

### (Phosphino)(Aryl)Carbenes: Effect of Aryl Substituents on Their Stabilization Mode

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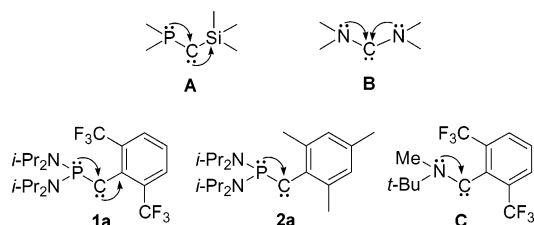
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**Abstract:** A broad range of (phosphino)(aryl)carbenes, **1b–d**, **10a,b**, and **14a,b**, were prepared by photolysis of their diazo precursors. The influence of the steric and electronic properties of the aryl ring on the structure and stability of these carbenes was studied both experimentally and theoretically. Among the different stabilization modes investigated, those featuring an acceptor as well as a spectator aryl substituent result in stable or at least persistent carbenes that could be completely characterized by classical spectroscopic methods. In marked contrast, the new substitution pattern featuring a donor aryl ring results in a very fleeting carbene.

#### Introduction

In the last 15 years, our understanding of carbene chemistry has advanced dramatically with the preparation of persistent triplet di(aryl)carbenes<sup>1</sup> and the isolation of singlet carbenes.<sup>2</sup> The former are potential building blocks for organic magnets,<sup>3</sup> while the latter, when used as ligands for transition metal centers, afford complexes with enhanced catalytic activity.<sup>4</sup>

Following the early predictions by Wanzlick,<sup>5</sup> the first isolated singlet carbenes **A**<sup>6</sup> and **B**<sup>7</sup> featured two heteroatomic substituents that both interact with the carbene center (Figure 1);



**Figure 1.** Structure of stable singlet carbenes **A–C**, **1a**, and **2a**.

however, totally different stabilization modes are involved for **A** (push–pull) and **B** (push–push). The range of stable carbenes was recently expanded to include monoheteroatom-substituted carbenes, for which the stabilization modes also differ significantly one to the another. A “push–pull” stabilization allowed for the preparation of the (aryl)carbene **1a**,<sup>8</sup> while for carbenes **2a**<sup>9</sup> and **C**,<sup>10</sup> a single electron-active substituent is involved and the aryl substituent remains merely a spectator.

To determine the electronic and steric factors that influence the stability and structure of these carbenes, we report here a detailed experimental and computational study of (phosphino)-(aryl)carbenes bearing different substituents on the aryl ring. Notably, a new substitution pattern featuring a donor aryl ring has been investigated.

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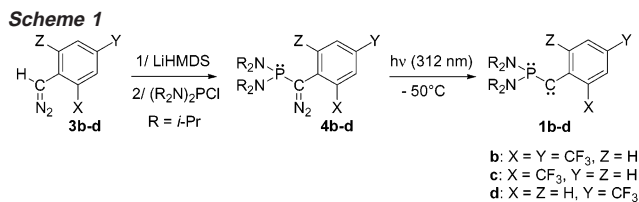
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**Table 1.** Selected NMR Data and Thermal Stability of Phosphinocarbenes R<sub>2</sub>PCR'

compound	R	R'	<sup>31</sup> P	<sup>13</sup> C	<sup>1</sup> J <sub>PC</sub>	T <sub>c</sub> (°C)	ref
<b>1a</b>	N( <i>i</i> -Pr) <sub>2</sub>	<i>o,o'</i> -(CF <sub>3</sub> ) <sub>2</sub> Ph	-22	146	271	80	8
<b>1b</b>	N( <i>i</i> -Pr) <sub>2</sub>	<i>o,p</i> -(CF <sub>3</sub> ) <sub>2</sub> Ph	-19	149	193	40	this work
<b>1c</b>	N( <i>i</i> -Pr) <sub>2</sub>	<i>o</i> -(CF <sub>3</sub> )Ph	-20	149	124	40	this work
<b>1d</b>	N( <i>i</i> -Pr) <sub>2</sub>	<i>p</i> -(CF <sub>3</sub> )Ph	-13	160	66	-20	this work
<b>2a</b>	N( <i>i</i> -Pr) <sub>2</sub>	<i>o,o',p</i> -Me <sub>3</sub> Ph	-23	151	65	40	9
<b>10a</b>	N( <i>i</i> -Pr) <sub>2</sub>	C <sub>6</sub> F <sub>5</sub>	9	133	58	20	this work
<b>10b</b>	N( <i>c</i> -Hex) <sub>2</sub>	C <sub>6</sub> F <sub>5</sub>	6			20	this work
<b>14a</b>	N( <i>i</i> -Pr) <sub>2</sub>	<i>o</i> -Me- <i>p</i> -(NMe <sub>2</sub> )Ph	-18			-70	this work
<b>14b</b>	N( <i>i</i> -Pr) <sub>2</sub>	<i>o</i> -MePh	-20	156	46	0	this work

## Results and Discussion

**(CF<sub>3</sub>-Substituted-aryl)carbenes 1a-1d.** The influence of the electronic and steric effects of electron-withdrawing substituents on the structure and stability of (phosphino)(aryl)carbenes was investigated by varying the number and position of CF<sub>3</sub> groups on the aryl ring. Three new diazo precursors **4b-d** were prepared in moderate yields by metalation of the corresponding aryl diazomethanes **3b-d**, followed by reaction with chlorobis(diisopropylamino)phosphine (Scheme 1). Photolysis of **4b-d** (312 nm) in deuterated toluene at low temperature allowed carbenes **1b-d** to be characterized by multinuclear NMR spectroscopy.

Thermal stabilities of **1b-d**, as determined qualitatively by variable-temperature <sup>31</sup>P NMR experiments, are very different. The indicated values T<sub>c</sub> correspond to the temperatures above which degradation occurs within a few hours (Table 1). From these values, it is clear that steric hindrance plays the key role in determining the stability of the carbenes. Indeed, T<sub>c</sub> significantly decreases for *o,p*-(CF<sub>3</sub>)<sub>2</sub> (**1b**) compared to *o,o'*-(CF<sub>3</sub>)<sub>2</sub> (**1a**) (by about 40 °C) and for *p*-CF<sub>3</sub> (**1d**) compared to *o*-CF<sub>3</sub>-substituted arylcarbene (**1c**) (by about 60 °C); moreover, the *o,p*-(CF<sub>3</sub>)<sub>2</sub> derivative (**1b**) has approximately the same stability as the *o*-CF<sub>3</sub>-substituted arylcarbene (**1c**). In all cases, the phosphino group affords the necessary stabilization, even to the extent that carbene **1d** featuring a naked aryl ring can be characterized spectroscopically at low temperature.

The <sup>31</sup>P and <sup>13</sup>C NMR spectroscopic data for carbenes **1a-d** are very similar (Table 1), the only noticeable difference being the magnitude of the <sup>1</sup>J<sub>PC</sub> coupling constant, which decreases progressively from **1a** to **1d**. Although these data are difficult to rationalize (the magnitude of the coupling constants depends on the influence of orbital, spin-dipolar, Fermi contact, and higher order quantum mechanical contributions), it is likely to indicate some modification in the electronic structure of (aryl)carbenes.

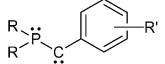
To gain more of an insight into the electronic role of the aryl substituents,<sup>11</sup> ab initio calculations at the B3LYP/6-31g\*

level were performed on the model (phosphino)(aryl)carbenes **1\*a-f**, featuring NH<sub>2</sub> groups at phosphorus, and on the experimentally observed carbene **1a**. Surprisingly, the optimized structures for **1\*a-e**, summarized in Table 2, are very similar whatever the position and the number of trifluoromethyl groups (P-C<sub>carb</sub> = 1.56–1.58 Å, C<sub>carb</sub>-C<sub>ipso</sub> = 1.42–1.44 Å, and P-C<sub>carb</sub>-C<sub>ipso</sub> = 141–146°), and isomeric carbenes **1\*a,b** and **1\*c-e** are very close in energy. This suggests that, despite the strong withdrawing effect of the CF<sub>3</sub> group, the CF<sub>3</sub>-substituted aryl rings provide only a weak withdrawing effect, which is further corroborated by comparing the optimized geometries of **1\*a-e** with that of the related (phenyl)carbene **1\*f**. A significant electronic contribution of the aryl substituent was only observed for **1a** featuring di(isopropyl)amino groups at phosphorus. Indeed, the steric repulsion between the bulky substituents at the phosphorus center and the aryl ring widens the P-C<sub>carb</sub>-C<sub>ipso</sub> bond angle (155°). As a result, the overlap between the carbene lone pair and the π-system of the aryl ring increases, as indicated by the significant shortening of the C<sub>carb</sub>-C<sub>ipso</sub> bond length (1.40 Å) observed in this case.

