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Air-stable helical bis(cyclopentadienylphosphazene) complexes of divalent ytterbium

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Experimental

*Synthesis of **2**:* To a mixture of Ph_2P-C_5Me_4H [1] (1.20 g, 3.92 mmol) and 1-AdN_3 [2] (830 mg, 4.69 mmol, 1.2 equiv), 10 ml toluene was added and the solution was refluxed with a gas-overpressure controller. After 14 h the reaction mixture turned dark brown. The solvent was completely removed *in vacuo* yielding a dark, oily residue which was triturated with 20 ml hexane, whereupon a yellow, crystalline solid slowly precipitates. The solid was filtered off, washed with hexane (2×5 ml) and dried *in vacuo*. The compound was isolated as a slightly air-sensitive, yellow, crystalline solid. Yield: 50% (900 mg). Mp 195–196°C.

^{1}H NMR for **2a** (300.1 MHz, $CDCl_3$): δ 1.40 [br s, 6H, C*H*$_2$(CH)$_2$], 1.79 [br s, 9H, NC(C*H*$_2$)$_3$, C*H*(CH$_2$)$_3$], 2.13 (s, 6H, *Me*C$_{C5}$), 2.30 (d, $^2J_{HP}$ 4.8 Hz, N*H*), 2.47 (s, 6H, *Me*C$_{C5}$), 6.97–7.02 (m, 6H, *m-/p-Ph*), 7.79–7.83 (m, 4H, *o-Ph*) ppm. ^{13}C{^{1}H} NMR for **2a** (75.5 MHz, $CDCl_3$): δ 11.3 (d, $^3J_{CP}$ 2.6 Hz, *α–Me*C$_{C5}$), 14.0 (s, *β–Me*C$_{C5}$), 29.8 [s, *C*H(CH$_2$)$_3$], 36.0 [s, *C*H$_2$(CH)$_2$], 44.7 [d, $^3J_{CP}$ 3.5 Hz, NC(*C*H$_2$)$_3$], 54.0 (d, $^2J_{CP}$ 4.6 Hz, N*C*), 75.7 (d, $^1J_{CP}$ 94 Hz, P*C*$_{C5}$), 118.6, 121.0 (2×d, J_{CP} 16 Hz, J_{CP} 18 Hz, 2×Me*C*$_{C5}$), 128.3 (d, $^3J_{CP}$ 12 Hz, *m-Ph*), 131.5 (d, $^1J_{CP}$ 100 Hz, *ipso-Ph*), 131.8 (d, $^4J_{CP}$ 2.8 Hz, *p-Ph*), 133.9 (d, $^2J_{CP}$ 10.1 Hz, *o-Ph*) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, C_6D_6): δ 12.3 (**2a**, 79%), -10.7 (**2b**, 9%), -25.6 (**2c**, 12%) ppm. EI-MS: m/z (%) = 455 (100) [M$^+$], 440 (35) [M$^+$ – Me], 320 (15) [M$^+$ – Ad]. Found (%): C 82.06, H 8.31, N 3.00. Calc. for $C_{31}H_{38}NP$ (455.63) (%): C 81.72, H 8.41, N 3.07.

‡ *Synthesis of **3** and **4**:* To a stirred solution of compound **1** or **2** (2.00 mmol) in 10 ml THF, a solution of [BnK] [3] (250 mg 1.92 mmol) in THF (10 ml) was added dropwise at ambient temperature, whereupon decoloration of the deep red solution takes place. To the obtained solution of the potassium salt, solid [$YbI_2(thf)_2$] [4] (570 mg, 1.90 mmol) was added at once at ambient temperature. The deep orange suspension was stirred for 1 h. The precipitate of KI was filtered off through a Celite©-pad and washed with THF (2×5 ml). The solvent was stripped off, yielding an orange, microcrystalline substance. The complex can be recrystallized from diethyl

