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Preliminary communication

Cyclooctatetraenide derivatives of divalent samarium

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Abstract

Owing to the lack of suitable precursor complexes and applicable synthetic methodology, few soluble divalent organosamarium compounds are known. Recently, a facile route to $SmI_2(THF)_2$ proceeding from the bulk metal powder and several organic halides has been described by Kagan & co-workers. We demonstrate herein that this material or the desolvated salt can be used directly in metathetical syntheses (as illustrated by the synthesis of insoluble $Sm(C_8H_8)$ and the THF-soluble $K_2Sm(C_8H_8)_2$).

The known divalent organometallic chemistry of the lanthanoid metals is dominated by derivatives of ytterbium and europium [1]. In contrast, few soluble divalent organosamarium compounds are known [2 *]. This disparity has arisen due to (1) the insolubility of bulk samarium metal in liquid ammonia (a property of both europium and ytterbium which has provided entry into several classes of divalent organometallics of these metals) [3a–d] and (2) the lack of suitable easily prepared divalent precursors which can be derivatized to yield divalent organometallics [4 *]. Recently, Watson [5] and Kagan et al. [6a,b] have described facile routes to the divalent halides LnX_2 (Ln = Yb, Eu, Sm; X = Br, I) proceeding from the bulk metal powder and several organic halides. Both Evans and Watson have used material prepared in this manner to synthesize soluble $(C_5Me_5)_3Sm(THF)_2$ [2a,7] previously accessible only by metal vaporization techniques. Kagan has also exploited the THF-solution stabilized SmI_2 in the synthesis of several divalent (albeit insoluble) samarium derivatives [6b].

To complement our investigations in divalent ytterbium and europium chemistry [3d], we have also begun to investigate the utility of samarium diiodide as a

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precursor to divalent samarium organometallics. We describe herein our approach to the synthetic exploitation of this important reagent and its use in the synthesis of the insoluble $Sm(C_8H_8)$ and the THF-soluble $K_2Sm(C_8H_8)_2$.

I. Results and discussion

THF solutions of samarium diiodide can be readily generated via the reported reaction of bulk samarium metal and diiodomethane or diiodoethane [6a,b]. Removal of excess metal by filtration yields blue-green solutions of SmI_2, which, as Kagan, Evans and Watson have demonstrated, can be used directly in metathetical syntheses. We find, however, that $SmI_2(THF)_2$ generated from iodomethane occasionally yields the diiodide contaminated with an unidentified trivalent impurity (as judged by its variable complexometric metal analysis and low magnetic moment). Consequently, to ensure exclusively divalent products using this starting material, the diiodide should be generated using diiodoethane. As described by Kagan, this material can be conveniently used in solution or as reported by Evans as the stable bis(tetrahydrofuranate). If desired, we further find that gentle heating (100–150 ° C) under high vacuum (10^{-4}–10^{-5} mmHg) generates the exclusively divalent forest-green desolvated salt (as determined by complexometric metal analysis) which retains solubility in THF and which can also be used directly in stoichiometric metatheses or as a starting material to generate other strong Lewis base adducts of this reagent. The viability of this reagent provides an important facile entry into divalent samarium chemistry and we report herein our use of $SmI_2(THF)_2$ to generate $Sm(C_8H_8)$ and olive-green $K_2Sm(C_8H_8)_2$ thereby completing the class of divalent cyclooctatetraenides.

$Yb(C_8H_8)$ and $Eu(C_8H_8)$ were first prepared by Hayes and Thomas in 1968 viz. the reaction of the respective metals and cyclooctatetraene in liquid ammonia [3a] $K_2Yb(C_8H_8)_2$ was recently reported by Streitwieser et al. by the 1/2 reaction of ytterbium and C_8H_8 in liquid ammonia [8]. Unlike $Yb(C_8H_8)$ and $Eu(C_8H_8)$, $K_2Yb(C_8H_8)_2$ is soluble in and can be crystallized from ethereal solvents. $Sm(C_8H_8)$ and $K_2Sm(C_8H_8)_2$, generated via the reaction of $SmI_2(THF)_2$ in THF and one and two equivalents of $K_2(C_8H_8)$ respectively [9 *], mirror these solubility properties. Olive-green $Sm(C_8H_8)$ is totally insoluble in THF and appears to slowly decompose in rigorously purified pyridine (although it is initially soluble). Attempts to trap a soluble $Sm(C_8H_8)$-containing species by conducting the reaction in the presence of strongly coordinating ligands, such as dimethylphosphinoethane (DMPE) or tetramethylethylenediamine (TMED), also fail to yield a soluble product. $K_2Sm(C_8H_8)_2$, in contrast, is slightly soluble in ether and soluble in THF. The olive-green complex is readily characterized by IR and ^1H NMR spectroscopy [10 *] and complete elemental analysis [11 *]. It is very air and moisture sensitive and exhibits similar spectral and chemical properties to $K_2Yb(C_8H_8)_2$.

