

The Synthesis of a New Soluble Samarium(II) Diorganoamide

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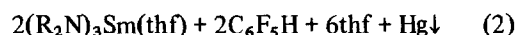
Samarium(II) compounds are important synthetic reagents [1–4]. For example, samarium diiodide is a very useful one-electron reductant in organic synthesis [1] and is a source of the very limited class of samarium(II) organometallics [4–6], whilst bis(pentamethylcyclopentadienyl)samarium(II) is readily 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 $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sm}$, which has been prepared by redox transmetallation from samarium metal and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Hg}$ [11] and by metathesis from SmI_2 [12], and isolated as $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{SmL}_2$ ($\text{L}_2 = (\text{MeOCH}_2)_2$ [11] or $\text{L} = \text{tetrahydrofuran (thf)}$ [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), $(\text{R}_2\text{N})_2\text{Sm}(\text{thf})_4$ (90%),



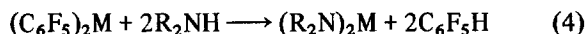
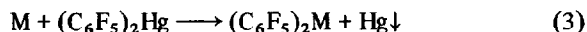
which had satisfactory C, H, Sm analyses and gave less intensely coloured $(\text{R}_2\text{N})_2\text{Sm}(\text{thf})_3$ (characterized by Sm analysis) on extended drying under vacuum. The compound is soluble in hot toluene and ethers and the colour is similar to that of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sm}$ [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 $\nu(\text{NH})$ 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 $(\text{R}_2\text{N})_2\text{Sm}(\text{thf})_3$ was provided by the effective magnetic moment, $3.82\ \mu_{\text{B}}$, at 294 K, which is within the range ($3.4\text{--}3.8\ \mu_{\text{B}}$ [12, 18]) for samarium(II) compounds and well outside that ($1.4\text{--}1.9\ \mu_{\text{B}}$ [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%).



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, $\mu_{\text{eff}}^{294\text{ K}}\ 1.58\ \mu_{\text{B}}$, indicative [18] of samarium(III), infrared absorption due to coordinated tetrahydrofuran [13], and the absence of $\nu(\text{NH})$ absorption. Oxidation of $(\text{R}_2\text{N})_2\text{Sm}$ by 2-phenylindole alone does not occur, since $(\text{C}_6\text{F}_5)_2\text{Hg}$, 2-phenylindole and samarium metal (mole ratio 1:3:4) in tetrahydrofuran under purified nitrogen at room temperature give $(\text{R}_2\text{N})_2\text{Sm}$ despite the presence of sufficient secondary amine for oxidation to samarium(III). The product is not derived from reduction of $(\text{R}_2\text{N})_3\text{Sm}$ 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 $(\text{R}_2\text{N})_2\text{Yb}(\text{thf})_4$ [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) ($\text{M} = \text{Yb}$) followed by ligand exchange (4) ($\text{M} = \text{Yb}$) [19].



Neither step can be independently demonstrated for $\text{M} = \text{Sm}$, since the reaction between $(\text{C}_6\text{F}_5)_2\text{Hg}$ and samarium metal is highly complex, giving (over a similar reaction time to that for the preparation of $(\text{C}_6\text{F}_5)_2\text{Yb}$ [16, 20]) a multitude of products including $\text{C}_6\text{F}_5\text{SmF}_2$ (a major product), $o\text{-HC}_6\text{F}_4\text{Sm}$ species, $\text{C}_{12}\text{F}_9\text{Sm}$ species, $o\text{-H}_2\text{C}_6\text{F}_4$ and $\text{C}_{18}\text{H}_2\text{F}_{12}$, which are considered to result from decomposition of initially formed $(\text{C}_6\text{F}_5)_n\text{Sm}$ ($n = 2$ or 3) [16]. Moreover, attempts to trap the initial redox transmetallation product by ligand exchange with

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).

Acknowledgements

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