Carbenes

Readily Available Onio-Substituted Methyleneiminium Salts: Single Precursors for a Variety of Aminocarbenes**

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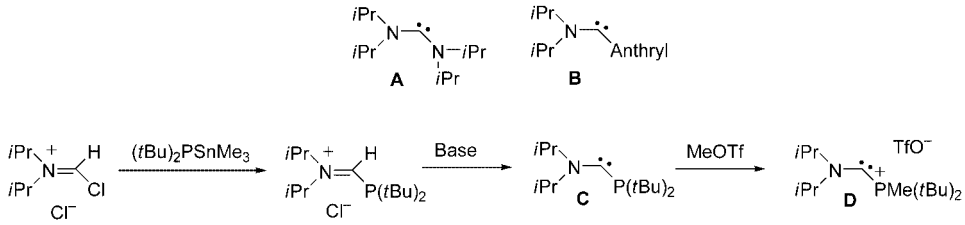
Due to their strong σ-donor properties, N-heterocyclic-carbenes (NHCs) have found numerous applications as ligands for transition-metal catalysts.[1] More recently, it has been found that acyclic diaminocarbenes **A** (see Scheme 1)[2] or even amino aryl carbenes **B**[3] also behave as strong-σ-donor weak-π-acceptor ligands and therefore could be considered as alternative ligands for catalysts;[4,5] to date, **A** is the most basic carbene ligand known.[4c] However, the range of acyclic amino carbenes (AAC) known is far surpassed by that of their NHCs counterparts. Obstacles to extending the range of available AACs reside in their supposed inherent instability,[6] but also in the lack of a general and convenient synthetic route for their preparation. We have recently reported that substitution reactions occur at the carbene center of the phosphonio-substituted carbene **D**, thus giving rise to new stable carbenes.[7] However, the synthesis of **D** requires several steps, which includes the preparation of a stannyl phosphane; a very fragile carbene intermediate **C**;[8] and most importantly, is limited to (methyl)di(*tert*-butyl)-phosphane as a leaving group. Indeed, to assure the stability of carbene **C**, bulky groups at phosphorus are required, and the addition of an organic group to the phosphane to form a quaternary P center is limited to methylation. (Methyl)di(*tert*-butyl)phosphane is 1) very basic, therefore not the perfect leaving group; 2) bulky, thus preventing the substitution reaction with sterically hindered nucleophiles; 3) features acidic methyl protons, which often react with the nucleophile (base) to afford undesirable products.

Herein, we report an easy entry to amino(phosphonio)-carbenes by using simple phosphanes and readily available reagents, and the subsequent substitution reactions at the carbene center.

As one of the most common synthetic routes to stable carbenes is based on the deprotonation of the corresponding iminium salt,[1] phosphonio iminium salts **3** were the obvious precursors to amino(phosphonio)carbenes. Based on the elegant work by Weiss and co-workers, we predicted that dications such as **3** should be accessible and stable as compounds that feature bis(onio)substituted sp^3- and even sp^2-carbon atoms have been isolated.[9] Indeed, we have found that Alder's dimer **1**[2,10] cleanly reacts at room temperature with the basic tricyclohexylphosphane, but also with very simple phosphanes such as triphenylphosphane, thus leading to the formation of the desired dications **3a,b** in 94 and 93% yield, respectively (Scheme 2). Although **3a,b** are water sensitive, giving back diisopropylamide when exposed to moisture, they are highly thermally stable (m.p.: **3a**: 217°C; **3b**: 172°C). Importantly, although the trifluoromethane sulfonate salts **3a,b** are barely soluble in most classical organic solvents, they are soluble in acetonitrile; thus, their purification is quite easy and large quantities can be prepared in a one-pot reaction from the amide (it is not necessary to isolate Alder's dimer **1**). However, in this reaction, half of the



Scheme 1. Carbenes **A** and **B**, and the synthesis of carbenes **C** and **D**.