Although, as mentioned above, numerous decomposition pathways were observed for **1b** and **1d**, gentle heating of carbene **1c** at 40 °C overnight affords the four-membered heterocycle **5c**, which was characterized spectroscopically (Scheme 2). The presence of an AX system in the <sup>31</sup>P NMR spectrum (δ <sup>31</sup>P 36.8 and 75.5, J<sub>PP</sub> = 52 Hz) suggested a novel two carbene unit coupling. Indeed, the previously reported C=C dimerization<sup>8</sup> and [2 + 2]-cycloaddition<sup>12</sup> pathways would have led to symmetrical structures featuring two magnetically equivalent phosphorus atoms. The structure of **5c** was deduced from the X-ray diffraction study performed on compound **6c**, which was obtained by treatment of **5c** with elemental sulfur (Figure 2, Table 3). Formally, compound **5c** results from the dimerization of **1c** with concomitant elimination of 1 equiv of the imine Me<sub>2</sub>C=N(*i*-Pr).<sup>13</sup> Mechanistically, it is likely that initial nucleophilic attack of the carbene on the electrophilic phosphorus center of another carbene molecule leads to the zwitterionic structure **7c**. The expected ring closure of **7c** is probably impeded by steric constraints, so that elimination of imine occurs to give the 1,3,3,5-diphosphabutadiene **8c**; an electrocyclization finally affords the four-membered diphosphorus-containing heterocycle **5c**.

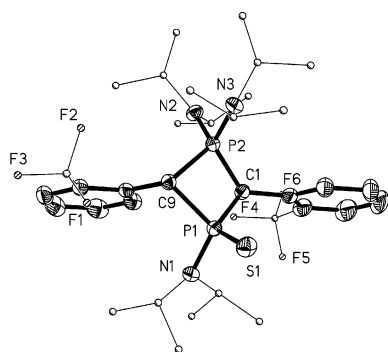
**(Pentafluorophenyl)- and (*p*-NR<sub>2</sub>-Substituted-aryl)carbenes 10a,b and 14a,b.** The synthesis of (phosphino)carbenes **1a-d** and **2a** demonstrates that observable (phosphino)(aryl)carbenes can be prepared whatever the steric bulk and the electronic properties—acceptor or spectator—of the aryl ring. Subsequently, the preparation of (phosphino)carbenes featuring a donor aryl substituent was investigated. Because fluorine atoms have potentially a π-donating effect and as C–F bonds are inert toward insertion of singlet<sup>10</sup> and even triplet carbenes,<sup>14</sup> the pentafluorophenyl substituent<sup>15</sup> was chosen for initial study.

- (11) Substituent effects have been studied computationally: (a) For (aryl)-(hydrogeno)carbenes, Geise, C. M. *J. Org. Chem.* **2000**, *65*, 8348. (b) For (aryl)(carbomethoxy)carbenes: Geise, C. M.; Wang, Y.; Mykhaylova, Frink, B. T.; Toscano, J. P.; Hadad, C. M. *J. Org. Chem.* **2002**, *67*, 3079.
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- (13) The structure of the imine Me<sub>2</sub>C=N(*i*-Pr) was deduced by comparison of its <sup>1</sup>H NMR data with those of an authentic sample.
- (14) (a) Tomioka, H.; Taketsuji, K. *J. Chem. Soc., Chem. Commun.* **1997**, 1745. (b) Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **1999**, *121*, 10213.
- (15) Fluorine combines σ-acceptor and π-donor properties, as illustrated by Taft constants (σ<sub>I</sub> = +0.5, σ<sub>R</sub> = -0.34 according to Ehrenson, S.; Brownless, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1). Accordingly, the pentafluorophenyl substituent could in principle behave as an acceptor, a spectator, or even as a donor.

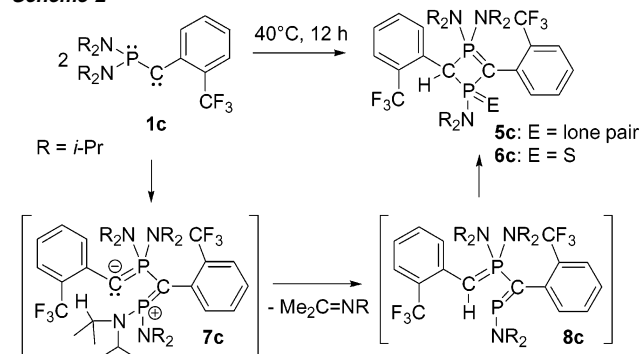
**Table 2.** Optimized Structures (at the B3LYP/6-31g\* Level) for (Phosphino)(aryl)carbenes<sup>a</sup>


compound	R	R'	PC	CC <sub>ipso</sub>	PCC <sub>ipso</sub>	ΣP	PCC <sub>ipso</sub> C <sub>o</sub>	PCC <sub>ipso</sub> C <sub>o'</sub>	E <sub>rel</sub> (kcal/mol)
<b>1*a</b>	NH <sub>2</sub>	<i>o,o'</i> -(CF <sub>3</sub> ) <sub>2</sub>	1.562	1.422	146.2	360.0	117.8	-65.7	+0.8
<b>1*b</b>	NH <sub>2</sub>	<i>o,p</i> -(CF <sub>3</sub> ) <sub>2</sub>	1.567	1.425	145.5	359.6	98.6	-85.2	0
<b>1*c</b>	NH <sub>2</sub>	<i>o</i> -CF <sub>3</sub>	1.568	1.433	145.2	359.8	126.6	-56.3	0
<b>1*d</b>	NH <sub>2</sub>	<i>p</i> -CF <sub>3</sub>	1.572	1.434	143.9	359.3	121.2	-61.6	+0.3
<b>1*e</b>	NH <sub>2</sub>	<i>m</i> -CF <sub>3</sub>	1.577	1.439	141.2	359.4	133.8	-48.6	+1.0
<b>1*f</b>	NH <sub>2</sub>	H	1.582	1.441	140.6	358.8	143.8	-38.2	
<b>1a</b>	N( <i>i</i> -Pr) <sub>2</sub>	<i>o,o'</i> -(CF <sub>3</sub> ) <sub>2</sub>	1.573	1.403	155.6	358.5	109.1	-74.8	
<b>10*</b>	NH <sub>2</sub>	F <sub>5</sub>	1.586	1.435	136.1	358.9	169.5	-12.4	
<b>10a</b>	N( <i>i</i> -Pr) <sub>2</sub>	F <sub>5</sub>	1.593	1.431	136.1	359.8	99.5	-87.4	
<b>14*</b>	NH <sub>2</sub>	<i>p</i> -NH <sub>2</sub>	1.613	1.431	140.7	344.9	151.2	-31.0	
<b>14**</b>	N( <i>i</i> -Pr) <sub>2</sub>	<i>p</i> -NH <sub>2</sub>	1.610	1.443	136.9	359.2	175.6	-4.4	

<sup>a</sup> PC and CC<sub>ipso</sub> bond lengths are given in angstroms; PCC<sub>ipso</sub> bond angles and PCC<sub>ipso</sub>C<sub>o</sub> and PCC<sub>ipso</sub>C<sub>o'</sub> dihedral angles are expressed in degrees. The sum of the bond angles around phosphorus is referred to as ΣP. Relative energies E<sub>rel</sub> are given for the isomeric structures (**1\*a,b**) and (**1\*c-e**). In each series, the most stable carbene is used as reference (**1\*a** and **1\*c**, respectively).



