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Diaminocarbene-phosphonium ylide: direct access to novel C,C-chelating ligands

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General remarks. THF and diethyl ether were dried and distilled over sodium/benzophenone, pentane, dichloromethane and acetonitrile over P_2O_5. All other reagents were used as commercially available. All reactions were carried out under argon atmosphere, using schlenk and vacuum line techniques. Column chromatography was carried out on silica gel (60 Å, C.C 70-200 μm). The following analytical instruments were used. ^{1}H, ^{13}C and ^{31}P NMR: Bruker AC 200, AM 250, DPX 300 or AMX 400. X-Ray diffraction: Ipds STOE. Mass spectrometry: Quadrupolar Nermag R10-10H. Elemental analyses: Perkin-Elmer 2400 CHN (flash combustion and detection by catharometry). NMR chemical shifts δ are in ppm, with positive values to high frequency relative to the tetramethylsilane reference; coupling constants J are in Hz.

2. Butyllithium (2.5 M, 12.23 mL, 30.6 mmol) was added to a solution of 1-phenylimidazole **1** (2.10 g, 14.6 mmol) in Et_2O (100 mL) at -78°C. The suspension was warmed to room temperature and stirred for 3 hours. Then diphenylchlorophosphine (2.69 mL, 14.6 mmol) was added dropwise at -78°C. The resulting suspension was slowly warmed to room temperature and stirred for 2 hours. After addition of methanol (0.65 mL, 16.0 mmol), the organic layer was washed with a saturated aqueous solution of NH_4Cl (3 x 20 mL) and dried with anhydrous $MgSO_4$. After evaporation of the solvent under vacuum, purification by chromatography on silica gel (pentane/ethyl acetate) gave **2** as a white solid residue, which was recrystallized at -20°C from THF/pentane (3.10 g, 65 %, m.p. 158-160°C).

^{31}P{^{1}H} NMR ($CDCl_3$, 25°C): δ = -16.8; ^{1}H NMR ($CDCl_3$, 25°C): δ = 6.92-6.93 (m, 1 H, H_{ar}), 7.06-7.09 (m, 2 H, H_{ar}), 7.23-7.40 (m, 13 H, H_{ar}), 7.46 (m, 1 H, H_{ar}); ^{13}C{^{1}H} NMR ($CDCl_3$, 25°C): δ = 121.1 (d, J_{CP} = 2.8, CH_{ar}), 127.1 (d, J_{CP} = 2.3, CH_{ar}), 128.7 (d, J_{CP} = 7.1, CH_{ar}), 128.9 (s, CH_{ar}), 129.0 (s, CH_{ar}), 129.2 (s, CH_{ar}), 129.8 (s, CH_{ar}), 134.0 (d, J_{CP} = 20.6, CH_{ar}), 134.5 (s, CH_{ar}), 135.7 (d, J_{CP} =

10.8, C_{ar}), 135.8 (d, J_{CP} = 19.2, C_{ar}), 138.0 (d, J_{CP} = 2.8, CH_{ar}), 141.3 (d, J_{CP} = 23.0, C_{ar}); MS (DCI/NH_3): *m/z*: 329 $[M + H]^+$; Anal. Calcd for $C_{21}H_{17}N_2P$: C, 76.82; H, 5.22; N, 8.53. Found: C, 76.56; H, 4.68; N, 8.35.

3. Methyl trifluoromethanesulfonate (0.60 mL, 5.5 mmol), was added at -78°C to a CH_2Cl_2 solution (30 mL) of **2** (0.90 g, 2.7 mmol). Then the suspension was warmed to room temperature and stirred for 12 hours. After filtration, the solid residue was washed with additionnal CH_2Cl_2 (30 ml) affording a white microcrystalline solid (1.71 g, 95 %). Recrystallization at -20°C from CH_2Cl_2 afforded **3** as colorless crystals (m.p. 185-187°C).

