New mono- and bis-carbene samarium complexes: synthesis, X-ray crystal structures and reactivity†

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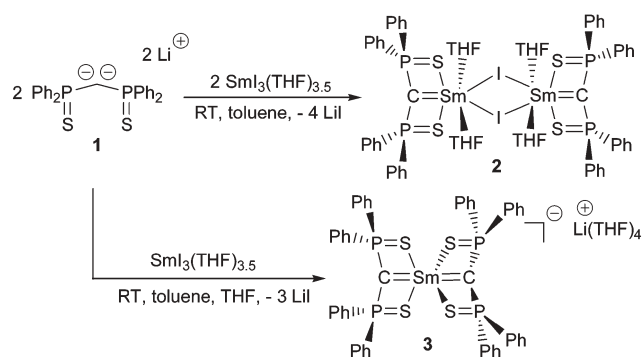
New samarium carbene complexes have been synthesized and characterized by X-ray diffraction analysis; the carbenic nature was assessed by reactivity studies.

Over the past decades, the chemistry of transition metal carbene complexes has been thoroughly explored[1] and recent studies have clearly demonstrated the relevance of carbenes as ancillary or active ligands in many catalytic processes of important synthetic value.[2] In contrast, examples of well-defined lanthanide species incorporating these ligands remain scarce.[3] Indeed, although several neutral donor carbene adducts are known,[4] only a few examples of lanthanide alkylidene complexes have been reported.[5,6] So far, the only structurally characterized complex was obtained by Cavell and coworkers after *in-situ* deprotonation of a bis(iminophosphorane)methylene ligand.[6] To date, neither the reactivity nor the electronic nature of the lanthanide–carbon multiple bond has been assessed in this type of complexes.

We recently reported on the quantitative synthesis of dianion **1** *via* the double deprotonation of the bis(diphenylthiophosphinoyl)-methane.[7] Preliminary studies on its coordination behaviour towards the [Pd(PPh₃)] fragment led to the discovery of a new type of bonding mode for the carbene moiety.[7] In order to explore the coordination ability of this dianion towards electron-deficient metal fragments, reaction of **1** with a samarium triiodide precursor was attempted. Herein, we report on the successful synthesis of new samarium carbene complexes (**2**, **3**) featuring anion **1** as ligand. As will be seen, this approach allowed us to isolate the first homoleptic samarium carbene complex **3** and to investigate the reactivity of complexes **2** and **3** towards electrophiles.

Addition of one equivalent of dianion **1** to SmI₃(THF)₃.₅ under an argon atmosphere yielded the quantitative formation of complex **2** (Scheme 1). After usual work-up aimed at the elimination of LiI salt, complex **2** was isolated as a yellow solid and fully characterized by NMR techniques (¹H, ¹³C and ³¹P).

In ³¹P NMR spectroscopy, complex **2** is characterized by a broad singlet markedly low-shifted relative to the dianionic precursor (**2**, 51.8 ppm; **1**, 20.6 ppm). Though no ¹³C NMR signal could be recorded for the carbenic carbon atom which is directly bound to the paramagnetic samarium(III) center, the absence of methylenic protons was confirmed by ¹H NMR. Crystals of **2** were

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Scheme 1

grown by cooling a solution of the complex in a diethyl ether/toluene/hexanes mixture (Fig. 1a).[8]

As can be seen, complex **2** crystallizes as an iodine-bridged dimer with two THF molecules bound to samarium. The coordination sphere of Sm adopts a distorted C2-symmetrical edge-capped octahedral geometry with the metal in the PCP plane. Considering the coordination number in complex **2**,[9] the most striking feature is the short Sm–C bond of 2.36 Å (av.) which possesses a multiple bond character, since it is considerably shorter than the average Sm–C distance (2.48 Å).[3] Compared to the bond length found in [Sm{C(Ph₂P=NSiMe₃)₂-K^3C,N,N'}(NCy₂)(THF)] (2.467(4) Å) synthesized by Cavell and coworkers,[6] a reduction of the bond length is observed in **2** which may be due to the planarity of the carbene fragment.[10]