**Figure 2.** Thermal ellipsoid diagram (50% probability) of **6c**. For clarity the *i*-Pr and CF<sub>3</sub> groups have been simplified. Selected bond lengths (in angstroms) and angles (in degrees): P(1)–C(1), 1.7619(16); P(1)–C(9), 1.8775(16); P(2)–C(1), 1.7291(16); P(2)–C(9), 1.8614(16); P(1)–C(1)–P(2), 93.65(8); C(1)–P(2)–C(9), 88.39(7); P(2)–C(9)–P(1), 85.83(7); C(9)–P(1)–C(1), 86.92(7).

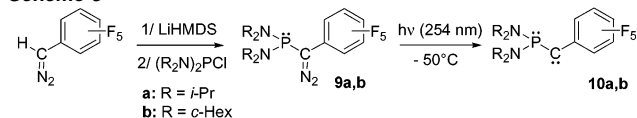
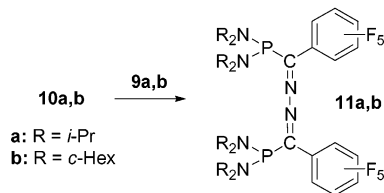
**Scheme 2**

Diazo compounds **9a,b** were prepared in moderate yields (34–37%) by metalation of the pentafluorophenyldiazomethane,<sup>16</sup> followed by coupling with chlorobis(diisopropylamino)phosphine (Scheme 3). Photolysis (254 nm) of **9a,b** in toluene at -50 °C affords carbenes **10a,b** in good yields (60–67%). The <sup>31</sup>P and <sup>13</sup>C NMR chemical shifts (**10a** δ <sup>31</sup>P 9.4, δ <sup>13</sup>C 133.3, <sup>1</sup>J<sub>PC</sub> = 58 Hz) are in the range typical for (phosphino)carbenes (Table 1). Carbenes **10a,b** are stable for days in solution at -30 °C and can even be observed by <sup>31</sup>P NMR up to room temperature where decomposition occurs within hours whatever the solvent (pentane, toluene, diethyl ether, tetrahydrofuran).

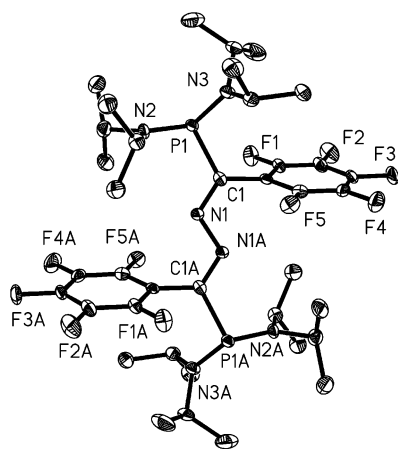
(16) Meese, C. O. *Liebigs Ann. Chem.* **1985**, 1711.

**Table 3.** Crystallographic Data for Compounds **6c** and **11a**

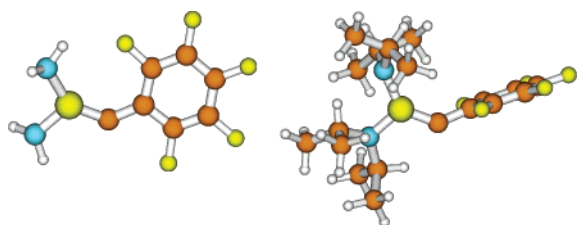
	<b>6c</b>	<b>11a</b>
formula	C <sub>34</sub> H <sub>51</sub> F <sub>6</sub> N <sub>3</sub> P <sub>2</sub> S	C <sub>38</sub> H <sub>56</sub> F <sub>10</sub> N <sub>6</sub> P <sub>2</sub>
formula weight	709.78	848.83
cryst system	monoclinic	triclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	11.422(2)	7.8502(4)
<i>b</i> , Å	28.059(5)	10.8228(6)
<i>c</i> , Å	11.827(2)	12.8265(7)
α, deg		98.102(1)
β, deg	95.211(3)	93.709(1)
γ, deg		105.260(1)
<i>V</i> , Å <sup>3</sup>	3774.8(11)	1034.91(10)
<i>Z</i>	4	1
<i>d</i> <sub>calcd</sub> , Mg/m <sup>3</sup>	1.249	1.362
absorp coeff, mm <sup>-1</sup>	0.227	0.186
no. of total reflns	26 846	11 619
no. of unique reflns	9350	11 621
R1 [ <i>I</i> > 2σ( <i>I</i> )]	0.0446	0.0866
wR2 (all data)	0.1086	0.2411
(Δ/ρ) <sub>max</sub> [e Å <sup>-3</sup> ]	0.380, -0.329	0.538, -0.652

**Scheme 3****Scheme 4**

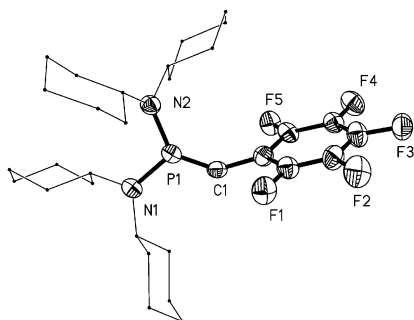
It should be noted that carbenes **10a,b** react cleanly with their diazo precursors at room temperature. Indeed, the corresponding azines **11a,b** are obtained in good yields (63–72%) when the photolytic degradation of the diazo compounds is performed to half conversion (Scheme 4). The structures of **11a,b** were deduced from multinuclear NMR spectroscopy and confirmed by an X-ray diffraction study for **11a** (Figure 3, Table 3). This carbene–diazo coupling is a reaction typical of transient carbenes,<sup>17</sup> something that has also recently been observed for a stable N-heterocyclic carbene.<sup>18</sup>



**Figure 3.** Thermal ellipsoid diagram (50% probability) of **11a**. Selected bond lengths (in angstroms) and angles (in degrees): P(1)–C(1), 1.859(4); C(1)–N(1), 1.292(5); N(1)–N(1A), 1.427(6); P(1)–C(1)–N(1), 119.8(3); C(1)–N(1)–N(1A), 113.2(3); N(2)–P(1)–N(3), 112.64(15); N(2)–P(1)–C(1), 105.27(15); N(3)–P(1)–C(1), 100.45(15).

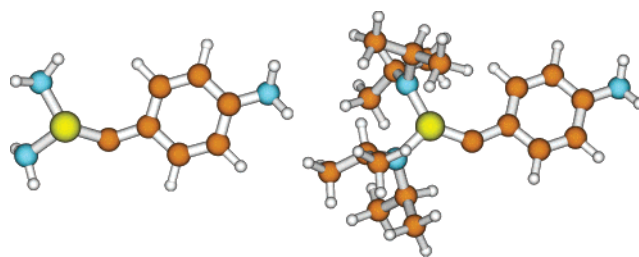


**Figure 4.** Optimized geometries of **10\*** (left) and **10a** (right).



**Figure 5.** Thermal ellipsoid diagram (30% probability) of **10b**. For clarity the *c*-Hex groups have been simplified.

