

for the manuscript

**New mono and bis-carbene samarium complexes:
Synthesis, X-Ray crystal structures and reactivity.**

by

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1°) General considerations.

All reactions were routinely performed under an inert atmosphere of argon or nitrogen by using Schlenk and glove-box techniques and dry deoxygenated solvents. Dry THF, ether and hexanes were obtained by distillation from Na/benzophenone. Dry dichloromethane was distilled on P₂O₅ and dry toluene on Na. Nuclear magnetic resonance spectra were recorded on a Bruker AC-300 SY spectrometer operating at 300.0 MHz for ¹H, 75.5 MHz for ¹³C and 121.5 MHz for ³¹P. Solvent peaks are used as internal reference relative to Me₄Si for ¹H and ¹³C chemical shifts (ppm); ³¹P chemical shifts are relative to a 85% H₃PO₄ external reference. Coupling constants are given in Hertz. The following abbreviations are used: s, singlet; d, doublet; t, triplet; m, multiplet; v, virtual.

2°) Synthesis and characterization of **2**, **3**, **4**, **5** and **6**.

Synthesis of 2: A solution of **1** in toluene (3.0 mL, 0.40 mmol) was added onto SmI₃(THF)_{3.5} (0.31 g, 0.40 mmol) and the reaction was stirred for 15 min. After centrifugation LiI salt was removed and diethyl ether (5 mL) was condensed onto the solution. After 24 hours, **2** was isolated as a yellow precipitate in 81% yield (0.28 g, 0.32 mmol). Selected data: ¹H NMR (300 MHz, [D8]toluene, 25°C, TMS): δ=8.4 (m, 4 H; ortho-aryl), 7.15-7.03 (m, 16 H; meta+para-aryl), 3.2 (br s, 8 H; THF), 1.04 ppm (br s, 8 H; THF); ³¹P NMR (121.5 MHz, [D8]Toluene, 25 °C, 85% H₃PO₄ as external standard): δ=51.8 ppm (br s); ¹³C NMR (75 MHz, [D8]Toluene, 25 °C, TMS): δ=141.2 (d, ²J(C,P)=75.5 Hz; ipso), 131.7 (s; ortho), 129.7 (s; para), 128.1 ppm (s; meta), C-Sm not observed.

Synthesis of 3: In a centrifugation tube two equivalents of **1** in toluene (6.0 mL, 0.80 mmol) were added onto SmI₃(THF)_{3.5} (0.31 g, 0.40 mmol) and the reaction was stirred for 5 min, at room temperature. LiI salt was eliminated via centrifugation. Evaporation of the solvent affords a yellow solid which was washed with a THF (0.5 mL) diethyl ether (10 mL) mixture. Pure complex **3** was isolated in 87% yield (0.47 g, 0.35 mmol). Selected data: ¹H NMR (300 MHz, [D8]Toluene, 25°C, TMS): δ=8.42 (br s, 16H; ortho), 7.11-7.05 (m, 24H; meta+para), 2.96 (br s, 16H; THF), 1.11 ppm (br s, 16H; THF); ³¹P{¹H} NMR (121.5 MHz, [D8]Toluene, 25°C, 85% H₃PO₄ as external standard): δ=46.2 ppm (br s); ¹³C{¹H} NMR (75.465 MHz, [D8]Toluene, 25°C, TMS): δ=144.1 (d, ¹J(C,P)=81.6 Hz; ipso), 131.6 (s; ortho), 129.0 (s; para), 127.8 (s; meta); 68.1 (s; THF), 25.1 ppm (s; THF).

Synthesis of 4: Benzophenone (0.01 g, 0.06 mmol) and samarium carbene (0.05 g, 0.06 mmol) were reacted in toluene for 1 hour upon which a white precipitate formed. After centrifugation the precipitate was removed and the solution evaporated giving the product as a pale yellow solid in 94% yield (0.034 g, 0.056 mmol). Selected data : ¹H NMR (300 MHz, [D8]Toluene, 25 °C, TMS): δ=8.2 (br s, 4 H; ortho-aryl), 7.1-6.7 ppm (m, 16 H; meta+para-aryl); ³¹P NMR (121.5 MHz, [D8]Toluene, 25 °C, H₃PO₄): δ=40.1 ppm (s); ¹³C NMR (75 MHz, [D8]Toluene, 25 °C, TMS): δ=177.5 (d, ²J(C,P) = 2.3 Hz, C=CPh₂), 142.7 (d, ¹J(C,P) = 11.5 Hz C=CPh₂), 132.2-125.6 ppm (phenyl).

Synthesis of 5: Addition of one equivalent of benzophenone (5.5 mg, 0.03 mmol) in a solution of **3** (40 mg, 0.03 mmol) in [D6]benzene (1 mL) yield the quantitative formation of **5** within 10 minutes. Selected data: ¹H NMR (300 MHz, [D6]benzene, 25°C, TMS): δ=8.67-6.42 ppm (m; H of phenyl); ³¹P{¹H} NMR (121.5 MHz, [D6]Benzene, 25°C, 85% H₃PO₄ as external standard): δ=49.4 (br s; PCCP), 43.9 ppm (br s; PCSmP); ¹³C{¹H} NMR (75.465 MHz, [D6]benzene, 25°C, TMS): δ=148.8 (t, ²J(C,P)=8.1 Hz; CO), 138.1 (d, ¹J(C,P)=101.8 Hz; SPCipso), 137.5 (d, ¹J(C,P)=88.9 Hz; SPCipso), 134.6 (s; OCCipso), 135.6-126.3 (m; ortho+meta+para aryl), 55.3 ppm (t, ¹J(C,P)=49.4 Hz; PCCO).

Synthesis of 6: Crystals of complex **6** were grown by diffusing a saturated solution of benzophenone in hexanes in a solution of complex **3** in toluene (0.07 mmol, 1 mL). Selected data: ³¹P NMR (121.5 MHz, [D8]Toluene, 25 °C, H₃PO₄): δ=50.2 ppm (s).