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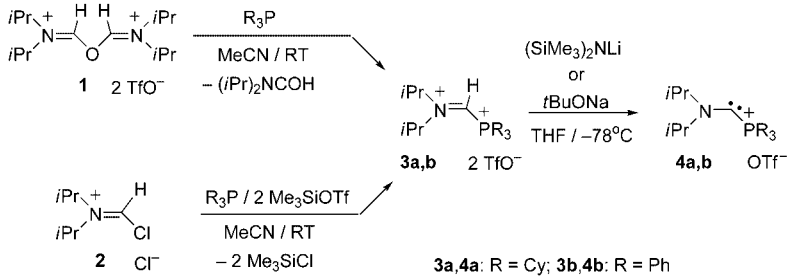


Scheme 2. Synthesis of **3a,b** and **4a,b**.

starting amide is lost. This is not significant when simple amides are used, but may become an important issue with more sophisticated amides. A way to bypass this obstacle is to treat an adduct of phosphane and trimethylsilyl triflate, generated in situ,[11] with the iminium chloride **2**. Using this route, we isolated **3a,b** in 89 and 94% yield, respectively, from the amide.

The acidity of the iminium protons of **3a,b** is indicated by the low field ^{1}H NMR chemical shifts (**3a**: 9.33 ppm, $J_{HP} = 19.3$ Hz **3b**: 9.66 ppm, $J_{HP} = 24.6$ Hz). Thus, the addition of one equivalent of sodium *tert*-butoxide and lithium bis(trimethylsilyl)amide to suspensions of dications **3a** and **3b** in tetrahydrofuran cleanly led to the formation of the corresponding amino(phosphonio)carbenes **4a** and **4b**, respectively. They have been isolated as air-sensitive orange–yellow crystals indefinitely stable in solution and in the solid state (m.p.: **4a**: 164 °C; **4b** 178 °C; Scheme 2).

The ^{13}C NMR signals for the carbene carbon atoms (**4a**: $\delta = 304.52$ ppm, $J_{CP} = 109.0$ Hz; **4b**: $\delta = 292.4$ ppm, $J_{CP} = 110.5$ Hz) are shifted considerably downfield relative to the resonances observed for their protonated precursors **3a,b** (**3a**: $\delta = 172.3$ ppm, $J_{CP} = 37.3$ Hz; **3b**: $\delta = 169.9$ ppm, $J_{CP} = 64.1$ Hz). In contrast, single-crystal X-ray diffraction studies[12] show very similar features for all four compounds **3a,b** and **4a,b** (Figure 1): no interaction with the counterion, a

