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Direct synthesis of *N*-phosphanyl-heterocyclic carbenes

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ABSTRACT

A direct method for the synthesis of *N*-phosphanyl-heterocyclic carbenes is described. The method is based on the reaction of lithium imidazolides and benzimidazolides having a bulky alkyl group at the nitrogen atom with di(*tert*-butyl)chlorophosphine leading directly to the carbenes.

Organolithiums prepared by direct deprotonation of acidic hydrogen using strong bases are excellent reagents for introducing a heterocyclic moiety into a complex structure.[1,2] Lithium derivatives of imidazole and benzimidazole play an important role in the synthesis of their various phosphorylated derivatives.[3] Also, their structures have been the subject of numerous theoretical and practical studies. It was found that lithium 1-methyl-(4-*tert*-butyl)imidazolide has carbene rather than carbanion nature. The ^{13}C NMR chemical shift of the C2 atom of lithium 1-methyl-(4-*tert*-butyl)imidazolide is found downfield (^{13}C $\delta = 195$) and the X-ray structural study supports quite strongly the carbene nature of lithium imidazolides.[3,4]

At the same time lithium *N*-methylimidazolide having an even more pronounced downfield shift of the C2 atom (^{13}C $\delta = 201.6$) reacts, for example, with *t*-Bu_2PCl, similar to a carbanion affording 2-phosphorylated imidazole,[5] but not the corresponding carbene which is a stable compound as described earlier by us.[6]

The difference in chemical shifts of the C2 carbon in the ^{13}C NMR spectra of the two lithium imidazolides—*N*-methylimidazolide and *N*-methyl-4-(*tert*-butyl)imidazolide—is probably due to the steric effect of the *tert*-butyl group which shields the adjacent nitrogen atom from lithium and imparts more anionic character to the molecule. It can be assumed that in *N*-*tert*-butylimidazolide the same effect from the *tert*-butyl group is extended to the second carbon atom, thus shielding the nitrogen to a greater extent from the lithium atom and rendering more carbene character to the molecule.

We found that lithium imidazolides **2a–d** bearing a bulky *N*-bound *tert*-butyl or adamantyl group reacted with di(*tert*-butyl) chlorophosphine to afford the corresponding carbenes **3a–d** (Scheme 1).[7]

On going to less sterically hindered imidazole **1e** bearing a 2,6-diethylphenyl group the same reaction with di(*tert*-butyl)chlorophosphine led to phosphine **4e** and not carbene **3e**.[8] This difference in activity is not due to thermal instability of the carbene **3e**, as the latter is easily obtained by the traditional method, that is, the action of sodium hexamethyldisilazide on the corresponding salt **5**.[6,9]

In the ^{13}C NMR spectra the chemical shifts of the carbene C2 atom occurred in the typical carbene range: δ 205 (**2b**), 234 (**3a**), 234 (**3b**), 223 (**3c**), 222 (**3d**), and 225 (**3e**). Carbenes **3a–e** were crystalline solids, sensitive to air, and distillable (for **3b–d**) in vacuo. Nevertheless, on heating over 150 °C they, like carbene **3** (R = Me, $n = 0$) prepared earlier by us,[6] were transformed into 2-phosphorylated imidazoles **4a–e**.[10]

It should be noted that the yields of the benzimidazol-2-ylidenes **3a,b** were in the range of 50% which is due to the poor stability of lithium benzimidazolides and their proclivity to ring-opening.[4]

In conclusion, we have reported a new method for the synthesis of *N*-phosphorylated carbenes circumventing the laborious stage of synthesis of the corresponding *N*-phosphorylated imidazolium salts. The method is promising and requires further theoretical and practical study.

