Supporting Information

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 SmI\(_3\)(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: \(^1\)H NMR (300 MHz, [D8]toluene, 25°C, TMS): \(\delta=8.4\) (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); \(^{31}\)P NMR (121.5 MHz, [D8]Toluene, 25 °C, 85% H\(_3\)PO\(_4\) as external standard): \(\delta=51.8\) ppm (br s); \(^{13}\)C NMR (75 MHz, [D8]Toluene, 25 °C, TMS): \(\delta=141.2\) (d, \(^2\)J(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 SmI\(_3\)(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: \(^1\)H NMR (300 MHz, [D8]Toluene, 25°C, TMS): \(\delta=8.42\) (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); \(^{31}\)P\(^{\{1\}H}\) NMR (121.5 MHz, [D8]Toluene, 25 °C, 85% H\(_3\)PO\(_4\) as external standard): \(\delta=46.2\) ppm (br s); \(^{13}\)C\(^{\{1\}H}\) NMR (75.465 MHz, [D8]Toluene, 25°C, TMS): \(\delta=144.1\) (d, \(^1\)J(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: \(^1\)H NMR (300 MHz, [D8]Toluene, 25 °C, TMS): \(\delta=8.2\) (br s, 4 H; ortho-aryl), 7.1-6.7 ppm (m, 16 H; meta+para-aryl); \(^{31}\)P\(^{\{1\}H}\) NMR (121.5 MHz, [D8]Toluene, 25 °C, 85% H\(_3\)PO\(_4\) as external standard): \(\delta=49.4\) (br s; PCCP), 43.9 ppm (br s; PCSmP); \(^{13}\)C\(^{\{1\}H}\) NMR (75.465 MHz, [D6]benzene, 25°C, TMS): \(\delta=177.5\) (d, \(^2\)J(C,P) = 2.3 Hz, C=CPh\(_2\)), 142.7 (d, \(^1\)J(C,P) = 11.5 Hz C=CPh\(_2\)), 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: \(^1\)H NMR (300 MHz, [D6]benzene, 25°C, TMS): \(\delta=8.67-6.42\) ppm (m; H of phenyl); \(^{31}\)P\(^{\{1\}H}\) NMR (121.5 MHz, [D6]Benzene, 25 °C, 85% H\(_3\)PO\(_4\) as external standard): \(\delta=49.4\) (br s; PCCP), 43.9 ppm (br s; PCSmP); \(^{13}\)C\(^{\{1\}H}\) NMR (75.465 MHz, [D6]benzene, 25°C, TMS): \(\delta=148.8\) (t, \(^3\)J(C,P)=8.1 Hz; CO), 138.1 (d, \(^1\)J(C,P)=101.8 Hz; SPCipso), 137.5 (d, \(^1\)J(C,P)=88.9 Hz; SPCipso), 134.6 (s; OCCipso), 135.6-126.3 (m; ortho+meta+para aryl), 55.3 ppm (t, \(^1\)J(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: \(^{31}\)P NMR (121.5 MHz, [D8]Toluene, 25 °C, H\(_3\)PO\(_4\)): \(\delta=50.2\) ppm (s).