In order to assert the strong Lewis basicity of dianion **1**, substitution of the three iodide ligands in SmI₃(THF)₃.₅ by two equivalents of the dianionic ligand **1** was attempted. This reaction resulted in the formation of the single new complex **3** which is characterized by a broad singlet at 46.2 ppm in ³¹P NMR. As for complex **2**, no resonance could be observed in the ¹³C NMR spectrum for the two carbenic centers. Crystals suitable for X-ray diffraction analysis were grown from a slow diffusion of hexanes into a solution of **3** in toluene (Fig. 1b).[8] This structure definitely establishes the coordination of two carbene ligands in **3**. Thus, **3** is the first homoleptic carbene complex in the lanthanide series. Though the NMR spectra revealed a symmetric structure in solution, the complex adopts an asymmetric geometry in the solid state. Both Sm–C bonds are significantly longer than in **2** (2.491(5) and 2.507(5) Å) and fall in the range of the average Sm–C single bond (2.48 Å).[3] This lengthening is consistent with the supplementary negative charge involved in complex **3**. However, the bond distance alone is not sufficient to fully determine the nature of the Sm–C bond as the distance depends on the coordination
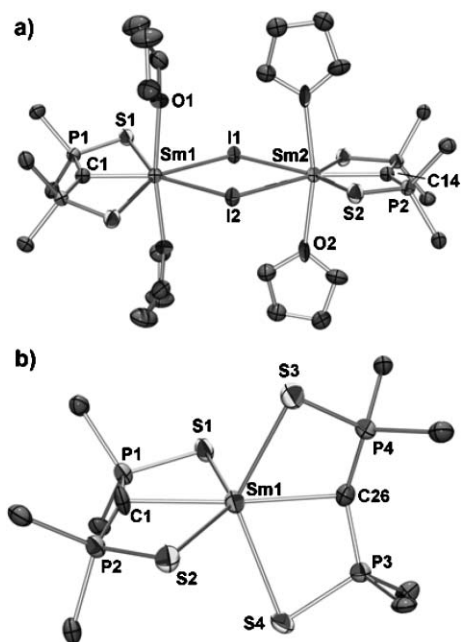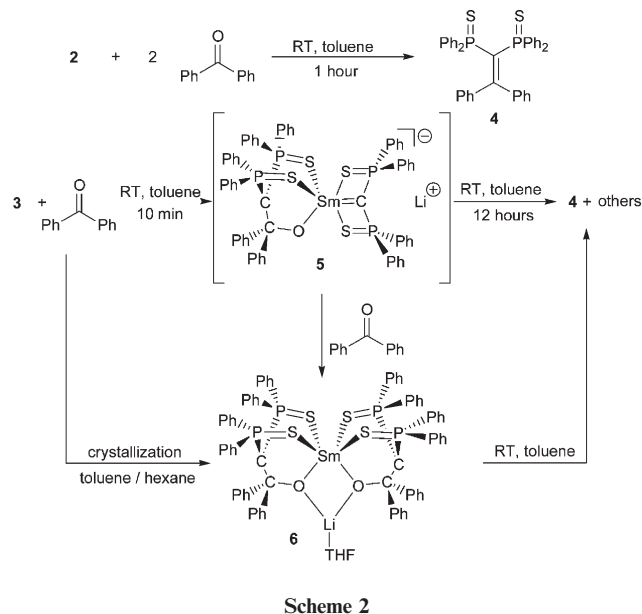
Scheme 2

Fig. 1 View of one molecule of **2** (a) and the anion of **3** (b) (ellipsoids set as 50% probability). The phenyl rings and co-crystallized solvent molecules are omitted for clarity (only ipso-carbon atoms are shown). Selected bond lengths [Å] and angles [°]: a) for **2** Sm1–C1 2.371(6), Sm2–C14 2.352(6), Sm1–S1 2.891(1), Sm1–S2 2.922(1), Sm1–I1 3.3021(4), Sm2–I1 3.2413(4), Sm1–O1 2.476(3), Sm1–O2 2.435(3), P1–C1–P1' 146.2(4), P2–C14–P2' 145.4(4), P1–C1–Sm1 106.9(2), P2–C14–Sm2 107.3(2); b) for **3** Sm1–C1 2.491(5), Sm1–C26 2.507(5), Sm1–S1 2.858(2), Sm1–S2 2.816(2), Sm1–S3 2.851(2), Sm1–S4 2.824(2), P1–C1–P2 156.4(4), P3–C2–P4 136.5(4), P1–C1–Sm1 99.1(3), P2–C1–Sm1 100.8(3), P4–C26–Sm1 97.8(2), P3–C26–Sm1 98.0(2), C1–Sm1–C26 160.4(2).

number at the metal center and on the resulting geometry.[9] The carbenic character of the Sm–C bond in **3** was therefore established *via* chemical reactivity tests (see below).