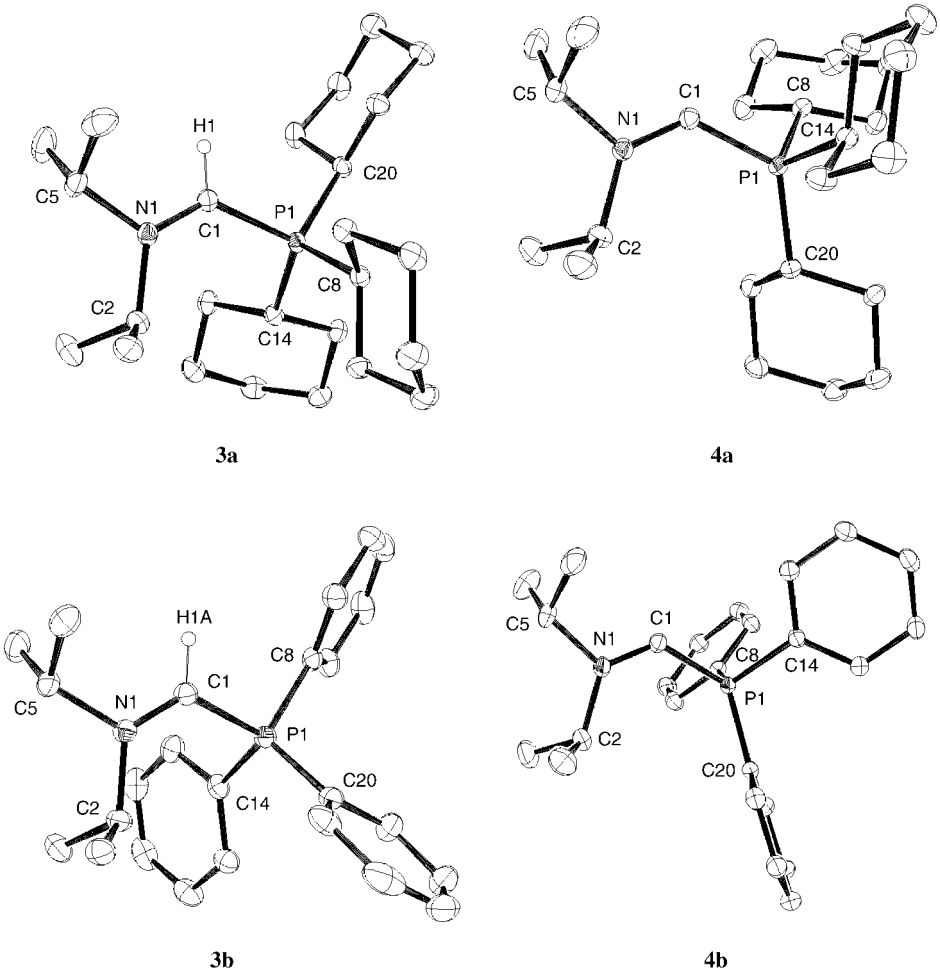
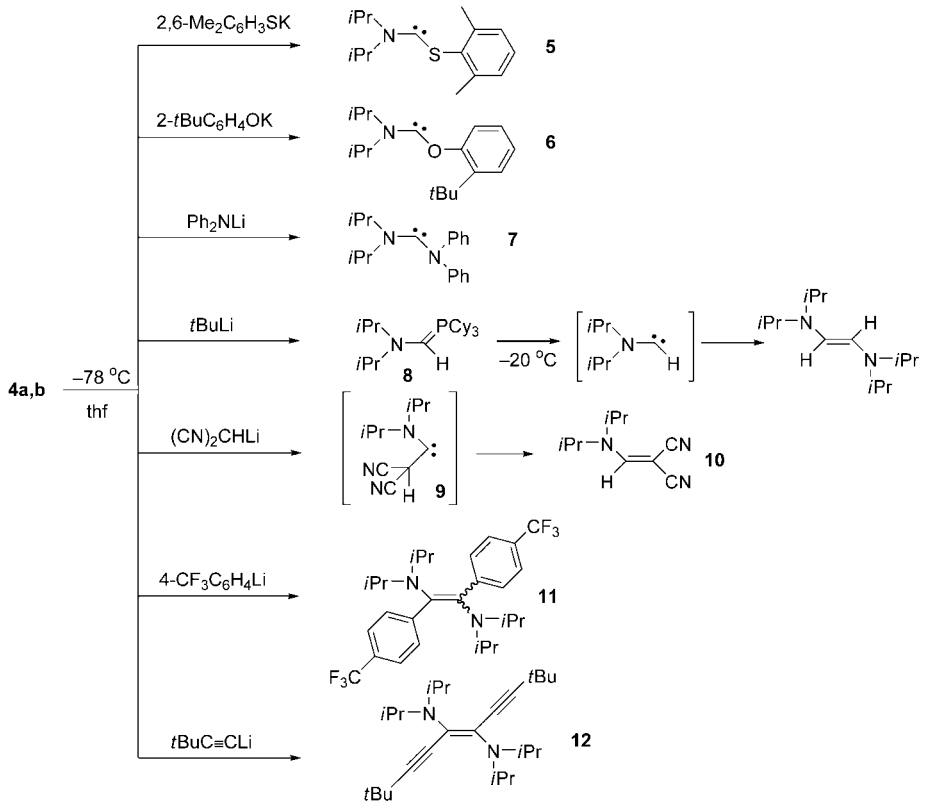