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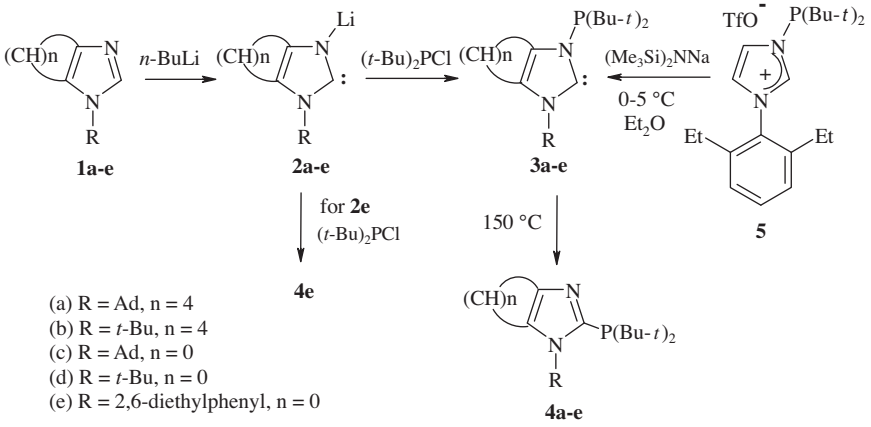

Scheme 1. Synthesis of carbenes **3**.