Interestingly, *ab initio* calculations carried out on the model (pentafluorophenyl)(phosphino)carbene **10\*** with NH<sub>2</sub> substituents at phosphorus predicted that, in contrast with carbenes **1\*a–d** and (phenyl)carbene **1\*f**, the plane of the aryl ring of **10\*** is rotated by only 11.5° with respect to that of the carbene (37.2° for **1\*f**) (Table 2, Figure 4). The almost coplanar orientation of the aryl ring with the P–C<sub>carbene</sub> bond is likely to result from a conjugation between the  $\pi$ -system of the aryl ring (which is enriched by the fluorine atoms) and the carbene vacant orbital. However, this interaction is probably weak since it is not visible on examination of the P–C<sub>carb</sub> and C<sub>carb</sub>–C<sub>ipso</sub> bond lengths. Experimentally, only poor-quality crystals of **10b** could be obtained from a pentane solution at –50 °C (Figure 5). Although the geometric parameters resulting from a study of



**Figure 6.** Optimized geometries of **14\*** (left) and **14\*\*** (right).

this crystalline sample cannot be discussed in detail, carbene **10b** clearly adopts a perpendicular rather than the expected coplanar structure in the solid state. The rotation of the aryl ring is probably induced by steric hindrance from the isopropyl groups. This hypothesis was corroborated by calculations on the isopropyl-substituted compound **10a** itself: the plane of the aryl ring was predicted to be rotated by 93° with respect to that of the carbene (Table 2). Due to this rotation of the aryl ring, carbenes **10a,b** adopt a similar structure to that of the (phosphino)(mesityl)carbene **2a**. The pentafluorophenyl ring merely behaves as a spectator substituent, thus no unequivocal conclusions can be drawn about (phosphino)carbenes featuring a donor aryl substituent.

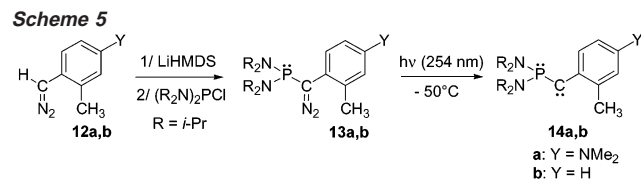
To try to force the aryl ring to behave as a  $\pi$ -donor substituent, one possibility is to introduce an amino group in the para position. This hypothesis was initially investigated theoretically on the model carbene **14\*** (Figure 6, Table 2).<sup>19</sup> Although neither a significant shortening of the C<sub>carb</sub>–C<sub>ipso</sub> nor an elongation of the P–C<sub>carb</sub> bond lengths could be observed, the  $\pi$ -system of the aryl ring was found to lie almost parallel to the empty 2p orbital of the carbene center. Moreover, a pyramidalization of the phosphorus atom was predicted, which clearly indicates a weaker donation of the phosphino group. For the bis(diisopropylamino)phosphino analogue **14\*\***, calculations found that the phosphorus center recovers its planar environment, but in marked contrast with that observed for **10a**, the aryl ring remains almost parallel to the carbene vacant orbital.

On taking into account the major role played by the steric bulk of the ortho substituents on the stability of (phosphino)-(aryl)carbenes (*vide supra*), we chose carbene **14a**, featuring an *o*-methyl substituent as a second target molecule; substituents at both ortho positions would certainly prevent the desired coplanar arrangement, as in the case of **10a,b**. The starting (aryl)diazomethane **12a** was prepared in 38% yield by solid–liquid phase transfer at 35 °C.<sup>20</sup> The introduction of the phosphino group was very tricky and could only be achieved in 15% yield by addition of chlorobis(diisopropylamino)phosphine and lithium diisopropylamide to an ether solution of **12a** at room temperature (Scheme 5). Diazo compound **13a** was characterized by multinuclear NMR spectroscopy. Photolysis of **13a** (254 nm) in toluene solution at –70 °C allowed for the characterization of the corresponding carbene **14a** by <sup>31</sup>P NMR spectroscopy ( $\delta$  <sup>31</sup>P –17.9). Any attempts to get <sup>13</sup>C NMR data were prevented by the extreme instability of **14a**, which decomposes within a few hours even at –70 °C. This peculiar

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instability of **14a** is likely to result from the donor group introduced in the aryl substituent. This hypothesis was confirmed by preparing the related (phosphino)(aryl)carbene **14b** featuring a methyl group in the ortho position but no amino group in the para position. Carbene **14b** was generated by photolysis (254 nm) of its diazo precursor at  $-60^\circ\text{C}$  and characterized spectroscopically. All the NMR data (Table 1) are very similar to those of the related (phosphino)(mesityl)carbene **2a**. In contrast to **14a**, carbene **14b** could be observed by  $^{31}\text{P}$  NMR up to  $0^\circ\text{C}$ , where it decomposes within a few hours.

## Conclusion

The phosphino group brings enough stabilization to singlet (aryl)carbenes to allow for their spectroscopic characterization under standard laboratory conditions. The phosphino group clearly behaves as a weak  $\pi$ - and  $\sigma$ -donor substituent, while the role of the aryl substituents strongly depends on both their electronic and steric properties. The most stable derivative **1a** features a push–pull cumulenonic structure, which is imposed by the bulky withdrawing 2,6-bis(trifluoromethyl)phenyl group. Despite their electron-withdrawing properties, less sterically hindered aryl groups behave as spectator substituents, as observed in **1b–d**. Carbenes **10a,b** are somewhat peculiar because steric factors induce the rotation of the potentially  $\pi$ -donating pentafluorophenyl ring, which finally behaves as only a spectator substituent. When the aryl substituent is strongly enriched electronically by an amino group, a push–push system is obtained. However, the phosphino and aryl  $\pi$ -donor groups do not have additive effects but rather an overall destabilizing effect,<sup>21</sup> making the resulting carbene **14a** extremely reactive. At the first glance, this is surprising since carbenes featuring two  $\pi$ -donor amino groups are highly stable. But this is more understandable if one considers the opposite inductive effects of phosphino ( $\sigma$ -donor) and amino ( $\sigma$ -acceptor) groups.

This understanding of the effects governing the stability of phosphinocarbenes will greatly facilitate the preparation of a variety of new stable or at least persistent carbenes. Having in hand such species will allow for the discovery of new types of reactions,<sup>22</sup> including those involving carbenes in excited states,<sup>23</sup> which have so far required rather sophisticated techniques.<sup>24</sup>

## Experimental Section

All manipulations were performed under an inert atmosphere of argon by standard Schlenk techniques. Dry, oxygen-free solvents were employed.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  NMR spectra were recorded on Bruker AC80, AC200, WM250, or AMX400 spectrometers.  $^1\text{H}$  and  $^{13}\text{C}$

chemical shifts are reported in parts per million (ppm) relative to Me<sub>4</sub>-Si as external standard.  $^{19}\text{F}$  NMR chemical shifts are given relative to an external standard of CF<sub>3</sub>CO<sub>2</sub>H.  $^{31}\text{P}$  NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H<sub>3</sub>PO<sub>4</sub>. Infrared spectra were recorded on a Perkin-Elmer FT-IR spectrometer 1725 X. Mass spectra were obtained on a Ribermag R10 10E instrument. Pentafluorophenyldiazomethane<sup>16</sup> and other starting (aryl)diazomethanes **3b–d** and **12a,b**<sup>25</sup> were prepared by decomposition of the corresponding tosylhydrazone salts.

**General Procedure for the Synthesis of Diazo Compounds 4b–d, 9a,b, and 13b.** A diethyl ether solution (4 mL) of the lithium salt of hexamethyldisilazane (0.27 g, 1.6 mmol) was added dropwise at  $-100^\circ\text{C}$  to a diethyl ether solution (20 mL) of the aryldiazomethane (1.6 mmol). After 30 min, a suspension of chlorobis(diisopropylamino)phosphine (0.43 g, 1.6 mmol) in diethyl ether (5 mL) was added. The solution was warmed to room temperature, and the solvent was removed under vacuum. The crude residue was extracted with pentane (30 mL) and quickly filtered through neutral activated alumina. Diazo compounds were obtained as deeply orange crystals from acetonitrile solutions at  $-30^\circ\text{C}$ .