ether. Yield for **3**: 82% (685 mg); for **4**: 60% (322 mg). **4** crystallizes from diethyl ether with additional solvent molecule in the lattice (**4**×½Et_2O) as was shown by NMR spectroscopy of briefly dried sample and X-ray diffraction analysis. Upon prolonged drying of the crystalline **4**×½Et_2O in a high vacuum, desolvatation with formation of powdery, solvent-free complex was observed. Desolvatation can also be achieved by heating a toluene solution to 70°C. The elemental analysis is given for the solvent-free complex. For **3**: ^{1}H NMR (300.1 MHz, C_6D_6): δ 1.44, 1.45 [2×d, $^2J_{HP}$ 12 Hz, 2×3H, *Me*(*Me*)P], 1.70 [m, 12H, NC(CH_2)$_3$, CH_2(CH)$_2$], 2.11 [br s, 3H, CH(CH$_2$)$_3$], 2.19, 2.25, 2.27, 2.29 (4×s, 4×3H, 4×*Me*C_{C5}) ppm. ^{13}C{^{1}H} NMR (75.0 MHz, C_6D_6): δ 11.9, 12.5 (2×d, $^3J_{CP}$ 1.7 Hz, α–*Me*C_{C5}), 13.8, 15.8 (2×s, 2×β–*Me*C_{C5}), 23.3, 23.6 [2×d, $^1J_{CP}$ 51 Hz, *Me*(*Me*)P], 30.8 [s, *C*H(CH$_2$)$_3$], 37.0 [s, *C*H$_2$(CH)$_2$], 48.8 [d, $^3J_{CP}$ 10 Hz, NC(*C*H$_2$)$_3$], 51.8 (d, $^2J_{CP}$ 7.4 Hz, N*C*), 90.6 (d, $^1J_{CP}$ 126 Hz, PC_{C5}), 115.9 (d, J_{CP} 13.2 Hz, MeC_{C5}), 116.3 (d, J_{CP} 12.7 Hz, MeC_{C5}), 118.9 (d, J_{CP} 15.4 Hz, MeC_{C5}), 120.0 (d, J_{CP} 14.9 Hz, MeC_{C5}) ppm. ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6): δ 0.5 ppm. Found (%): C 60.40, H 8.02, N 3.26. Calc. for $C_{42}H_{66}N_2P_2Yb$ (833.99) (%): C 60.49, H 7.98, N 3.36. For **4**: ^{1}H NMR (300.1 MHz, C_6D_6): δ 1.12 [t, $^3J_{HH}$ 6.9 Hz, 3H, CH_3CH$_2$)$_2$O], 1.44 (s, 3H, *Me*C_{C5}), 1.64, 1.75 [2×d, $^3J_{HH}$ 14 Hz, 6H, CH_2(CH)$_2$], 2.03–2.19 [m, 9H, CH(CH$_2$)$_3$, NC(CH_2)$_3$], 2.16, 2.28, 2.62 (3×s, 3×3H, 3×*Me*C_{C5}), 3.27 [qt, $^3J_{HH}$ 6.9 Hz, 2H, (CH$_3$CH_2)$_2$O], 7.10–7.22 (m, 6H, *m-/p-Ph*), 7.70 (dd, $^3J_{HH}$ 7.4 Hz, $^3J_{HP}$ 12 Hz, 2H, *o-Ph*), 8.12–8.19 (m, 2H, *o-Ph*) ppm. ^{13}C{^{1}H} NMR (75.0 MHz, C_6D_6): δ 12.3 (s, *Me*C_{C5}), 12.6, 12.9 (2×d, $^3J_{CP}$ 2.2 Hz, $^3J_{CP}$ 1.7 Hz, 2×*Me*C_{C5}), 15.5 [s, (*C*H$_3$CH$_2$)$_2$O], 16.7 (s, *Me*C_{C5}), 30.8 [s, *C*H(CH$_2$)$_3$], 37.0 [s, *C*H$_2$(CH)$_2$], 48.8 [d, $^3J_{CP}$ 10.3 Hz, NC(*C*H$_2$)$_3$], 52.5 (d, $^2J_{CP}$ 8.5 Hz, N*C*), 65.9 [s, (CH$_3$*C*H$_2$)$_2$O], 91.0 (d, $^1J_{CP}$ 137 Hz, PC_{C5}), 117.9 (d, J_{CP} 10.6 Hz, MeC_{C5}), 118.3 (d, J_{CP} 15.1 Hz, MeC_{C5}), 119.2 (d, J_{CP} 16.2 Hz, MeC_{C5}), 121.7 (d, J_{CP} 14.5 Hz, MeC_{C5}), 127.9, 128.1 (2×s, 2×*p-Ph*), 130.3, 131.0 (2×d, $^3J_{CP}$ 2.2 Hz, 2×*m-Ph*), 133.7, 134.8 (2×d, $^2J_{CP}$ 10.3 Hz, 2×*o-Ph*), 138.0, 138.8 (2×d, $^1J_{CP}$ 80 Hz, $^1J_{CP}$ 72 Hz, 2×*ipso-Ph*) ppm. ^{31}P{^{1}H} NMR (121.0 MHz, C_6D_6): δ 3.1 ppm. Found (%): C 68.27, H 7.37, N 2.72. Calc. for $C_{62}H_{74}N_2P_2Yb$ (1082.28) (%): C 68.81, H 6.89, N 2.59.

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