$^{31}P\{^1H\}$ NMR (CD_3CN, 25°C): δ = +20.5; ^1H NMR (CD_3CN, 25°C): δ = 2.76 (d, J_{HP} = 14.0, 3 H, CH_3P), 3.69 (s, 3 H, CH_3N), 7.21-7.25 (m, 2 H, H_{ar}), 7.67-7.76 (m, 9 H, H_{ar}), 7.92-7.94 (m, 3 H, H_{ar}), 7.97-8.02 (m, 1 H, H_{ar}), 8.10-8.14 (m, 1 H, H_{ar}), 8.45 (brs, 1 H, NCHN); $^{13}C\{^1H\}$ NMR (CD_3CN, 25°C): δ = 10.1 (d, J_{CP} = 58.1, CH_3P), 36.3 (s, CH_3N), 117.7 (d, J_{CP} = 85.4, C_{ar}), 118.4 (d, J_{CP} = 88.7, C_{ar}), 121.0 (q, J_{CF} = 321.9, $CF_3SO_3^-$), 124.5 (s, CH_{ar}), 130.5 (d, J_{CP} = 13.2, CH_{ar}), 131.8 (d, J_{CP} = 6.7, CH_{ar}), 132.8 (d, J_{CP} = 12.0, CH_{ar}), 133.2 (d, J_{CP} = 11.2, CH_{ar}), 135.6 (d, J_{CP} = 2.6, CH_{ar}), 136.7 (d, J_{CP} = 8.9, CH_{ar}), 137.1 (s, CH_{ar}), 137.5 (d, J_{CP} = 3.1, C_{ar}), 137.7 (s, C_{ar}); MS(FAB^+): *m/z*: 507 $[M - CF_3SO_3^-]^+$; Anal. Calcd for $C_{25}H_{23}N_2PF_6S_2O_6$: C, 45.73; H, 3.53; N, 4.26. Found: C, 45.35; H, 3.30; N, 4.18.

4a,b. A mixture of $[Pd(allyl)Cl]_2$ (0.27 g, 0.7 mmol), complex **3** (0.97 g, 1.5 mmol), and NEt_3 (0.23 mL, 1.6 mmol), was dissolved in CH_3CN (20 mL) and stirred at room temperature for 1 hour. After evaporation of the solvent, the crude residue was washed with water (20 mL). Then the organic layer was extracted with CH_2Cl_2 (20 mL) and dried with anhydrous $MgSO_4$. The remaining solid residue was purified by chromatography on silica gel (CH_2Cl_2/acetone) affording a grey solid as a mixture (50/50) of two diastereoisomers **4a,b** (0.86 g, 85 %). Recrystallization at room temperature from ethanol gave colorless crystals (m. p. 160°C decomp).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = +21.70; +21.73; ^1H NMR ($CDCl_3$, 25°C): δ = 2.28 (d, J_{HH} = 12.0, 1 H, CH_{2allyl}), 2.54 (d, J_{HP} = 13.9, 3 H, CH_3P), 2.55 (m, 1 H, CH_{2allyl}), 2.56 (d, J_{HP} = 14.0, 3 H, CH_3P), 2.97 (d, J_{HH} = 13.6, 1 H, CH_{2allyl}), 3.19 (d, J_{HH} = 13.6, 1 H, CH_{2allyl}), 3.58 (m, 2 H, CH_{2allyl}), 3.78 (s, 3 H, CH_3N), 3.93 (s, 3 H, CH_3N), 4.04 (d, J_{HH} = 5.5, 1 H, CH_{2allyl}), 4.09 (d, J_{HH} = 7.4, 1 H, CH_{2allyl}), 5.14

(m, 1 H, CH_{allyl}), 5.34 (m, 1 H, CH_{allyl}), 6.37 (d, J_{HH} = 1.7, 1 H, H_{ar}), 6.45 (d, J_{HH} = 1.7, 1 H, H_{ar}), 7.20-7.33 (m, 4 H, H_{ar}), 7.53-7.72 (m, 22 H, H_{ar}), 7.79-7.82 (m, 2 H, H_{ar}), 7.84-7.91 (m, 2 H, H_{ar}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = 8.2 (d, J_{CP} = 55.4, CH_3P), 8.3 (d, J_{CP} = 55.6, CH_3P), 38.5 (s, CH_3N), 38.6 (s, CH_3N), 50.3 (s, CH_{2allyl}), 51.1 (s, CH_{2allyl}), 73.2 (s, CH_{2allyl}), 73.7 (s, CH_{2allyl}), 115.3 (s, CH_{allyl}), 117.9 (d, J_{CP} = 88.2, C_{ar}), 118.3 (d, J_{CP} = 87.9, C_{ar}), 118.5 (d, J_{CP} = 86.8, C_{ar}), 118.6 (d, J_{CP} = 89.4, C_{ar}), 120.7 (q, J_{CF} = 320.8, $CF_3SO_3^-$), 120.8 (d, J_{CP} = 90.6, C_{ar}), 120.9 (d, J_{CP} = 92.6, C_{ar}), 122.9 (s, CH_{ar}), 123.1 (s, CH_{ar}), 124.8 (s, CH_{ar}), 130.3 (d, J_{CP} = 13.2, CH_{ar}), 130.5 (d, J_{CP} = 12.3, CH_{ar}), 130.7 (d, J_{CP} = 10.3, CH_{ar}), 130.9 (d, J_{CP} = 12.9, CH_{ar}), 131.0 (d, J_{CP} = 13.0, CH_{ar}), 131.6 (d, J_{CP} = 7.4, CH_{ar}), 131.8 (d, J_{CP} = 7.4, CH_{ar}), 132.8 (d, J_{CP} = 10.5, CH_{ar}), 132.9 (d, J_{CP} = 10.5, CH_{ar}), 133.2 (d, J_{CP} = 10.8, CH_{ar}), 133.3 (d, J_{CP} = 10.8, CH_{ar}), 135.1 (s, CH_{ar}), 135.6 (s, CH_{ar}), 135.9 (d, J_{CP} = 9.3, CH_{ar}), 136.0 (d, J_{CP} = 9.5, CH_{ar}), 136.1 (s, CH_{ar}), 143.1 (d, J_{CP} = 3.6, C_{ar}), 143.2 (d, J_{CP} = 3.8, C_{ar}), 181.8 (s, NCN), 182.0 (s, NCN); MS(FAB^+): *m/z*: 539 [M^+]; HRMS (ES^+) calcd for $C_{26}H_{27}N_2PClPd$ 539.0635; found, 539.0653.