These successful syntheses demonstrate the utility of $SmI_2(THF)_2$ in the preparation of new divalent samarium species and serve to re-emphasize the necessity of saturating lanthanoid coordination spheres with solubility-enhancing ligands (i.e. two $C_8H_8{}^{2-}$ vs. one $C_8H_8{}^{2-}$) if soluble characterizable materials are to be isolated. This effect has also been successfully exploited by Deacon and co-workers with the synthesis of soluble $KSm(C_5H_5)_3$ [2d] (in contrast to the insoluble $Sm(C_5H_5)_2$). Further synthetic efforts are focussed on the synthesis and characterization of additional classes of divalent samarium derivatives and are under active investigation.

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References and Notes

1 See references cited in T.J. Marks and R.D. Ernst in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon Press, New York, 1982; Vol. 3, Chapter 21.

2 Known soluble complexes of divalent samarium are restricted to cyclopentadienide and substituted-cyclopentadienide species e.g. (a) $(C_5Me_5)_2Sm(THF)_2$, $[(C_5Me_5)SmI(THF)_2]_2$ W.J. Evans, J.W. Grate, H.W. Choi, I. Bloom, W.E. Hunter and J.L. Atwood, J. Am. Chem. Soc., 107 (1985) 941; (b) $(C_5Me_4Et)_2Sm(THF)_2$, $(C_5Me_4Et)_2Sm$, W.J. Evans, I. Bloom, W.E. Hunter, J.L. Atwood, Organometallics, 4 (1985) 112; (c) $(C_5Me_5)_2Sm$, W.J. Evans, L.A. Hughes and T.P. Hanusa, J. Am. Chem. Soc., 106 (1984) 4270; (d) $KSm(C_5H_5)_3$, G.B. Deacon, G.N. Pain and T.D. Tuong, Polyhedron, 4 (1985) 1149.

3 (a) R.G. Hayes and J.L. Thomas, J. Am. Chem. Soc., 91 (1969) 6876; (b) E.O. Fischer and H. Fischer, J. Organomet. Chem., 3 (1965) 181; F. Calderazzo, R. Pappalardo and S. Losi, J. Inorg. Nucl. Chem., 28 (1966) 987; (c) E. Murphy and G.E. Toogood, Inorg. Nucl. Chem. Lett., 7 (1971) 755; (d) A.L. Wayda, J.L. Dye and R.D. Rogers, Organometallics, 3 (1984) 1605.

4 LnX_2 (Ln = Eu, Yb; X = Cl, Br, I) can be readily prepared via the reaction of the respective metal-ammonia solutions with NH_4X (J.K. Howell and L.L. Pytlewski, J. Less. Common Metals, 18 (1969) 437). The insolubility of bulk samarium metal precludes the corresponding synthesis of SmX_2 by this route.

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6 (a) J.L. Namy, P. Girard and H.B. Kagan, Nouv. J. Chim., 5 (1977) 1; (b) J.L. Namy, P. Girard, H.B. Kagan and P.E. Caro, ibid., 7 (1981) 479.

7 P.L. Watson, private communication.

8 S.A. Kinsley, A. Streitwieser and A. Zalkin, Organometallics, 4 (1985) 52.

9 In a typical synthesis, forest-green SmI_2 was dissolved in THF to yield a deep blue-purple solution. $K_2C_8H_8$, one or two equivalents (prepared by the 8 h ambient temperature reaction of freshly scraped potassium metal and dried, degassed C_8H_8 in THF) was slowly dripped into the stirred SmI_2 solution. In both reactions the addition of the $K_2C_8H_8$ solution resulted in precipitation of solid and a color change of the resultant slurry to olive-green/brown. The reactions were then normally stirred overnight at ambient temperature in the dry box before work-up. Crude products were isolated by filtration (of insoluble product in the case of $Sm(C_8H_8)$) or by rotary evaporation of solvent (from the dark-brown filtrate in the case of $K_2Sm(C_8H_8)_2$). Analytically pure $K_2Sm(C_8H_8)_2$ was isolated by washing the crude dark brown product with a small amount of diethyl ether to remove a very soluble brown impurity containing K, Sm and I (by X-ray fluorescence). Continued extraction of the remaining solid yielded an olive-green solution. Removal of solvent gave analytically pure olive-green $K_2Sm(C_8H_8)_2$ in 20% yield.

10 The infrared spectrum is obtained on a Nujol mull of the complex and exhibits bands characteristic of $C_8H_8{}^{2-}$. IR (cm^{-1}): 882(s), 739(m), 688(s); ^1H NMR (THF-d_8): δ 5.78 (s, C_8H_8) ppm.

11 Found: K, 17.05; Sm, 32.90; C, 42.57; H, 3.61. $K_2SmC_{16}H_{16}$ calcd.: K, 17.89; Sm, 34.42; C, 43.99; H, 3.69%.