Figure 1. Selected bond distances [Å] and bond angles [°]: **3a**: N(1)-C(1) 1.283, P(1)-C(1) 1.849; N(1)-C(1)-P(1) 129.64, C(1)-N(1)-C(5) 119.1, C(1)-N(1)-C(2) 125.41, C(2)-N(1)-C(5) 115.48, C(14)-P(1)-(C8) 112.02, C(20)-P(1)-C(8) 108.92, C(20)-P(1)-C(14) 111.43. **4a**: N(1)-C(1) 1.281, P(1)-C(1) 1.792; N(1)-C(1)-P(1) 129.3, C(1)-N(1)-C(5) 115.4, C(1)-N(1)-C(2) 129.1, C(2)-N(1)-C(5) 115.5, C(8)-P(1)-C(14) 107.18, C(1)-P(1)-C(20) 126.01, C(8)-P(1)-C(20) 113.17. **3b**: N(1)-C(1) 1.275, P(1)-C(1) 1.844; N(1)-C(1)-P(1) 125.64, C(1)-N(1)-C(2) 124.00, C(1)-N(1)-C(5) 119.94, C(2)-N(1)-C(5): 116.05, C(20)-P(1)-C(8) 111.20, C(20)-P(1)-C(14) 111.65, C(8)-P(1)-C(14) 110.52. **4b**: N(1)-C(1) 1.282, P(1)-C(1) 1.775; N(1)-C(1)-P(1) 129.14, C(1)-N(1)-C(2): 128.05, C(1)-N(1)-C(5): 115.97, C(2)-N(1)-C(5): 115.98, C(14)-P(1)-C(8): 108.42, C(14)-P(1)-C(20): 105.63, C(8)-P1)-C(20): 109.06.

short CN bond (**3a**: 1.283; **4a**: 1.281; **3b**: 1.275; **4b**: 1.282 Å), a long CP bond (**3a**: 1.849; **4a**: 1.792; **3b**: 1.844; **4b**: 1.775 Å), and an acute angle about the iminium and carbene centers (**3a**: 129.6; **4a**: 129.3; **3b**: 125.6; **4b**: 129.4°). Notably, the similarities observed between the carbenes **4a,b**, which feature two phosphanes that are very different in nature, suggest that there is only a slight, if any, interaction between the phosphonio group and the carbene center.

Since large quantities of amino(phosphonio)carbenes **4a,b** were now available, we were able to investigate the scope of the substitution reaction at the carbene center. As already observed with the previously reported onio–carbene **D**, the potassium salts of 2,6-dimethylthiophenol and 2-*tert*-butylphenol react cleanly with **4a,b** in THF at −78 °C; multinuclear NMR spectroscopy showed the quantitative formation of carbenes **5**[7] and **6**,[10b] along with the corresponding phosphane (Scheme 3). As Ph_2NLi is too basic to promote substitution with **D**, a study of its reactivity was of interest. Again, the reaction of Ph_2NLi with **4a,b** at −78 °C, yields exclusively the unsymmetrical diamino carbene **7** that has been fully characterized in solution by multinuclear NMR spectroscopy (m.p.: 75 °C). To define the limit of the method, carbenes **4a,b** were then treated with *tert*-butyl lithium. Although in the case of **4b**, a complex mixture was obtained, for **4a** the corresponding phosphorus ylide **8** was formed quantitatively (^{31}P NMR: $\delta = 14.9$ ppm, d, $^2J_{CP} = 50$ Hz). Not surprisingly, the latter is unstable[13] and dissociates at −20 °C within ten minutes into the phosphane and the diisopropylaminocarbene, which dimerizes.[14] To prevent this reduction reaction, the use of a secondary alkyl lithium was explored.



Scheme 3. Reactivity of **4a,b**.

Addition of the lithium salt of malonitrile to **4a,b** cleanly afforded enamine **10**, which demonstrates that the desired substitution reaction occurred, and that the primary formed carbene **9** is unstable towards a 1,2-hydrogen shift.[15,16] Substitution reactions also take place with aryl and alkynyl lithium salts, thus leading to transient carbenes, which dimerize into alkenes **11** and **12**, respectively.