**4b:** mp  $66^\circ\text{C}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>)  $\delta$  71.0 (s);  $^{19}\text{F}$  NMR (CDCl<sub>3</sub>)  $\delta$  14.5 (s), 12.3 (s);  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  1.04 (d, 12 H,  $^3J_{\text{HH}} = 6.6$  Hz, CH<sub>3</sub>), 1.29 (d, 12 H,  $^3J_{\text{HH}} = 6.6$  Hz, CH<sub>3</sub>), 3.46 (septet, 4 H,  $^3J_{\text{HH}} = 6.6$  Hz, CH), 7.64 (d, 1 H,  $^3J_{\text{HH}} = 8.5$  Hz, H<sub>ortho</sub>), 7.88 (s, 1 H, H<sub>meta</sub>), 7.99 (d, 1 H,  $^3J_{\text{HH}} = 8.5$  Hz, H<sub>meta</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (CDCl<sub>3</sub>)  $\delta$  24.5 (d,  $^3J_{\text{CP}} = 7$  Hz, CH<sub>3</sub>), 25.1 (d,  $^3J_{\text{CP}} = 6$  Hz, CH<sub>3</sub>), 48.2 (d,  $^2J_{\text{CP}} = 13$  Hz, CH), 50.8 (d,  $^1J_{\text{CP}} = 42$  Hz, CN<sub>2</sub>), 124.1 (q,  $^1J_{\text{CF}} = 272$  Hz, CF<sub>3</sub>), 124.1 (q,  $^1J_{\text{CF}} = 274$  Hz, CF<sub>3</sub>), 125.8 (q,  $^2J_{\text{CF}} = 31$  Hz, C<sub>para</sub>), 126.3 (qd,  $^3J_{\text{CP}} = 3$  Hz,  $^2J_{\text{CF}} = 33$  Hz, C<sub>ortho</sub>), 127.9 (d,  $^4J_{\text{CP}} = 3$  Hz, C<sub>meta</sub>), 128.6 (d,  $^3J_{\text{CP}} = 27$  Hz, C<sub>ortho</sub>), 129.6 (s, C<sub>meta</sub>), 137.0 (d,  $^2J_{\text{CP}} = 24$  Hz, C<sub>ipso</sub>); IR (diethyl ether)  $\nu_{\text{CN}_2}$  2046. Anal. Calcd for C<sub>21</sub>H<sub>31</sub>F<sub>6</sub>N<sub>4</sub>P: C 52.06, H 6.45, N 11.56. Found: C 51.84, H 6.20, N 11.90.

**4c:** mp  $108^\circ\text{C}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  66.8 (s);  $^{19}\text{F}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  14.4 (s);  $^1\text{H}$  NMR (CDCl<sub>3</sub>)  $\delta$  0.97 (d, 12 H,  $^3J_{\text{HP}} = 6.6$  Hz, CH<sub>3</sub>), 1.25 (d, 12 H,  $^3J_{\text{HH}} = 6.6$  Hz, CH<sub>3</sub>), 3.43 (septet, 4 H,  $^3J_{\text{HH}} = 6.6$  Hz, CH), 7.17 (pt, 1 H,  $^3J_{\text{HH}} = 7.6$  Hz, H<sub>arom</sub>), 7.40 (pt, 1 H,  $^3J_{\text{HH}} = 7.6$  Hz, H<sub>arom</sub>), 7.62 (d, 1 H,  $^3J_{\text{HH}} = 7.6$  Hz, H<sub>arom</sub>), 7.83 (pt, 1 H,  $^3J_{\text{HH}} = 7.6$  Hz, H<sub>arom</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  24.4 (d,  $^3J_{\text{CP}} = 7$  Hz, CH<sub>3</sub>), 24.5 (d,  $^3J_{\text{CP}} = 6$  Hz, CH<sub>3</sub>), 48.0 (d,  $^2J_{\text{CP}} = 12$  Hz, CH), 49.5 (d,  $^1J_{\text{CP}} = 24$  Hz, CN<sub>2</sub>), 124.8 (d,  $^1J_{\text{CF}} = 3$  Hz, C<sub>arom</sub>), 126.4 (q,  $^2J_{\text{CF}} = 30$  Hz, C<sub>ortho</sub>), 125.3 (q,  $^1J_{\text{CF}} = 274$  Hz, CF<sub>3</sub>), 127.3 (q,  $^4J_{\text{CF}} = 6$  Hz, C<sub>meta</sub>), 129.0 (d,  $^3J_{\text{CP}} = 21$  Hz, C<sub>ortho</sub>), 131.3 (s, C<sub>arom</sub>), 132.3 (qd,  $^2J_{\text{CP}} = 22$  Hz,  $^3J_{\text{CF}} = 2$  Hz, C<sub>ipso</sub>); IR (tetrahydrofuran)  $\nu_{\text{CN}_2}$  2042. Anal. Calcd for C<sub>20</sub>H<sub>32</sub>F<sub>3</sub>N<sub>4</sub>P: C 57.68, H 7.74, N 13.46. Found: C 57.45, H 7.34, N 13.71.

**4d:** mp  $73^\circ\text{C}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR (C<sub>7</sub>D<sub>8</sub>)  $\delta$  62.6 (s);  $^{19}\text{F}$  NMR (C<sub>7</sub>D<sub>8</sub>)  $\delta$  14.9 (d,  $^7J_{\text{FP}} = 9$  Hz);  $^1\text{H}$  NMR (C<sub>7</sub>D<sub>8</sub>)  $\delta$  1.15 (d, 6 H,  $^3J_{\text{HH}} = 6.6$  Hz, CH<sub>3</sub>), 1.25 (d, 6 H,  $^3J_{\text{HH}} = 6.6$  Hz, CH<sub>3</sub>), 3.38 (septet, 4 H,  $^3J_{\text{HH}} = 6.6$  Hz, CH), 7.30 (d, 2 H,  $^3J_{\text{HH}} = 8.4$  Hz, H<sub>arom</sub>), 7.44 (d, 2 H,  $^3J_{\text{HH}} = 8.4$  Hz, H<sub>arom</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (C<sub>7</sub>D<sub>8</sub>)  $\delta$  24.0 (d,  $^2J_{\text{CP}} = 7$  Hz, CH<sub>3</sub>), 25.1 (d,  $^2J_{\text{CP}} = 7$  Hz, CH<sub>3</sub>), 48.2 (d,  $^1J_{\text{CP}} = 12$  Hz, CH), 53.1 (d,  $^1J_{\text{CP}} = 50$  Hz, CN<sub>2</sub>), 123.4 (d,  $^3J_{\text{CP}} = 11$  Hz, C<sub>ortho</sub>), 126.1 (q,  $^2J_{\text{CF}} = 4$  Hz, C<sub>meta</sub>), 125.5 (q,  $^1J_{\text{CF}} = 271$  Hz, CF<sub>3</sub>), 125.6 (q,  $^2J_{\text{CF}} = 31$  Hz, C<sub>para</sub>), 138.3 (d,  $^2J_{\text{CP}} = 29$  Hz, C<sub>ipso</sub>); IR (diethyl ether)  $\nu_{\text{CN}_2}$  2032. Anal. Calcd for C<sub>20</sub>H<sub>32</sub>F<sub>3</sub>N<sub>4</sub>P: C 57.68, H 7.74, N 13.46. Found: C 57.99, H 8.12, N 13.14.

**9a:** mp  $63^\circ\text{C}$  (decomp);  $^{31}\text{P}\{^1\text{H}\}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  66.0 (t,  $^4J_{\text{PF}} = 61$  Hz);  $^{19}\text{F}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$   $-87.5$  (t, 2 F,  $^3J_{\text{FF}} = 22$  Hz, F<sub>meta</sub>),  $-82.6$  (t, 1 F,  $^3J_{\text{FF}} = 22$  Hz, F<sub>para</sub>),  $-62.7$  (dd, 2 F,  $^3J_{\text{FF}} = 22$  Hz,  $^4J_{\text{FF}} = 61$  Hz,

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$F_{ortho}$ );  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.11 (d, 12 H,  $^3J_{\text{HH}} = 6.6$  Hz,  $\text{CH}_3$ ), 1.23 (d, 12 H,  $^3J_{\text{HH}} = 6.6$  Hz,  $\text{CH}_3$ ), 3.38 (septet d, 4 H,  $^3J_{\text{HH}} = 6.6$  Hz,  $^3J_{\text{HP}} = 11.8$  Hz, CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  24.2 (d,  $^3J_{\text{CP}} = 9$  Hz,  $\text{CH}_3$ ), 24.7 (d,  $^3J_{\text{CP}} = 7$  Hz,  $\text{CH}_3$ ), 42.4 (md,  $^1J_{\text{CP}} = 54$  Hz, CP), 48.2 (d,  $^2J_{\text{CP}} = 13$  Hz, CH), 109.2 (md,  $^2J_{\text{CP}} = 21$  Hz,  $\text{C}_{ipso}$ ), 138.3 (md,  $^1J_{\text{CF}} = 252$  Hz,  $\text{C}_{arom}$ ), 139.6 (md,  $^1J_{\text{CF}} = 252$  Hz,  $\text{C}_{arom}$ ), 144.8 (md,  $^1J_{\text{CF}} = 248$  Hz,  $\text{C}_{arom}$ ); IR (diethyl ether)  $\nu_{\text{CN}_2} = 2051$ . Anal. Calcd for  $\text{C}_{19}\text{H}_{28}\text{F}_5\text{N}_4\text{P}$ : C 52.05, H 6.44, N 12.78. Found: C 52.34, H 6.68, N 12.52.