So far, no data on the electronic nature and reactivity of carbene lanthanide complexes have been reported. Since both complexes **2** and **3** were obtained from coordination of dianion **1** to the electron-deficient samarium(III) center, one could expect that these species exhibit a reactivity similar to that of Schrock-type carbene complexes.[11] In order to assess the nucleophilicity of **2**, reaction with benzophenone was attempted. As expected, this Wittig-like reaction resulted in the formation of the tetra-substituted olefin **4** which was fully characterized by NMR techniques and X-ray crystallography (see Supporting Information) (Scheme 2). This reaction, which has never been reported before for the lanthanide series, clearly demonstrates the carbenic nature of complex **2**.[12]

Since the reaction was fast, no intermediate could be observed in ^{31}P NMR. In order to shed some light on the synthetic pathway, we attempted the same reaction with anionic complex **3**. Indeed, the driving force of this reaction being the formation of polymeric samarium oxide, we expected that the overall negative charge in **3** would kinetically stabilize a monomeric intermediate which would not easily rearrange into the highly energetic samarium oxide. Addition of one equivalent of benzophenone to **3** in toluene led to the immediate disappearance of the signal of complex **3** in the ^{31}P NMR spectrum with the concomitant appearance of a new complex (**5**) characterized by two broad singlets at 43.9 and

49.4 ppm. NMR spectra (^{1}H, ^{13}C and ^{31}P) recorded for this compound support the structure assigned for complex **5** (Scheme 2) which involves the addition of one benzophenone molecule onto one carbene moiety of complex **3**. However, rearrangement of this kinetic isomer (**5**) to the more stable final products (**4**, samarium oxide and other intractable products) occurs in solution over a period of about ten hours at room temperature. Our efforts have thus concentrated on trapping this intermediate by crystallization. However, slow diffusion of a saturated solution of benzophenone in hexanes onto a solution of complex **3** in toluene resulted in the growth of pale yellow crystals of the unexpected complex **6**, within one hour (Fig. 2).[8]

As can be seen, complex **6** features two benzophenone units. Dissolution of these crystals in toluene showed a singlet at 50.2 ppm in ^{31}P NMR which readily disappeared to yield **4** and by-products. This structure confirms **6** as an intermediate involved
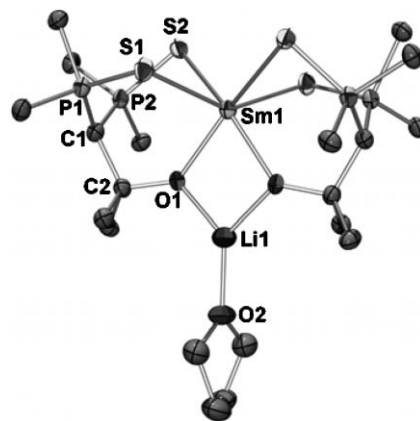

Fig. 2 View of one molecule of **6** (ellipsoids set as 50% probability). The phenyl rings are omitted for clarity (only ipso-carbon atoms are shown). Selected bond lengths [Å] and angles [°]: Sm1–S1 2.843(1), Sm1–S2 2.856(1), Sm1–O1 2.237(2), P2–S2 2.022(1), P1–S1 2.031(1), C1–P2 1.768(4), C1–P1 1.755(4), C1–C2 1.558(5), C2–O1 1.418(4), O1–Li1 1.908(2), P1–C1–P2 112.5(2), P2–C1–C2 114.4(2), P1–C1–C2 117.8(2), C1–C2–O1 110.0(3).

in the transformation of carbene complex **3** into **4**.[13] Indeed, a new C–C sigma bond has formed (1.56 Å *vs.* 1.37 Å in final product **4**) whilst the Sm=C bond has been cleaved (3.57 Å *vs.* 2.46 Å in reactant **3**). Simultaneously, the benzophenone C=O bond is significantly elongated (1.42 Å in **6** *vs.* 1.22 Å in free benzophenone) and a new energetic Sm–O interaction arises (2.24 Å). Metalla-oxetanes have often been proposed as intermediates in the reaction of early transition metal carbene complexes with carbonyl compounds.[11,14] Due to their instability, few related intermediates have been isolated so far.[11] In our case, the structure of **6** supports the idea that this transformation very likely proceeds through the formation of an open metalla-oxetane in which the samarium carbene bond is cleaved because of geometrical constraints. The sp³ character found for C1 and C2 atoms (Fig. 2, $\Sigma\alpha_C = 345°$) is consistent with a significant remaining negative charge induced by such a cleavage.