In summary, we have developed a new route for the synthesis of amino(phosphonio)carbenes, by deprotonation of readily available dicationic precursors. The onio–carbenes are excellent building blocks for the synthesis of new stable and transient acyclic monoamino carbenes. The only limitation observed for this route is with tertiary alkyl carbenes, which remain unknown and constitute an exciting synthetic challenge.

Experimental Section

All manipulations were performed under argon by using standard Schlenk techniques. Dry, oxygen-free solvents were employed.

Synthesis of C-phosphonio iminium salts **3a,b**: R_3P (20 mmol), was added at room temperature to an acetonitrile solution (120 mL) of **1** (20 mmol) and the mixture was stirred for 1 h. Alternatively, an acetonitrile solution (30 mL) of trimethylsilyltrifluoromethane sulfonate (8.9 g, 40 mmol) and R_3P (20 mmol) was added, at room temperature to an acetonitrile solution (50 mL) of iminum chloride **2**[17] (3.7 g, 20 mmol) and the reaction mixture stirred for 1 hour. The solvent was evaporated under vacuum, and the residue was washed with THF (150 mL) affording white microcrystalline solids. **3a**: $^{31}P\{^1H\}$ NMR (CD_3CN): $\delta = 43.86$ ppm; ^{1}H NMR (CD_3CN): $\delta = 1.64$–2.20 (m, 30 H, CH_2), 1.83 and 1.86 (d, 6 H, J(H,H) = 6.5 Hz, CH_3CH), 3.50 (m, 3 H, Cy-C*H*), 4.70 (sept, 1 H, J(H,H) = 6.5 Hz, C*H*N), 5.09 (sept d, 1 H, J(H,H) = 6.5 Hz, J(H,P) = 2.9 Hz, C*H*N), 9.33 ppm (d, 1 H, J(P,H) = 19.3 Hz, =C*H*); $^{13}C\{^1H\}$ NMR (CD_3CN): $\delta = 21.26$ and 24.90 (s, *C*H$_3$CH), 25.86 (s, CH_2), 27.21 (d, J(C,P) = 14.5 Hz, CH_2), 28.81 (br, CH_2), 35.40 (d, J(C,P) = 29.0 Hz, Cy-*C*H), 66.00 (br, *C*HN), 69.67 (s, *C*HN), 123.31 (q, J(C,F) = 319.4 Hz, CF_3), 172.29 ppm (d, J(C,P) = 37.3 Hz, =*C*H). **3b**: $^{31}P\{^1H\}$ NMR (CD_3CN): $\delta = 21.50$ ppm; ^{1}H NMR (CD_3CN) $\delta = 1.25$ and 1.72 (d, 6 H, J(H,H) = 6.7 Hz, CH_3CH), 4.52 (sept, 1 H, J(H,H) = 6.7 Hz, C*H*N), 4.87 (sept d, 1 H, J(H,H) = 6.7 Hz, J(H,P) = 3.1 Hz, C*H*N), 7.85–8.09 (m, 15 H, Ph), 9.66 ppm (d, 1 H, J(P,H) = 24.6 Hz, =C*H*); $^{13}C\{^1H\}$ NMR (CD_3CN): $\delta =$ 24.04 and 26.29 (s, *C*H$_3$CH), 68.00 (d, J(C,P) = 3.2 Hz, CHN), 67.45 (d, J(C,P) = 6.7 Hz, *C*HN), 121.89 (q, J(C,F) = 320.7 Hz, CF_3), 114.04 (d, J(C,P) = 88.2 Hz, C_{ipso}), 132.50 (d, J(C,P) = 13.4 Hz, C_{meta}), 136.08 (d, J(C,P) = 12.0 Hz, C_{ortho}), 138.54 (s, C_{para}),

169.93 ppm (d, J(C,P) = 64.1 Hz, =*C*H).