**9b**: mp 84 °C (decomp);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  67.2 (t,  $^4J_{\text{PF}} = 58$  Hz);  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  -87.5 (t, 2 F,  $^3J_{\text{FF}} = 22$  Hz,  $F_{meta}$ ), -82.6 (t, 1 F,  $^3J_{\text{FF}} = 22$  Hz,  $F_{para}$ ), -62.4 (dd, 2 F,  $^3J_{\text{FF}} = 22$  Hz,  $^4J_{\text{FF}} = 58$  Hz,  $F_{ortho}$ );  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  0.95–1.83 (m, 40 H,  $\text{CH}_2$ ), 2.93 (m, 4 H, CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  25.6 (s,  $\text{CH}_2$ ), 25.8 (s,  $\text{CH}_2$ ), 26.8 (s,  $\text{CH}_2$ ), 27.3 (s,  $\text{CH}_2$ ), 35.3 (d,  $^3J_{\text{CP}} = 7$  Hz,  $\text{CH}_2$ ), 35.8 (d,  $^3J_{\text{CP}} = 7$  Hz,  $\text{CH}_2$ ), 56.7 (d,  $^2J_{\text{CP}} = 11$  Hz, CH), 58.0 (d,  $^2J_{\text{CP}} = 10$  Hz, CH); IR (pentane)  $\nu_{\text{CN}_2} = 2051$ . Anal. Calcd for  $\text{C}_{31}\text{H}_{44}\text{F}_5\text{N}_4\text{P}$ : C 62.19, H 7.41, N 9.36. Found: C 62.47, H 7.68, N 9.02.

**13b**: mp 104 °C;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  64.4 (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.96 (d, 12 H,  $^3J_{\text{HH}} = 6.5$  Hz,  $\text{CH}_3$ ), 1.25 (d, 12 H,  $^3J_{\text{HH}} = 6.5$  Hz,  $\text{CH}_3$ ), 2.31 (s, 3 H,  $\text{CH}_3$ ), 3.42 (septet, 4 H,  $^3J_{\text{HH}} = 6.5$  Hz, CH), 7.11 (br s, 3 H,  $\text{H}_{arom}$ ), 7.63 (br s, 1 H,  $\text{H}_{arom}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.4 (s,  $\text{CH}_3$ ), 24.4 (d,  $^3J_{\text{CP}} = 7$  Hz,  $\text{CH}_3$ ), 47.8 (d,  $^2J_{\text{CP}} = 12$  Hz, CH), 50.9 (d,  $^1J_{\text{CP}} = 17$  Hz,  $\text{CN}_2$ ), 125.7 (s,  $\text{CH}_{arom}$ ), 125.9 (d,  $J_{\text{CP}} = 2$  Hz,  $\text{CH}_{arom}$ ), 127.9 (d,  $^3J_{\text{CP}} = 14$  Hz,  $\text{CH}_{arom}$ ), 130.8 (s,  $\text{CH}_{arom}$ ), 130.9 (d,  $^2J_{\text{CP}} = 21$  Hz,  $\text{C}_{ipso}$ ), 135.9 (s,  $\text{C}_{arom}$ ); IR (diethyl ether)  $\nu_{\text{CN}_2} = 2032$ . Anal. Calcd for  $\text{C}_{20}\text{H}_{35}\text{N}_4\text{P}$ : C 66.27, H 9.73, N 15.46. Found: C 65.94, H 9.38, N 15.72.

**Synthesis of the Diazo Compound 13a.** To a diethyl ether solution (5 mL) of diazo compound **12a** (17 mg, 0.1 mmol) were successively added at room temperature chlorobis(diisopropylamino)phosphine (27 mg, 0.1 mmol) and a diethyl ether solution (3 mL) of lithium diisopropylamide (12 mg, 0.11 mmol). The solvent was removed under vacuum. The crude residue was extracted with pentane (10 mL) and quickly filtered over neutral activated alumina. Diazo compound **13a** was obtained as deep purple crystals (15% yield) from an acetonitrile solution at -30 °C: mp 113 °C;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  62.90 (s);  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  1.10 (d, 12 H,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CH}_3$ ), 1.25 (d, 12 H,  $^3J_{\text{HH}} = 6.8$  Hz,  $\text{CH}_3$ ), 2.40 (s, 3 H,  $\text{CH}_3$ ), 2.50 (s, 6 H,  $\text{CH}_3\text{N}$ ), 3.42 (septet, 4 H,  $^3J_{\text{HH}} = 6.8$  Hz, CH), 6.51 (s, 1 H,  $\text{H}_{arom}$ ), 6.54 (d, 1 H,  $^3J_{\text{HH}} = 8.0$  Hz,  $\text{H}_{arom}$ ), 7.72 (d, 1 H,  $^3J_{\text{HH}} = 8.0$  Hz,  $\text{H}_{arom}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  20.9 (s,  $\text{CH}_3$ ), 24.5 (d,  $^3J_{\text{CP}} = 2.8$  Hz,  $\text{CH}_3$ ), 40.2 (s,  $\text{CH}_3\text{N}$ ), 48.06 (d,  $^2J_{\text{CP}} = 12.0$  Hz, CH), 49.6 (d,  $^1J_{\text{CP}} = 15.7$  Hz,  $\text{CN}_2$ ), 104.7 (s,  $\text{C}_{para}$ ), 111.1 (s,  $\text{C}_{meta}$ ), 115.0 (s,  $\text{C}_{meta}$ ), 128.8 (br s,  $\text{C}_{arom}$ ), 129.3 (br s,  $\text{C}_{arom}$ ), 129.6 (d,  $^3J_{\text{CP}} = 9.2$  Hz,  $\text{C}_{ortho}$ ); IR (diethyl ether)  $\nu_{\text{CN}_2} = 2029$ .

**General Procedure for the Synthesis of Carbenes 1b–d, 10a,b, and 14a,b.** A toluene solution (1 mL) of the diazo precursor (20 mg) was irradiated (254 or 312 nm) at -60 °C. The reaction was controlled by  $^{31}\text{P}$  NMR spectroscopy to ensure completion.

**1b** ( $h\nu$  312 nm, 223 K):  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  -19.3 (s);  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  14.5 (d,  $^7J_{\text{FP}} = 5$  Hz,  $\text{CF}_3$ ), 11.3 (d,  $^5J_{\text{FP}} = 9$  Hz,  $\text{CF}_3$ );  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  1.50 (d, 24 H,  $^3J_{\text{HH}} = 6.7$  Hz,  $\text{CH}_3$ ), 3.20 (septet d, 4 H,  $^3J_{\text{HH}} = 6.7$  Hz,  $^3J_{\text{HP}} = 21$  Hz, CH), 6.63 (dd, 1 H,  $^4J_{\text{HP}} = 3.0$  Hz,  $^3J_{\text{HH}} = 8.5$  Hz,  $\text{H}_{ortho}$ ), 7.24 (s, 1 H,  $\text{H}_{meta}$ ), 7.30 (d, 1 H,  $^3J_{\text{HH}} = 8.5$  Hz,  $\text{H}_{meta}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  22.3 (s,  $\text{CH}_3$ ), 48.9 (s, CH), 115.3 (qd,  $^3J_{\text{CF}} = 29$  Hz,  $^3J_{\text{CP}} = 22$  Hz,  $\text{C}_{ortho}$ ), 116.9 (qd,  $^3J_{\text{CF}} = 33$  Hz,  $^5J_{\text{CP}} = 6$  Hz,  $\text{C}_{para}$ ), 125.9 (q,  $^1J_{\text{CF}} = 272$  Hz,  $\text{CF}_3$ ), 126.0 (q,  $^1J_{\text{CF}} = 270$  Hz,  $\text{CF}_3$ ), 123.1 (d,  $^3J_{\text{CP}} = 23$  Hz,  $\text{C}_{ortho}$ ), 124.5 (m,  $\text{C}_{meta}$ ), 127.8 (s,  $\text{C}_{meta}$ ), 144.4 (d,  $^2J_{\text{CP}} = 17$  Hz,  $\text{C}_{ipso}$ ), 149.2 (d,  $^1J_{\text{CP}} = 193$  Hz,  $\text{C}_{carbene}$ ).

