

The Synthesis of a New Soluble Samarium(II) Diorganoamide

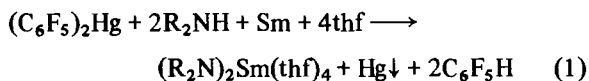
G. B. DEACON and C. M. FORSYTH

Chemistry Department, Monash University, Clayton, Vic.
3168, Australia

(Received June 14, 1988)

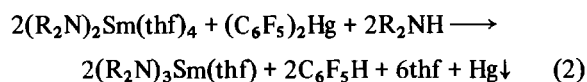
Samarium(II) compounds are important synthetic reagents [1–4]. For example, samarium diiodide is a very useful one-electron reductant in organic synthesis [1] and is a source of the very limited class of samarium(II) organometallics [4–6], whilst bis(pentamethylcyclopentadienyl)samarium(II) is readily 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%),



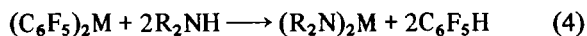
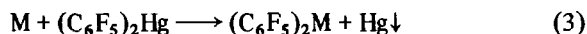
which had satisfactory C, H, Sm analyses and gave less intensely coloured $(\text{R}_2\text{N})_2\text{Sm}(\text{thf})_3$ (characterized by Sm analysis) on extended drying under vacuum. The compound is soluble in hot toluene and ethers and the colour is similar to that of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sm}$ [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 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%).



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

We are grateful to the Australian Research Grants Scheme for support, and for a Commonwealth Postgraduate Research Award (to C.M.F.).

References

- 1 H. B. Kagan and J. L. Namy, in K. A. Gschneidner and I. Eyring (eds.), 'Handbook of the Physics and Chemistry of Rare Earths', Vol. 6, Elsevier, Amsterdam, 1984, Chap. 50.
- 2 T. J. Marks and R. D. Ernst, in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.), 'Comprehensive Organometallic Chemistry', Vol. 3, Pergamon, Oxford, 1982, Chap. 21.
- 3 H. Schumann and W. Genthe, in K. A. Gschneidner and I. Eyring (eds.), 'Handbook of the Physics and Chemistry of Rare Earths', Vol. 7, Elsevier, Amsterdam, 1984, Chap. 53.
- 4 W. J. Evans, *Polyhedron*, **6**, 803 (1987).
- 5 J. L. Namy, R. Girard, H. B. Kagan and R. Caro, *Nouv. J. Chem.*, **5**, 479 (1981).
- 6 A. L. Wayda, S. Cheng and I. Mukerji, *J. Organomet. Chem.*, **330**, C17 (1987).
- 7 R. G. Finke, S. R. Keenan, D. A. Shiraldi and P. L. Watson, *Organometallics*, **6**, 1356 (1987).
- 8 W. J. Evans and D. K. Drummond, *Organometallics*, **7**, 797 (1988).
- 9 W. J. Evans, R. A. Keyer, H. Zhang and J. L. Atwood, *J. Chem. Soc., Chem. Commun.*, 837 (1987).
- 10 G. W. Watt and E. W. Gillow, *J. Am. Chem. Soc.*, **91**, 775 (1969).
- 11 Yu. F. Rad'kov, E. A. Fedorova, S. Ya. Khorshev, G. S. Kalinina, M. N. Bochkarev and G. A. Razuvaev, *J. Gen. Chem. USSR*, 1911 (1985).
- 12 W. J. Evans, D. K. Drummond, H. Zhang and J. L. Atwood, *Inorg. Chem.*, **27**, 575 (1988).
- 13 J. Lewis, J. R. Miller, R. L. Richards and A. Thompson, *J. Chem. Soc.*, 5850 (1958).
- 14 D. C. Stewart and D. Kato, *Anal. Chem.*, **30**, 164 (1958).
- 15 G. S. Ofelt, *J. Chem. Phys.*, **38**, 2171 (1963).
- 16 G. B. Deacon, A. J. Koplick, W. D. Raverty and D. G. Vince, *J. Organomet. Chem.*, **182**, 121 (1979).
- 17 D. F. Evans, G. V. Fazackerley and R. F. Phillips, *J. Chem. Soc. A*, 1931 (1971).
- 18 W. J. Evans and M. A. Hozbor, *J. Organomet. Chem.*, **326**, 299 (1987).
- 19 G. B. Deacon, C. M. Forsyth and R. H. Newnham, *Polyhedron*, **5**, 1143 (1987).
- 20 G. B. Deacon, W. D. Raverty and D. G. Vince, *J. Organomet. Chem.*, **135**, 103 (1977).
- 21 G. B. Deacon and R. H. Newnham, *Aust. J. Chem.*, **38**, 1757 (1985).