Synthesis of phosphonio carbenes **4a,b**: A 1/1 mixture of *t*BuONa and **3a**, or $(Me_3Si)_2NLi$ and **3b** (1.2 mmol) was cooled to −78 °C, and THF (6 mL) was added. The suspension was brought to room temperature and stirred for 30 min. The solvent was removed under vacuum and the residue was washed with Et_2O (2 mL). Orange solids, containing NaOTf or LiOTf, were obtained (quantitative reaction by ^{31}P NMR) and used for the substitution reactions without purification. Single crystals were grown by slow diffusion of a THF solution of the solids in ether. **4a**: $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 15.16 ppm; ^{1}H NMR ([D$_8$]THF): δ = 1.14–1.89 (m, 30 H, CH_2), 1.38 and 1.45 (d, 6 H, J(H,H) = 6.7 Hz, CH_3CH), 2.76 (m, 3 H, Cy-C*H*), 4.31 ppm (br, 2 H, C*H*N); $^{13}C\{^1H\}$ NMR ([D$_8$]THF): δ = 20.70 and 23.29 (s, *C*H$_3$CH), 26.84 (s, CH_2), 27.47 (d, J(C,P) = 11.7 Hz, CH_2), 28.59 (d, J(C,P) = 3.4 Hz, CH_2), 34.62 (d, J(C,P) = 36.9 Hz, CH), 44.74 and 48.10 (br, CH_3CH), 122.33 (q, J(C,F) = 321.9 Hz, CF_3), 304.52 ppm (d, J(C,P) = 109.0 Hz, $C_{carbene}$); **4b**: $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = −2.46 ppm; ^{1}H NMR ([D$_8$]THF): δ = 1.37 (d, 12 H, J(H,H) = 6.5 Hz, CH_3CH), 4.46 (br, 2 H, C*H*N), 7.63–7.76 ppm (m, 15 H, Ph); $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 220 K): δ = 21.51 (s, *C*H$_3$CH), 59.31 (br. CH_3CH), 73.52 (br. CH_3CH), 122.00 (q, J(C,F) = 321.1 Hz, CF_3), 123.14 (d, J(C,P) = 81.1 Hz, C_{ipso}), 132.00 (d, J(C,P) = 10.4 Hz, C_{meta}), 134.72 (d, J(C,P) = 10.4 Hz, C_{ortho}), 135.37 (s, C_{para}), 292.40 ppm (d, J(C,P) = 110.5 Hz, $C_{carbene}$); at room temperature, the signals of the isopropyl carbon are too broad to be observed.