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7. 1-(1-Adamantyl)-3-[di(*tert*-butyl)phosphanyl]benzimidazol-2-ylidene (**3a**): To a solution of 1-(*tert*-butyl)benzimidazole or 1-(1-adamantyl)benzimidazole (**1a**) (5 mmol) in THF (15 mL) at −25 °C, *n*-BuLi (2.5 M solution in hexane 2 mL, 5 mmol) was added dropwise over 1 min. The reaction mixture was stirred for 1 h until the temperature had increased to −15 °C, then the brown solution was cooled to −70 °C and a solution of di(*tert*-butyl)chlorophosphine (0.9 g, 5 mmol) in hexane (7 mL) was added. After warming to 15 °C, the mixture was stirred overnight (for **3a**) or for 4 days (for **3b**). The solvents were removed in vacuo, the residue was rinsed with hot pentane (30 mL) and the solid residue filtered and washed with pentane (2 × 20 mL). The filtrate was concentrated in vacuo, and the residue was distilled (for **3b**). In the case of **3a** the filtrate was concentrated to 8 mL and cooled to −18 °C for 24 h to afford crystals. Yield (1.05 g, 54%), mp 126–128 °C (pentane); [Found: C, 76.48; H, 9.12; N, 7.16; P, 7.65. $C_{25}H_{37}N_2P$ requires C, 75.72; H, 9.40; N, 7.06; P, 7.81]; ^{1}H NMR (500 MHz, C_6D_6): δ 8.05 (d, 1H, J = 9 Hz, CH), 7.56 (d, 1H, J = 8.5 Hz, CH), 7.01 (t, 1H, J = 7.5 Hz, CH), 7.02 (t, 1H, J = 7.5 Hz, CH), 2.48 (s, 6H, CH_2-Ad), 1.62 (br s, 6H, CH_2-Ad), 1.83 (br s, 3H, CH-Ad), 1.36 (d, 18H, J = 12.5 Hz, *t*-Bu); ^{13}C NMR (125 MHz, C_6D_6): δ 233.8 (d, J = 4 Hz), 143.9 (d, J = 24 Hz), 132.6 (d, J = 2.5 Hz), 128.2, 120.8 (d, J = 75.5 Hz), 113.6, 113.2 (d, J = 16 Hz), 58.3, 43.2, 36.5, 35.0 (d, J = 24 Hz), 30.0, 29.1 (d, J = 16 Hz); ^{31}P NMR (81 MHz, C_6D_6): δ 77.1.
   1-*tert*-Butyl-3-[di(*tert*-butyl)phosphanyl]benzimidazol-2-ylidene (**3b**): Yield (920 mg, 57%); bp 110 °C/0.05 Torr; mp 62–64 °C (pentane); [Found: C, 72.43; H, 9.03; N, 8.47; P, 9.37. $C_{19}H_{31}N_2P$ requires C, 71.66; H, 9.81; N, 8.80; P, 9.73]; ^{1}H NMR (300 MHz, C_6D_6): δ 8.02 (d, 1H, J = 7.5 Hz, CHAr), 7.36 (d, 1H, J = 7.8 Hz, CHAr), 7.08 (m, 1H, CHAr), 6.99 (d, 1H, CHAr), 1.66 (s, 9H, *t*-Bu), 1.34 (d, 18H, J = 12.6 Hz, *t*-Bu); ^{13}C NMR (125 MHz, C_6D_6): 234.1 (d, J = 4 Hz), 143.9 (d, J = 24 Hz), 132.7 (d, J = 2.5 Hz), 121.1, 120.7, 113.2, 113.1 (d, J = 17.6 Hz), 57.3, 34.9 (d, J = 24 Hz), 30.2, 29.1 (d, J = 15 Hz); δ ^{31}P NMR (81 MHz, C_6D_6): δ 77.9.
   1-(1-Adamantyl)-3-[di(*tert*-butyl)phosphanyl]imidazol-2-ylidene (**3c**): To a solution of 1-(*tert*-butyl)imidazole or 1-(1-adamantyl)imidazole (5 mmol) in THF (10 mL) at −45 °C, *n*-BuLi (2.5 M solution in hexane 2 mL, 5 mmol) was added dropwise over 2 min. The reaction mixture was stirred until the temperature had increased to −40 °C, then the light yellow solution was cooled to −60 °C and a solution of di(*tert*-butyl)chlorophosphine (0.9 g, 5 mmol) in hexane (7 mL) was added. After warming to room temperature the mixture was stirred overnight. The solvents were removed in vacuo, the residue was rinsed with pentane (40 mL), the solid residue filtered and washed again with pentane (2 × 20 mL). The filtrate was concentrated in vacuo and the residue distilled. Yield (1.17 g, 68%), bp 140–145 °C/0.05 Torr; mp 40–42 °C (pentane); [Found: C, 73.42; H, 9.86; N, 7.91; P, 8.57. $C_{21}H_{35}N_2P$ requires C, 72.79; H, 10.18; N, 8.08; P, 8.94]; ^{1}H NMR (300 MHz, C_6D_6): δ 7.07 (dd, 1H, J_1 = 1.5 Hz, J_2 = 4.5 Hz, CHIm), 6.73 (m, 1H, CHIm), 2.14 (m, 6H, CH_2-Ad), 1.98 (br s, 3H, CH-Ad), 1.56 (m, 6H, CH_2-Ad), 1.37 (d, 18H, J = 12.3 Hz, *t*-Bu); ^{13}C NMR (125 MHz, C_6D_6): δ 222.0, 126.4 (d, J = 33 Hz), 113.1 (d, J = 7.5 Hz), 55.9, 44.4, 36.2, 34.6 (d, J = 24 Hz), 29.9, 29.1 (d, J = 16 Hz); ^{31}P NMR (81 MHz, C_6D_6): δ 97.9.
   1-*tert*-Butyl-3-[di(*tert*-butyl)phosphanyl]imidazol-2-ylidene (**3d**): Yield (1.15 g, 86%); bp 85 °C/0.05 Torr; [Found: C, 67.39; H, 10.1; N, 10.13; P, 11.27. $C_{15}H_{29}N_2P$ requires C, 67.13; H, 10.89; N, 10.44; P, 11.54]; ^{1}H NMR (500 MHz, C_6D_6): δ 7.05 (dd, J_1 = 1.5 Hz, J_2 = 4.5 Hz, CH), 6.75 (d, J = 1.2 Hz, CH), 1.49 (s, 9H, *t*-Bu), 1.35 (d, 18H, J = 12.3 Hz, *t*-Bu); ^{13}C NMR (125 MHz, C_6D_6): δ 222.7 (br s), 126.8 (d, J = 32.7 Hz), 113.7 (d, J = 6.3 Hz), 55.6, 34.6 (d, J = 24 Hz), 31.0, 29.0 (d, J = 16 Hz); ^{31}P NMR (81 MHz, C_6D_6): δ 98.4.
