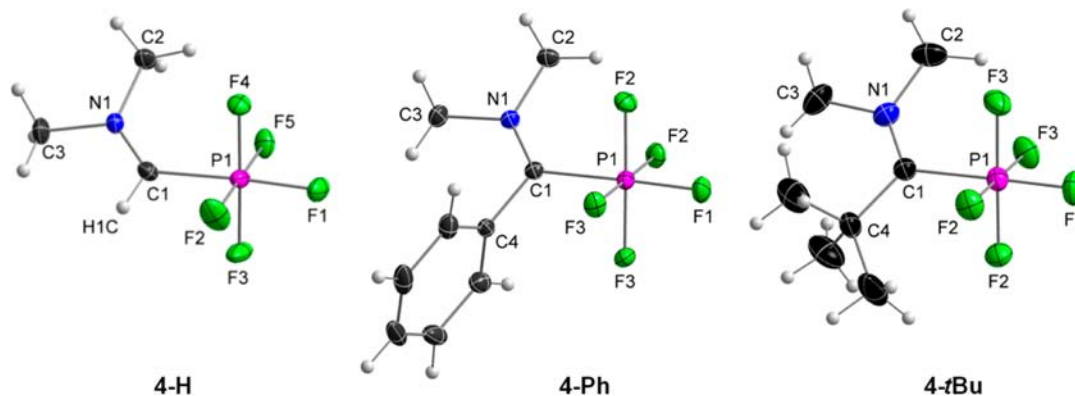


Figure 2. Crystal structures of compounds **4-H**, **4-Ph**, and **4-*t*Bu** (thermal ellipsoids set at the 50% probability level; hydrogen atoms fixed in size). Only one of the two independent molecules in the asymmetric unit of compound **4-H** is shown.

In summary, we have successfully extended the family of carbene precursors for main-group-element compounds to now include the asymmetric (difluoroorganyl)dialkylamines with only one amino group attached to the $-CF_2$ function. We have also presented an improved synthesis of the starting materials.

■ ASSOCIATED CONTENT

📄 Supporting Information

Text, figures, tables, and CIF files giving experimental details for the synthesis of compounds **3-R** and **4-R** and X-ray crystallographic and NMR spectroscopic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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