General procedure for the substitution reactions**:** A THF solution (2 mL) of the nucleophile (1.2 mmol) was added to a suspension of carbene **4a** or **4b** (1.2 mmol) in 2 mL of THF at −78 °C. The mixture was warmed to room temperature and stirred for 30 minutes. According to NMR spectroscopy, all the reactions are quantitative. Carbene **7**: ^{1}H NMR ([D$_8$]THF): δ = 0.84 and 1.42 (d, 6 H, J(H,H) = 6.4 Hz, CH_3CH), 3.71 and 3.75 (sept, 1 H, J(H,H) = 6.4 Hz, C*H*N), 7.07–7.27 ppm (m, 10 H, Ph); $^{13}C\{^1H\}$ NMR ([D$_8$]THF): δ = 20.94 and 26.41 (s, *C*H$_3$CH), 49.42 and 50.78 (s, *C*HN), 125.27, 125.55, 129.47 and 151.27 (s, Ph), 258.20 ppm (s, $C_{carbene}$). Enamine **10**: ^{1}H NMR ($CDCl_3$): δ = 1.30 and 1.32 (d, 6 H, J(H,H) = 6.5 Hz, CH_3CHN), 3.75 and 4.77 (sept, 1 H, J(H,H) = 6.5 Hz, CH_3CH*N*), 7.03 ppm (s, 1 H, =CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 20.49 and 23.88 (s, *C*H$_3$CHN), 48.88 and 50.85 (s, CH_3*C*HN), 49.02 (s, =*C*$(CN)_2$), 115.78 and 118.22 (s, CN), 153.19 ppm (s, =CH). Dimer **11**: *E*/*Z* = 3/1; ^{1}H NMR (C_6D_6): δ(*E*) = 0.69 (d, 24 H, J(H,H) = 6.4 Hz, CH_3CHN), 3.05 (sept, 4 H, J(H,H) = 6.4 Hz, CH_3C*H*N), 7.42 and 7.45 ppm (d, 4 H, J(H,H) = 9.4 Hz, H_{arom}); δ(*Z*) = 1.07 (d, 24 H, J(H,H) = 7.0 Hz, CH_3CHN), 3.73 (sept, 4 H, J(H,H) = 7.0 Hz, CH_3C*H*N), 7.03 and 7.07 ppm (d, 4 H, J(H,H) = 9.4 Hz, H_{arom}); $^{13}C\{^1H\}$ NMR (C_6D_6): δ(*E*) = 23.62 (s, *C*H$_3$CHN), 52.16 (s, CH_3*C*HN), 125.15 (s, C_{ortho}), 125.58 (q, J(C,F) = 272.8 Hz, CF_3), 129.29 (q, J(C,F) = 31.1 Hz, C_{para}), 132.12 (s, C_{meta}), 140.37 (s, =C), 149.02 ppm (s, C_{ipso}); δ(*Z*) = 24.46 (s, *C*H$_3$CHN), 48.21 (s, CH_3*C*HN), 124.35 (s, C_{ortho}), 133.66 (s, C_{meta}), 134.86 (s, =C), 147.95 ppm (s, C_{ipso}); $^{19}F\{^1H\}$ NMR (C_6D_6): δ(*E*) = 1.09; (*Z*): 1.37 ppm. Dimer **12**: ^{1}H NMR (C_6D_6): δ = 1.23 (s, 18 H, CH_3C), 1.31 (d, 24 H, J(H,H) = 6.4 Hz, CH_3CHN), 3.50 ppm (sept, 4 H, J(H,H) = 6.4 Hz, CH_3C*H*N); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 22.50 (s, *C*H$_3$CHN), 28.91 (s, CH_3*C*), 31.36 (s, *C*H$_3$C), 50.62 (s, CH_3*C*HN), 80.55 (s, C≡C), 106.60 (s, C≡C), 134.53 ppm (s, C=C).

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[12] The Bruker SMART-1000[18a] X-ray diffraction instrument with Mo radiation was used for data collection of compounds **3a**, **3b**, **4a**, and **4b.** All data frames were collected by using ω-scan mode (−0.3° ω-scan width, hemisphere of reflections) and integrated by using the Bruker SAINTPLUS program.[18b] The intensity data were corrected for Lorentzian polarization and absorption corrections were performed by using the SADABS program incorporated in the SAINTPLUS program. The Bruker SHELXTL program[18c] was used for direct methods of phase determination and structure refinement. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of the four compounds were refined by means of a full-matrix least-squares procedure on F^2. All H atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. Crystal data for **3a:** size 0.56 × 0.44 × 0.28 mm^3, orthorhombic, space group *Pbca*, a = 14.709(3) Å, b = 15.705(4) Å, c = 28.878(6) Å, $\alpha = \beta = \gamma$ = 90°, V = 6671(3) Å^3, ρ_{calcd} = 1.378 g cm^{-3}, $2\theta_{max}$ = 56.56°, Mo radiation (λ = 0.71073 Å), low temperature = 223(2) K, total reflections collected = 69549, independent reflections = 8276 (R_{int} = 0.0377, R_{sig} = 0.0203), 6571 (79.4%) reflections were greater than $2\sigma(I)$, index ranges $-19 \le h \le 19$, $-20 \le k \le 20$, $-36 \le l \le 38$, absorption coefficient μ = 0.280 mm^{-1}; max/min transmission = 0.9256/0.8588, 513 parameters were refined and converged at $R1$ = 0.0460, $wR2$ = 0.1131, with intensity $I > 2\sigma(I)$, the final difference map was 0.538/−0.327 e Å^{-3}. **3b:** size 0.51 × 0.30 × 0.13 mm^3, monoclinic, space group $P2(1)/c$, a =