**1c** ( $h\nu$  312 nm, 223 K):  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  -20.1 (s);  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  12.5 (d,  $^5J_{\text{FP}} = 10$  Hz);  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  1.11 (d, 24 H,  $^3J_{\text{HH}} = 6.5$  Hz,  $\text{CH}_3$ ), 3.20 (septet, 4 H,  $^3J_{\text{HH}} = 6.5$  Hz, CH), 6.56 (pt, 1 H,  $^3J_{\text{HH}} = 7.6$  Hz,  $\text{H}_{arom}$ ), 6.96 (d, 1 H,  $^3J_{\text{HH}} = 7.9$  Hz,  $\text{H}_{arom}$ ), 7.15 (pt, 1 H,  $^3J_{\text{HH}} = 7.6$  Hz,  $\text{H}_{arom}$ ), 7.64 (d, 1 H,  $^3J_{\text{HH}} = 7.9$  Hz,  $\text{H}_{arom}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  22.5 (s,  $\text{CH}_3$ ), 48.6 (s, CH), 116.7 (d,  $^5J_{\text{CP}} = 7$  Hz,

$\text{CH}_{arom}$ ), 116.3 (qd,  $^2J_{\text{CF}} = 27$  Hz,  $^3J_{\text{CP}} = 6$  Hz,  $\text{C}_{arom}$ ), 123.7 (d,  $^3J_{\text{CP}} = 26$  Hz,  $\text{CH}_{arom}$ ), 125.6 (q,  $^1J_{\text{CF}} = 276$  Hz,  $\text{CF}_3$ ), 126.5 (s,  $\text{CH}_{arom}$ ), 131.5 (s,  $\text{CH}_{arom}$ ), 142.7 (d,  $^2J_{\text{CP}} = 6$  Hz,  $\text{C}_{ipso}$ ), 148.6 (d,  $^1J_{\text{CP}} = 124$  Hz,  $\text{C}_{carbene}$ ).

**1d** ( $h\nu$  312 nm, 223 K):  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  -12.9 (q,  $^7J_{\text{FP}} = 11$  Hz);  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  14.9 (d,  $^7J_{\text{FP}} = 9$  Hz);  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  1.05 (d, 24 H,  $^3J_{\text{HH}} = 6.4$  Hz,  $\text{CH}_3$ ), 3.10 (septet, 4 H,  $^3J_{\text{HH}} = 6.4$  Hz, CH), 6.84 (d, 2 H,  $^3J_{\text{HH}} = 8.4$  Hz,  $\text{H}_{arom}$ ), 7.46 (d, 2 H,  $^3J_{\text{HH}} = 8.4$  Hz,  $\text{H}_{arom}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  22.7 (s,  $\text{CH}_3$ ), 48.5 (s, CH), 125.7 (q,  $^1J_{\text{CF}} = 297$  Hz,  $\text{CF}_3$ ), 118.9 (qd,  $^2J_{\text{CF}} = 32$  Hz,  $^5J_{\text{CP}} = 8$  Hz,  $\text{C}_{para}$ ), 120.8 (d,  $^3J_{\text{CP}} = 28$  Hz,  $\text{CH}_{arom}$ ), 131.1 (s,  $\text{CH}_{arom}$ ), 150.8 (s,  $\text{C}_{ipso}$ ), 159.7 (d,  $^1J_{\text{CP}} = 66$  Hz,  $\text{C}_{carbene}$ ).

**10a** ( $h\nu$  254 nm, 223 K):  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ , 193 K)  $\delta$  9.4 (q,  $J_{\text{PF}} = 18$  Hz);  $^{19}\text{F}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  -98.8 (ttd, 1 F,  $^3J_{\text{FF}} = 22$  Hz,  $^4J_{\text{FF}} = 7$  Hz,  $^6J_{\text{FF}} = 18$  Hz,  $F_{para}$ ), -91.6 (t, 2 F,  $^3J_{\text{FF}} = 22$  Hz,  $F_{meta}$ ), -71.2 (ddd, 2 F,  $^3J_{\text{FF}} = 22$  Hz,  $^4J_{\text{FF}} = 7$  Hz,  $^4J_{\text{FP}} = 18$  Hz,  $F_{ortho}$ );  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ , 193 K)  $\delta$  1.03 (d, 24 H,  $^3J_{\text{HH}} = 6.5$  Hz,  $\text{CH}_3$ ), 3.10 (septet d, 4 H,  $^3J_{\text{HH}} = 6.5$  Hz,  $^3J_{\text{HP}} = 20.1$  Hz, CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ , 193 K)  $\delta$  22.5 (s,  $\text{CH}_3$ ), 48.6 (s, CH), 121.2 (t,  $^2J_{\text{CF}} = 19$  Hz,  $\text{C}_{ipso}$ ), 133.2 (md,  $^1J_{\text{CF}} = 239$  Hz,  $\text{C}_{arom}$ ), 133.3 (d,  $^1J_{\text{CP}} = 55$  Hz,  $\text{C}_{carb}$ ), 138.0 (md,  $^1J_{\text{CF}} = 250$  Hz,  $\text{C}_{arom}$ ), 138.5 (md,  $^1J_{\text{CF}} = 239$  Hz,  $\text{C}_{arom}$ ).

**10b** ( $h\nu$  254 nm, 293 K):  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  5.9 (q,  $J_{\text{PF}} = 17$  Hz).

**14a** ( $h\nu$  254 nm, 203 K):  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  -17.9 (s).

**14b** ( $h\nu$  254 nm, 223 K):  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  -19.8 (s);  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  1.02 (d, 24 H,  $^3J_{\text{HH}} = 6.0$  Hz,  $\text{CH}_3$ ), 2.47 (d, 3 H,  $^5J_{\text{HP}} = 3.6$  Hz,  $\text{CH}_3$ ), 3.25 (septet, 4 H,  $^3J_{\text{HH}} = 6.0$  Hz, CH), 7.02 (br s, 1 H,  $\text{H}_{arom}$ ), 7.14 (br s, 1 H,  $\text{H}_{arom}$ ), 7.37 (br s, 2 H,  $\text{H}_{arom}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_7\text{D}_8$ )  $\delta$  23.5 (s,  $\text{CH}_3$ ), 23.6 (s,  $\text{CH}_3$ ), 44.8 (s, CH), 119.1 (d,  $^5J_{\text{CP}} = 10$  Hz,  $\text{CH}_{arom}$ ), 121.8 (d,  $^3J_{\text{CP}} = 26$  Hz,  $\text{CH}_{arom}$ ), 127.3 (d,  $^3J_{\text{CP}} = 23$  Hz,  $\text{C}_{arom}$ ), 129.9 (d,  $^2J_{\text{CP}} = 4$  Hz,  $\text{C}_{ipso}$ ), 130.3 (s,  $\text{CH}_{arom}$ ), 137.5 (s,  $\text{CH}_{arom}$ ), 156.1 (d,  $^1J_{\text{CP}} = 46$  Hz,  $\text{C}_{carbene}$ ).