8. 2-[Di(*tert*-butyl)phosphanyl]-1-(2,6-diethylphenyl)-1*H*-imidazole (**4e**). To a solution of 1-(2,6-diethylphenyl)-1*H*-imidazole (1.0 g, 5 mmol) in THF (15 mL) at −45 °C, *n*-BuLi (2.5 M solution in hexane 2 mL, 5 mmol) was added dropwise over 2 min. The reaction mixture was stirred for 30 min at −40 °C then heated to room temperature and stirred for another 30 min. The mixture was cooled to −60 °C and a solution of di(*tert*-butyl)chlorophosphine (0.9 g, 5 mmol) in hexane (7 mL) was added. The mixture was allowed to warm to rt and stirred for 30 min then H_2O (2 mL) was added. The organic layer was separated, and the aqueous layer extracted with benzene. The combined organic layers were dried over Na_2SO_4 and evaporated in vacuo. The residue was distilled, bp 130 °C/0.05 Torr. Yield (1.50 g, 88%), mp 71–72 °C (pentane). [Found; C, 73.97; H, 9.31; N, 7.90; P, 9.43. $C_{21}H_{33}N_2P$ requires C, 73.22; H, 9.66; N, 8.13; P, 8.99]; ^{1}H NMR (300 MHz, C_6D_6): δ 7.42 (s, 1H, CHIm), 7.36 (t, 1H, J = 7.5 Hz, CHAr), 7.19 (d, 2H, J = 7.5 Hz, CHAr), 6.99–7.01 (m, 1H, CHIm), 2.37 (m, 2H, Et), 2.18 (m, 2H, Et), 1.19 (d, 18H, J = 15.3 Hz, *t*-Bu), 1.12 (t, 6H, J = 7.5 Hz, Et); ^{13}C NMR (125 MHz, C_6D_6): δ 141.6, 136.1, 135.5 (d, J = 88 Hz), 129.3, 128.7 (d, J = 12.8 Hz), 127.0, 125.8, 40.7 (d, J = 35 Hz), 28.5 (d, J = 2.5 Hz), 24.7, 15.1; ^{31}P NMR (81 MHz, C_6D_6): δ 11.4.
9. 3-[Di(*tert*-butyl)phosphanyl]-1-(2,6-diethylphenyl)-1*H*-imidazol-3-ium triflate (**5**). To a mixture of 1-(2,6-diethylphenyl)imidazole (1.09 g, 5.45 mmol) and sodium trifluoromethansulfonate (dried at 200 °C at 0.05 Torr for 2 h) (2.46 g, 10.9 mmol), a solution of di(*tert*-butyl)bromophosphine (1.23 g, 5.45 mmol) in THF (50 mL) was added. The reaction mixture was stirred for 12 h at room temperature (18 °C). The solvent was removed in vacuo (on heating to 30–35 °C), and the residue was washed with pentane (2 × 20 mL) and filtered. The solid residue was dried at 30–35 °C in vacuo (0.05 Torr) and then rinsed with CH_2Cl_2. The filtrate was concentrated in vacuo, the residue rinsed again with Et_2O, and the solid residue dried at 30–35 °C in vacuo (0.05 Torr). Yield (1.27 g, 47%), mp 125–127 °C. [Found: C, 54.1; H, 6.62; N, 5.36; P, 6.75. $C_{22}H_{34}F_3N_2O_3PS$ requires C, 53.43; H, 6.93; N, 5.66; P, 6.26]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (br s, 1H), 8.07 (br s, 1H), 7.67 (br s, 1H), 7.44 (t, 1H, J = 7.8 Hz, CHAr), 7.22 (d, 2H, J = 7.8 Hz, CHAr), 2.21–2.29 (m, 4H, Et), 1.28 (d, 18H, J = 13.5 Hz), 1.08 (t, 6H, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.0 (d, J = 24 Hz), 140.5, 131.7, 131.5, 127.9, 127.4, 126.8, 123.3 (q, J = 319 Hz, CF_3), 35.3 (d, J = 30 Hz), 28.4 (d, J = 15 Hz), 24.0, 14.7; ^{31}P NMR (81 MHz, $CDCl_3$): δ 121.9.
   3-[Di(*tert*-butyl)phosphanyl]-1-(2,6-diethylphenyl)imidazol-2-ylidene (**3e**). To a suspension of salt **5** (1.18 g, 2.4 mmol) in Et_2O (7 mL) at 0 °C was added dropwise over 2 min a solution of sodium hexamethyldisilazide (430 mg, 2.3 mmol) in Et_2O (7 mL). After 30 min the solvent was removed in vacuo, the residue was extracted with degassed pentane (15 mL), the solid was removed by filtration, rinsed with pentane (2 × 10 mL), and the filtrate evaporated to 5 mL. Crystals precipitated after freezing at 18 °C were collected. Yield (450 mg, 57%), mp 96–98 °C. [Found: C, 73.41; H, 9.15; N, 8.05; P, 8.81. $C_{21}H_{33}N_2P$ requires C, 73.22; H, 9.66; N, 8.13; P, 8.99]; ^{1}H NMR (300 MHz, C_6D_6): δ 7.12–7.15 (m, 1H + C_6D_6, CHAr), 7.01–7.06 (m, 3H, 2CHAr + CHIm), 6.41 (s, 1H, CHIm), 2.38 (m, 4H, Et), 1.36 (d, 18H, J = 12.6 Hz, *t*-Bu), 1.08 (t, 6H, J = 7.5 Hz, Et); ^{13}C NMR (125 MHz, C_6D_6): 225.1, 141.4, 140.0, 129.4 (d, J = 102 Hz), 128.1,