8.4220(12) Å, $b = 19.597(3)$ Å, $c = 18.867(3)$ Å, $\beta = 101.212(3)°$, $V = 3054.5(8)$ Å^3, $\rho_{calcd} = 1.465$ g cm^{-3}, $2\theta_{max} = 52.74°$, Mo-radiation ($\lambda = 0.71073$ Å), low temperature = 223(2) K, total reflections collected = 17766, independent reflections = 6234 ($R_{int} = 0.0274$, $R_{sig} = 0.0303$), 4972 (79.8 %) reflections were greater than $2\sigma(I)$, index ranges $-10 \le h \le 10$, $-23 \le k \le 24$, $-20 \le l \le 23$, absorption coefficient $\mu = 0.305$ mm^{-1}; max/min transmission = 0.9615/0.8601, 422 parameters were refined and converged at $R1 = 0.0387$, $wR2 = 0.0960$, with intensity $I > 2\sigma(I)$, the final difference map was 0.402/−0.306 e Å^{-3}. **4a:** size $0.48 \times 0.14 \times 0.08$ mm^3, monoclinic, space group $P2(1)/n$, $a = 10.4384(14)$ Å, $b = 9.7257(10)$ Å, $c = 28.325(4)$ Å, $\beta = 91.238(2)°$, $V = 2874.9(6)$ Å^3, $\rho_{calcd} = 1.251$ g cm^{-3}, $2\theta_{max} = 52.74°$, Mo-radiation ($\lambda = 0.71073$ Å), low temperature = 223(2) K, total reflections collected = 26302, independent reflections = 5865 ($R_{int} = 0.0589$, $R_{sig} = 0.0486$), 4157 (70.9 %) reflections were greater than $2\sigma(I)$, index ranges $-13 \le h \le 12$, $-12 \le k \le 12$, $-35 \le l \le 35$, absorption coefficient $\mu = 0.215$ mm^{-1}; max/min transmission = 0.9830/0.9040, 367 parameters were refined and converged at $R1 = 0.0574$, $wR2 = 0.1479$, with intensity $I > 2\sigma(I)$, the final difference map was 1.043/−0.611 e Å^{-3}. **4b:** size $0.68 \times 0.42 \times 0.41$ mm^3, monoclinic, space group $P2(1)/n$, $a = 8.3940(11)$ Å, $b = 10.5726(14)$ Å, $c = 29.903(4)$ Å, $\beta = 97.160(3)°$, $V = 2633.1(6)$ Å^3, $\rho_{calcd} = 1.321$ g cm^{-3}, $2\theta_{max} = 56.56°$, Mo-radiation ($\lambda = 0.71073$ Å), low temperature = 228(2) K, total reflections collected = 19642, independent reflections = 6509 ($R_{int} = 0.0263$, $R_{sig} = 0.0273$), 5494 (84.4 %) reflections were greater than $2\sigma(I)$, index ranges $-11 \le h \le 10$, $-14 \le k \le 14$, $-22 \le l \le 39$, absorption coefficient $\mu = 0.233$ mm^{-1}; max/min transmission = 0.9056/0.7309, 320 parameters were refined and converged at $R1 = 0.0470$, $wR2 = 0.1251$, with intensity $I > 2\sigma(I)$, the final difference map was 0.501/−0.541 e Å^{-3}. CCDC-233824 (**3a**), CCDC-233825 (**3b**), CCDC-233826 (**4a**) and CCDC-233827 (**4b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[15] a) The activation energies for 1,2-hydrogen shifts[16a] are essentially zero for simple alkylcarbenes but increase significantly for heteroatom-substituted alkylcarbenes.[16b,c]

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