5a,b. A 1/1 mixture of KHMDS and complex **4a,b** (1.16 g, 1.7 mmol) was cooled to -78ºC and THF (20 mL) was added. The suspension was warmed to room temperature and stirred for 1 hour. After evaporation of the solvent, the solid residue was purified by chromatography on silica gel (CH_2Cl_2/acetone) affording a grey solid as a mixture of two diastereoisomers **5a,b** (70/30) (0.87 g, 79 %). Recrystallization at -20ºC from CH_3CN/Et_2O gave colorless crystals (m. p. 170ºC decomp).

NMR assignment: [a]major isomer (70 %), [b]minor isomer (30 %): $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = +34.2[a]; +34.1[b]; ^1H NMR ($CDCl_3$, 25°C): δ = 1.55[a] (dd, J_{HP} = 8.9, J_{HH} = 13.2, 1 H, CH_2P), 1.77[b] (dd, J_{HP} = 9.3, J_{HH} = 13.1, 0.7 H, CH_2P), 2.06[b] (dd, J_{HP} = 8.7, J_{HH} = 13.1, 0.7 H, CH_2P), 2.19[a] (d, J_{HH} = 13.4, 1 H, CH_{2allyl}), 2.24[a] (dd, J_{HP} = 8.8, J_{HH} = 13.2, 1 H, CH_2P), 2.41[a] (d, J_{HH} = 13.1, 1 H, CH_{2allyl}), 2.64[b] (d, J_{HH} = 12.8, 0.7 H, CH_{2allyl}), 2.77[b] (d, J_{HH} = 13.2, 0.7 H, CH_{2allyl}), 3.28[a] (s, 3 H, CH_3), 3.42[b] (s, 2.1 H, CH_3), 3.54[b] (d, J_{HH} = 6.8, 0.7 H, CH_{2allyl}), 3.68[a,b] (m, 1.7 H, CH_{2allyl}), 3.80[a] (d, J_{HH} = 7.2, 1 H, CH_{2allyl}), 4.87[b] (m, 0.7 H, CH_{allyl}), 5.28[a] (m, 1 H, CH_{allyl}), 6.66[b] (d, J_{HH} = 1.60, 0.7 H, H_{ar}), 6.67[a] (d, J_{HH} = 1.50, 1 H, H_{ar}), 7.12-7.85[a,b] (m, 25.5 H, H_{ar}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C): δ = -11.2[a] (d, J_{CP} = 39.0, CH_2P), -10.9[b] (d, J_{CP} = 38.4, CH_2P), 38.1[a] (s, CH_3N), 38.3[b] (s, CH_3N), 57.9[a] (s, CH_{2allyl}), 59.5[a] (s, CH_{2allyl}), 59.9[b] (s, CH_{2allyl}), 61.4[b] (s, CH_{2allyl}), 117.4[a] (s, CH_{allyl}), 117.7[b] (s, CH_{allyl}), 121.0 (q, J_{CF} = 320.8, $CF_3SO_3^-$), 122.1 (d, J_{CP} = 91.5, C_{ar}), 122.8 (d, J_{CP} = 85.0, C_{ar}), 122.9 (d, J_{CP} = 102.0, C_{ar}),