**Thermal Rearrangement of Carbene 1c.** A toluene solution (1 mL) of carbene **1c** (31 mg, 0.07 mmol) was heated at 40 °C overnight. Compound **5c** was characterized spectroscopically without further purification. Excess elemental sulfur (10 mg, 0.3 mmol) was then added at room temperature to the toluene solution of **5c**. After 2 h, the solvent was removed under vacuum and the crude residue was purified by column chromatography (pentane/diethyl ether 95/5,  $R_f = 0.2$ ). Derivative **6c** was isolated as yellow crystals (68% yield) from a saturated diethyl ether solution. **5c**:  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  75.5 (qd,  $J_{\text{PP}} = 52$  Hz,  $^5J_{\text{FP}} = 14$  Hz), 36.8 (d,  $J_{\text{PP}} = 52$  Hz);  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  18.0 (d,  $^5J_{\text{FP}} = 14$  Hz), 17.9 (s). **6c**: mp 188 °C (decomp);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  63.6 (d,  $J_{\text{PP}} = 95$  Hz), 42.5 (d,  $J_{\text{PP}} = 95$  Hz);  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  22.0 (s), 17.5 (s);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.31 (s, 6 H,  $\text{CH}_3$ ), 0.48 (s, 6 H,  $\text{CH}_3$ ), 1.06 (s, 6 H,  $\text{CH}_3$ ), 1.24 (s, 6 H,  $\text{CH}_3$ ), 1.46 (s, 6 H,  $\text{CH}_3$ ), 1.57 (s, 6 H,  $\text{CH}_3$ ), 3.61 (br s, 2 H, CH), 4.00 (br s, 2 H, CH), 4.64 (br s, 2 H, CH), 4.95 (pt, 1 H,  $^2J_{\text{HP}} = 15.3$  Hz,  $\text{H}_{cycle}$ ), 7.31–8.85 (br s, 8 H,  $\text{H}_{arom}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  22.8 (s,  $\text{CH}_3$ ), 22.9 (s,  $\text{CH}_3$ ), 30.0 (d,  $^3J_{\text{CP}} = 3$  Hz,  $\text{CH}_3$ ), 23.4 (d,  $^3J_{\text{CP}} = 5$  Hz,  $\text{CH}_3$ ), 24.0 (s,  $\text{CH}_3$ ), 24.2 (d,  $^3J_{\text{CP}} = 4$  Hz,  $\text{CH}_3$ ), 25.6 (s,  $\text{CH}_3$ ), 46.7 (d,  $^2J_{\text{CP}} = 4$  Hz, CH), 48.1 (br s, CH), 49.0 (br s, CH), 58.9 (dd,  $J_{\text{CP}} = 38$  Hz,  $J_{\text{CP}} = 54$  Hz,  $\text{CH}_{cycle}$ ), 125.3 (s,  $\text{CH}_{arom}$ ), 125.5 (s,  $\text{CH}_{arom}$ ), 126.9 (q,  $J_{\text{CF}} = 2$  Hz,  $\text{CH}_{arom}$ ), 128.3 (s,  $\text{CH}_{arom}$ ), 130.7 (s,  $\text{CH}_{arom}$ ), 131.2 (s,  $\text{CH}_{arom}$ ), 134.2 (q,  $J_{\text{CF}} = 4$  Hz,  $\text{CH}_{arom}$ ), 141.0 (q,  $J_{\text{CF}} = 5.2$  Hz,  $\text{CH}_{arom}$ ). Anal. Calcd for  $\text{C}_{34}\text{H}_{51}\text{F}_6\text{N}_3\text{P}_2\text{S}$ : C 57.53, H 7.24, N 5.92. Found: C 57.92, H 7.61, N 5.67.

**Reaction of Carbene 10a with Its Diazo Precursor 9a.** A pentane solution (2 mL) of diazo compound **9a** (0.10 g, 0.23 mmol) was irradiated ( $\lambda$  300 nm) at -50 °C for 8 h. The reaction was monitored by  $^{31}\text{P}$  NMR and the irradiation was continued to half conversion. This mixture was then held at room temperature for 14 h before the solvent was removed in vacuo. Yellow crystals of **11a** were obtained (0.06 g; 63%) from a saturated diethyl ether/acetonitrile solution at -30 °C: mp 151 °C (decomp);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  56.8 (t,  $^4J_{\text{PF}} = 49$  Hz);  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  -88.3 (dd, 4 F,  $^3J_{\text{FF}} = 20$  Hz,  $^3J_{\text{FF}} = 17$  Hz,  $F_{meta}$ ),

−80.8 (t, 2 F,  $^3J_{\text{FF}} = 20$  Hz,  $F_{\text{para}}$ ), −58.1 (m, 4 F,  $F_{\text{ortho}}$ ); MS (EI,  $\text{NH}_3$ )  $m/z$  849, 231, 132; IR (pentane)  $\nu_{\text{C=N}} = 1518$ . Anal. Calcd for  $\text{C}_{38}\text{H}_{56}\text{F}_{10}\text{N}_6\text{P}_2$ : C 53.77, H 6.65, N 9.90. Found: C 53.48, H 6.34, N 10.24.

**Reaction of Carbene 10b with Its Diazo Precursor 9b.** A diethyl ether solution (2 mL) of diazo compound **9b** (0.10 g, 0.17 mmol) was irradiated ( $\lambda$  300 nm) at −50 °C for 8 h. The reaction was monitored by  $^{31}\text{P}$  NMR and the irradiation was continued until half conversion was achieved. This mixture was then maintained at room temperature for 14 h before the solvent was removed in vacuo. Yellow crystals of **11b** were obtained (0.07 g; 72%) from a saturated diethyl ether solution at −30 °C: mp 244 °C (decomp);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  70.0 (t,  $^4J_{\text{PF}} = 32$  Hz);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ )  $\delta$  −87.2 (t, 2 F,  $^3J_{\text{FF}} = 23$  Hz,  $F_{\text{meta}}$ ), −80.3 (t, 1 F,  $^3J_{\text{FF}} = 23$  Hz,  $F_{\text{para}}$ ), −59.3 (d, 2 F,  $^3J_{\text{FF}} = 23$  Hz,  $F_{\text{ortho}}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.09–1.73 (m, 40 H,  $\text{CH}_2$ ), 2.70 (m, 4 H, CH); IR ( $\text{CDCl}_3$ )  $\nu_{\text{C=N}} = 1516$ . Anal. Calcd for  $\text{C}_{62}\text{H}_{88}\text{F}_{10}\text{N}_6\text{P}_2$ : C 63.68, H 7.59, N 7.19. Found: C 64.02, H 7.86, N 6.84.

**X-ray Crystallographic Studies of Compounds 6c, 10b, and 11a.** Crystal data for all structures are presented in Table 3. Data were collected at low temperatures on a Bruker-AXS CCD 1000 diffractometer with Mo  $K\alpha$  ( $\lambda = 0.71073$  Å). The structures were solved by direct methods by means of SHELXS-97<sup>26</sup> and refined with all data on  $F^2$  by means of SHELXL-97.<sup>27</sup> All non-hydrogen atoms were refined anisotropically. **11a** shows two different orientations of a nonmerohedral twin in the reciprocal space. By using the program package GEMINI,<sup>28</sup> we were able to separate the two domains. The refinement by using HKLF 5 in SHELXL gave occupancies of about 60 to 40 for the two orientations.

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**Computational Details.** All calculations were performed with the Gaussian 98 set of programs.<sup>29</sup> The various structures were fully optimized at the B3LYP level. This density functional is built with Becke's three-parameter exchange functional<sup>30</sup> and the Lee–Yang–Parr correlation functional.<sup>31</sup> All heavy main-group atoms were augmented by a single set of polarization functions [basis set 6–31g-(d)]. The energy optimizations were conducted by analytically determined nuclear gradients. All of the investigated structures were characterized by vibrational analysis within the harmonic approximation. The force constants were derived from analytically computed gradients.

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**Supporting Information Available:** X-ray crystallographic data for compounds **6c**, **10b**, and **11a** (print/PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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