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The Synthesis of a New Soluble Samarium(II) Diorganoamide

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Samarium(II) compounds are important synthetic reagents [1–4]. For example, samarium diiodide is a very useful one-electron reductant in organic synthesis [1] and is a source of the very limited class of samarium(II) organometallics [4–6], whilst bis(pentamethylcyclopentadienyl)samarium(II) is readily oxidised to novel samarium(III) organometallics [4, 7–9]. Some potentially important samarium(II) compounds, e.g. samarium diacetate [5] and bis(cyclopentadienyl)samarium(II) [5, 10] are insoluble in organic solvents and this restricts purification and preparative use. The sole known bis(diorganoamido)samarium(II) compound is $[(Me_3Si)_2N]_2Sm$, which has been prepared by redox transmetallation from samarium metal and $[(Me_3Si)_2N]_2Hg$ [11] and by metathesis from SmI_2 [12], and isolated as $[(Me_3Si)_2N]_2SmL_2$ ($L_2 = (MeOCH_2)_2$ [11] or L = tetrahydrofuran (thf) [12]). We now report a 'one-pot' synthesis of bis(2-phenylindol-1-yl)samarium(II) from samarium metal.

Reaction of bis(pentafluorophenyl)mercury, 2-phenylindole and samarium (mole ratio, 1:2:4) in tetrahydrofuran for 12 h at room temperature under purified nitrogen gave a dark brown–purple reaction mixture, which was filtered to remove precipitated mercury and the excess of samarium. The filtrate was evaporated to dryness under vacuum at room temperature, giving intensely air-sensitive, deep purple, bis(2-phenylindol-1-yl)tetrakis(tetrahydrofuran)samarium(II), $(R_2N)_2Sm(thf)_4$ (90%),

$$(C_6F_5)_2Hg + 2R_2NH + Sm + 4thf \longrightarrow (R_2N)_2Sm(thf)_4 + Hg\downarrow + 2C_6F_5H \quad (1)$$

which had satisfactory C, H, Sm analyses and gave less intensely coloured $(R_2N)_2Sm(thf)_3$ (characterized by Sm analysis) on extended drying under vacuum. The compound is soluble in hot toluene and ethers and the colour is similar to that of $[(Me_3Si)_2N]_2Sm$ [11, 12]. Infrared absorption at 1035 and 885 cm^{-1} can be attributed [13] to ring stretching modes of coordinated tetrahydrofuran, and the absence of ν(NH) absorption established loss of the NH proton in reaction (1). Visible maxima are at 490 and 585 nm in tetrahydrofuran and the absence of peaks at 1000–1300 nm eliminates [14–16] samarium(III). Confirmation of the oxidation state of $(R_2N)_2Sm(thf)_3$ was provided by the effective magnetic moment, 3.82 μ_B, at 294 K, which is within the range (3.4–3.8 μ_B [12, 18]) for samarium(II) compounds and well outside that (1.4–1.9 μ_B [18]) for samarium(III). Further, the samarium(II) diorganoamide underwent oxidation and ligand exchange on reaction with bis(pentafluorophenyl)mercury and 2-phenylindole under purified nitrogen in tetrahydrofuran over 72 h, giving air-sensitive orange tris(2-phenylindol-1-yl)(tetrahydrofuran)samarium(III) (67%).

$$2(R_2N)_2Sm(thf)_4 + (C_6F_5)_2Hg + 2R_2NH \longrightarrow 2(R_2N)_3Sm(thf) + 2C_6F_5H + 6thf + Hg\downarrow \quad (2)$$

The product was identified by a samarium analysis, near infrared absorption at 1170 and 1220 nm characteristic [14, 16] of samarium(III), ^1H NMR spectroscopy, $\mu_{eff}^{294\,K}$ 1.58 μ_B, indicative [18] of samarium(III), infrared absorption due to coordinated tetrahydrofuran [13], and the absence of ν(NH) absorption. Oxidation of $(R_2N)_2Sm$ by 2-phenylindole alone does not occur, since $(C_6F_5)_2Hg$, 2-phenylindole and samarium metal (mole ratio 1:3:4) in tetrahydrofuran under purified nitrogen at room temperature give $(R_2N)_2Sm$ despite the presence of sufficient secondary amine for oxidation to samarium(III). The product is not derived from reduction of $(R_2N)_3Sm$ by the excess of samarium metal, since this compound does not react with samarium in tetrahydrofuran at room temperature.

Although reaction (1) parallels our earlier synthesis of $(R_2N)_2Yb(thf)_4$ [19], the outcome is surprising both in terms of the clean reaction (high yield) and the oxidation state of the product. The 'one-pot' synthesis of the ytterbium(II) diorganoamide has been shown to proceed via the known [16, 20] redox transmetallation (3) (M = Yb) followed by ligand exchange (4) (M = Yb) [19].

$$M + (C_6F_5)_2Hg \longrightarrow (C_6F_5)_2M + Hg\downarrow \quad (3)$$

$$(C_6F_5)_2M + 2R_2NH \longrightarrow (R_2N)_2M + 2C_6F_5H \quad (4)$$

Neither step can be independently demonstrated for M = Sm, since the reaction between $(C_6F_5)_2Hg$ and samarium metal is highly complex, giving (over a similar reaction time to that for the preparation of $(C_6F_5)_2Yb$ [16, 20]) a multitude of products including $C_6F_5SmF_2$ (a major product), o-HC_6F_4Sm species, $C_{12}F_9Sm$ species, o-$H_2C_6F_4$ and $C_{18}H_2F_{12}$, which are considered to result from decomposition of initially formed $(C_6F_5)_nSm$ (n = 2 or 3) [16]. Moreover, attempts to trap the initial redox transmetallation product by ligand exchange with

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cyclopentadiene or indene after short reaction times gave the samarium(III) organometallics $(C_5H_5)_3Sm$ and $(C_9H_7)_3Sm$ in modest yields [21]. Thus, the reaction of samarium with $(C_6F_5)_2Hg$ and 2-phenylindole was expected to be complex and to give some $(R_2N)_3Sm$. Formation of $(R_2N)_2Sm$ in reaction (1), together with the failure of samarium metal to reduce $(R_2N)_3Sm$ (above), is strong evidence that the $Sm/(C_6F_5)_2Hg$ redox transmetallation gives $(C_6F_5)_2Sm$ [reaction (3), M = Sm] as the initial product, which then undergoes ligand exchange (4) (M = Sm). It has been shown that samarium metal does not react with 2-phenylindole under the conditions of reaction (1).

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