In conclusion, dianionic ligand **1** has proved to be a versatile precursor to access new samarium carbene complexes. Among these, complex **3** is the first homoleptic samarium carbene derivative. For the first time, structural, spectroscopic and reactivity studies have clearly demonstrated the carbenic nature of a samarium–carbon bond. Moreover, these complexes exhibit a marked nucleophilic character and react with benzophenone similarly to Schrock-type complexes. Isolation of an intermediate complex (**6**) clearly shows that this transformation, hitherto unknown in the lanthanide series, involves an open form of metalla-oxetane.

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8 Crystal data for **2**: $C_{66}H_{74}I_2O_4P_4S_4Sm_2,4(C_7H_8)$; $M_r = 2106.41$; monoclinic; $a = 23.3380(10)$, $b = 27.1900(10)$, $c = 18.1090(10)$ Å; $\beta = 128.1740(10)°$; $V = 9033.7(7)$ Å³; $T = 150.0(1)$ K; space group $C2/c$; $Z = 4$; $\mu = 2.183$ cm⁻¹; 15765 reflections measured, 9222 unique, 6040 used reflections, criterion $I > 2\sigma$ (*I*); *R*1 = 0.0362; *wR*2 = 0.0737. Crystal data for **3**: $C_{50}H_{40}P_4S_4Sm,C_{16}H_{32}LiO_4$; $M_r = 1338.65$; triclinic; $a = 14.969(3)$, $b = 15.159(2)$, $c = 16.2692(16)$ Å; $\alpha = 77.918(10)$, $\beta = 88.901(12)$, $\gamma = 61.756(11)°$; $V = 3166.6(8)$ Å³; $T = 150.0(1)$ K; space group P-1; $Z = 2$; $\mu = 1.207$ cm⁻¹; 25383 reflections measured, 25429 unique, 22457 used reflections, criterion $I > 2\sigma$ (*I*); *R*1 = 0.0559; *wR*2 = 0.1756. Crystal data for **6**: $C_{80}H_{68}LiO_3P_4S_4Sm$; $M_r = 1486.80$; monoclinic; $a = 20.1140(10)$, $b = 11.6210(10)$, $c = 29.9670(10)$ Å; $\beta = 108.1840(10)°$; $V = 6654.8(7)$ Å³; $T = 150.0(1)$ K; space group $C2/c$; $Z = 4$; $\mu = 1.156$ cm⁻¹; 25884 reflections measured, 7570 unique, 6745 used reflections, criterion $I > 2\sigma$ (*I*); *R*1 = 0.0393; *wR*2 = 0.1115. Crystal data for **4**: $C_{38}H_{30}P_2S_2$; $M_r = 612.68$; monoclinic; $a = 8.7650(10)$, $b = 18.7960(10)$, $c = 19.3020(10)$ Å; $\beta = 100.167(2)°$; $V = 3130.0(4)$ Å³; $T = 150.0(1)$ K; space group $P2_1/n$; $Z = 4$; $\mu = 0.299$ cm⁻¹; 11978 reflections measured, 7149 unique, 4539 used reflections, criterion $I > 2\sigma$ (*I*); *R*1 = 0. 0424; *wR*2 = 0.0929. CCDC 275470 (**2**), CCDC 275471 (**3**), CCDC 275472 (**4**) and CCDC 275473 (**6**) contain the supplementary crystallographic data for this paper. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b510327d.

9 So far, the shortest Sm–C bond (2.332(2) Å) has been reported by Hitchcock *et al.* for [Sm(CH(SiMe₃)₂)₃], in which the low coordination number ($n = 3$ compared to $n = 7$ in **2**) leads to strong samarium–alkyl interactions. See: P. B. Hitchcock, M. F. Lappert, R. G. Smith, R. A. Bartlett and P. P. Power, *J. Chem. Soc., Chem. Commun.*, 1988, 1007–1009.

10 In **2**, the samarium atom lies in the SPCPS plane and the sum of the angles around the carbene atom equals 360°. In contrast, Cavell's system forms an "open book" structure and the angles at the carbene sum up to 321°; see ref. 6.

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12 Note that compound **4** could not be obtained by reacting dianion **1** with benzophenone.

13 Addition of an excess of benzophenone to complexes **3** or **5** yielded small amounts of **6** and a faster decomposition of complex **5** into **4**, compared to the stoichiometric reaction between **3** and benzophenone.

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