126.6, 119.5 (d, J = 7.5 Hz), 34.6 (d, J = 25 Hz), 28.9 (d, J = 16 Hz), 24.8, 15.3; δ ^{31}P NMR (81 MHz, C_6D_6): δ 99.4.

10. Thermal isomerization of carbenes **3a**–**e**. A solution of carbene (100 mg) in benzene-d_6 (0.7 mL) was heated in a sealed tube at 150 °C. For **4a**—the reaction was complete in 1 h 20 min, for **4b**—2 h, for **4c**—30 min, for **4d**—1 h, for **4e**—3 h. The solvent was removed in vacuo and the residue was distilled or recrystallized to give the target compound. 1-(1-Adamantyl)-2-[di(*tert*-butyl)phosphanyl]-1*H*-benzimidazole (**4a**). Yield (91%), mp 171–172 °C (hexane). [Found: C, 74.96; H, 9.11; N, 7.01; P, 7.74. $C_{25}H_{37}N_2P$ requires C, 75.72; H, 9.40; N, 7.06; P, 7.81]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87–7.78 (m, 2H, CHAr), 7.20–7.17 (m, 2H, CHAr), 2.71 (s, 6H, CH_2-Ad), 2.31 (br s, 3H, CH-Ad), 1.85 (d, 6H, J = 12.3 Hz, CH_2-Ad), 1.26 (d, 18H, J = 12.0 Hz, *t*-Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2 (d, J = 42 Hz), 144.7, 134.3 (d, J = 2.5 Hz), 121.5, 120.83, 120.79, 115.5, 61.8 (d, J = 2.5 Hz), 44.9 (d, J = 12.5 Hz), 36.2, 34.9 (d, J = 24 Hz), 30.7 (d, J = 15 Hz), 30.3; ^{31}P NMR (81 MHz, C_6D_6): δ 25.8. ^{31}P NMR (81 MHz, $CDCl_3$): δ 26.1.