123.8-124.0 (m, CH_{ar}), 124.2 (s, CH_{ar}), 127.5 (d, J_{CP} = 69.5, C_{ar}), 127.6 (d, J_{CP} = 68.3, C_{ar}), 127.7 (d, J_{CP} = 6.3, CH_{ar}), 127.8 (d, J_{CP} = 6.3, CH_{ar}), 128.8 (d, J_{CP} = 12.1, CH_{ar}), 128.9 (d, J_{CP} = 12.1, CH_{ar}), 129.1 (d, J_{CP} = 12.5, CH_{ar}), 129.2 (d, J_{CP} = 12.5, CH_{ar}), 129.6 (d, J_{CP} = 11.0, CH_{ar}), 130.1 (d, J_{CP} = 8.8, CH_{ar}), 130.2 (d, J_{CP} = 8.8, CH_{ar}), 132.5 (d, J_{CP} = 9.3, CH_{ar}), 132.7 (d, J_{CP} = 2.7, CH_{ar}), 132.8 (d, J_{CP} = 2.2, CH_{ar}), 133.1 (s, CH_{ar}) 135.0 (d, J_{CP} = 10.1, CH_{ar}), 135.2 (d, J_{CP} = 12.5, CH_{ar}), 135.3 (s, CH_{ar}), 135.4 (d, J_{CP} = 1.9, CH_{ar}), 142.6[b] (d, J_{CP} = 1.2, C_{ar}), 142.8[a] (d, J_{CP} = 1.2, C_{ar}), 180.7[b] (d, J_{CP} = 7.8, NCN), 181.2[a] (d, J_{CP} = 8.6, NCN); MS(FAB$^+$): *m/z*: 503 [M^+]; HRMS (ES^+) calcd for $C_{26}H_{26}N_2PPd$ 503.0868; found, 503.0898.

Catalytic allylic substitution of 3-acetoxy-1,3-diphenylpropene by dimethyl malonate.

To a stirred solution of complex **5a,b** (0.023 g, 0.035 mmol) and 3-acetoxy-1,3-diphenylpropene (0.18 g, 0.71 mmol) in THF (2 mL) at room temperature was added a THF solution (3 mL) of the nucleophile generated from dimethylmalonate (0.16 mL, 1.42 mmol) and NaH (0.034 g, 1.42 mmol). The resulting mixture was stirred for 12 h at 60°C. The reaction was then quenched with aqueous solution of NH_4Cl and extracted with CH_2Cl_2 (10 mL). After drying over $MgSO_4$, the organic layer was evaporated under vacuum. ^1H NMR spectroscopy indicates complete conversion of 3-acetoxy-1,3-diphenylpropene to (*E*)-Dimethyl 1,3-diphenylpro-2-enylpropanediolate, which was identified by comparison with an authentic sample.

Crystal structure determination of compounds 3, 4a-b, and 5a-b.

Intensity data for **3** and **4a-b** were collected at low temperature on an Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo Ka radiation source and equipped with an Oxford Cryosystems Cryostream Cooler Device. Data for **5a-b** were collected at a low temperature on an IPDS STOE diffractometer equipped with an Oxford Cryosystem Cryostream Cooler Device.

Structures were solved by direct methods using SIR92, and refined by full-matrix least-squares procedures on F using the programs of the PC version of CRYSTALS. Atomic scattering factors were taken from the International tables for X-ray Crystallography.

Crystal data for **3**. $C_{23}H_{23}N_2P$, $2(CF_3SO_3)$, M = 656.56 g mol^{-1}, Monoclinic, a = 14.8559(8) Å, b = 13.0168(7) Å, c = 15.3373(9) Å, β = 107.695(5)°, V = 2825.5(3) $Å^3$, T = 180 K, space group P $2_1/c$,

Z = 4, μ(Mo-Kα) = 0.328 mm^{-1}, 25883 reflections measured, 7540 unique (Rint = 0.04), 3856 reflections used in the calculations [$I > 2.5\sigma(I)$], R1 = 0.0583, wR2 = 0.0616.

Crystal data for **4a-b**. $C_{26}H_{27}ClN_2PPd$, $2(C_2H_6O)$, CF_3SO_3, M = 781.55 g mol^{-1}, Triclinic, a = 9.6679(4) Å, b = 14.2740(8) Å, c = 14.8838(7) Å, α = 61.390(5)°, β = 82.991(4)°, γ = 72.475(4)°, V = 1718.87(17) $Å^3$, T = 160 K, space group P -1, Z = 2, μ(Mo-Kα) = 0.782 mm^{-1}, 16470 reflections measured, 9131 unique (Rint = 0.02), 7437 reflections used in the calculations [$I > 3\sigma(I)$], R1 = 0.0329, wR2 = 0.0336.

Crystal data for **5a-b**. $C_{26}H_{26}N_2PPd$, CF_3SO_3, M = 652.95 g mol^{-1}, Triclinic, a = 13.131(1) Å, b = 13.216(2) Å, c = 16.126(2) Å, α = 100.10(1)°, β = 98.43(1)°, γ = 91.50(1)°, V = 2721.6(5) $Å^3$, T = 180 K, space group P -1, Z = 4, μ(Mo-Kα) = 0.87 mm^{-1}, 27069 reflections measured, 9946 unique (Rint = 0.08), 3475 reflections used in the calculations [$I > 3\sigma(I)$], R1 = 0.0687, wR2 = 0.0781. The asymmetric unit contains two non-equivalent molecules.