1-*tert*-Butyl-2-[di(*tert*-butyl)phosphanyl]-1*H*-benzimidazole (**4b**). Yield 95%, bp 110 °C/0.05 Torr, mp 103–104 °C (pentane). [Found: C, 71.22; H, 9.41; N, 8.75; P, 9.87. $C_{19}H_{31}N_2P$ requires C, 71.66; H 9.81; N, 8.80; P, 9.73%]; ^{1}H NMR (300 MHz, C_6D_6): δ 8.05–8.02 (m, 1H, CHAr), 7.59–7.56 (m, 1H, CHAr), 7.19–7.11 (m, 2H, CHAr), 1.76 (s, 9H, *t*-Bu), 1.37 (d, 18H, J = 12.0 Hz); ^{13}C NMR (125 MHz, C_6D_6): δ 155.0 (d, J = 38 Hz), 145.0, 135.2 (d, J = 1.25 Hz), 122.1, 121.2, 121.0, 114.8, 59.2 (d, J = 1.25 Hz), 34.6 (d, J = 23 Hz), 32.9 (d, J = 14 Hz), 30.6 (d, J = 16 Hz); ^{31}P NMR (81 MHz, C_6D_6): δ 23.0. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86–7.79 (m, 2H, CHAr), 7.25–7.23 (m, 2H, CHAr), 2.03 (s, 9H, *t*-Bu), 1.32 (d, 18H, J = 12.0 Hz, *t*-Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.3 (d, J = 39 Hz), 144.6 (d, J = 1.25 Hz), 135.1 (d, J = 1.25 Hz), 121.9, 120.9, 120.8, 114.9, 59.8 (d, J = 1.25 Hz), 34.8 (d, J = 23 Hz), 33.4 (d, J = 12.5 Hz), 30.7 (d, J = 15 Hz); ^{31}P NMR (81 MHz, $CDCl_3$): δ 23.7.

1-(1-Adamantyl)-2-[di(*tert*-butyl)phosphanyl]-1*H*-imidazole (**4c**). Yield 90%, mp 91–92 °C (pentane, at −18 °C). [Found: C, 73.24; H, 9.78; N, 7.90; P, 9.11. $C_{21}H_{35}N_2P$ requires C, 72.79; H, 10.18; N, 8.08; P, 8.94]; ^{1}H NMR (300 MHz, C_6D_6): δ 7.19 (s, 2H, CHIm), 2.46 (br s, 6H, CH_2-Ad), 2.22 (br s, 3H, CH-Ad), 1.75 (d, 6H, CH_2-Ad), 1.22 (d, 18H, J = 12.3 Hz, *t*-Bu); ^{13}C NMR (125 MHz, C_6D_6): δ 145.8 (d, J = 29 Hz), 127.7, 118.1 (d, J = 2.5 Hz), 58.3 (d, J = 1.25 Hz), 44.3 (d, J = 11 Hz), 36.0, 34.6 (d, J = 16 Hz), 30.8 (d, J = 14 Hz), 30.2; ^{31}P NMR (81 MHz, C_6D_6): δ 13.8. 1-*tert*-Butyl-2-[di(*tert*-butyl)phosphanyl]-1*H*-imidazole (**4d**). Yield 98%, bp 90 °C/0.05 Torr. [Found: C, 68.14; H 10.12; N, 10.12; P, 12.07. $C_{15}H_{29}N_2P$ requires C, 67.13; H 10.89; N, 10.44; P, 11.54]; ^{1}H NMR (500 MHz, C_6D_6): δ 7.19 (s, 1H, CHIm), 6.84 (s, 1H, CHIm), 1.51 (s, 9H, *t*-Bu), 1.29 (d, 18H, J = 12.0 Hz, *t*-Bu); ^{13}C NMR (125 MHz, C_6D_6): δ 145.6 (d, J = 25 Hz), 128.0, 118.8, 56.6, 34.5 (d, J = 19 Hz), 32.0 (d, J = 10 Hz), 30.8 (d, J = 14 Hz); ^{31}P NMR (81 MHz, C_6D_6): δ 11.5. 2-[Di(*tert*-butyl)phosphanyl]-1-(2,6-diethylphenyl)-1*H*-imidazole (**4e**): Yield 90%, bp 130 °C/ 0.05 Torr, mp 69–71 °C (pentane).