

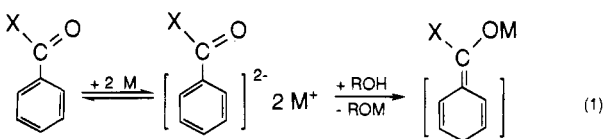
Protonation at the Aromatic Ring of Samarium Benzophenone Dianion Species. Isolation and Structural Characterization of a Samarium(III) Enolate Complex

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The reduction of aromatic compounds into their dihydro derivatives by dissolving metal/alcohol systems (the Birch reduction) is a useful methodology in organic synthesis.¹ Of particular importance is the reduction of aromatic carbonyl compounds such as aromatic acids,² esters,³ amides,^{2d,4} and monoaryl ketones,⁵ which usually generates *in situ* useful metal enolate intermediates that upon further reaction with electrophiles yield a variety of cyclohexadiene derivatives.^{1f,g} One of the possible processes to generate these metal enolate intermediates is thought to be the monoprotection of dianionic species at the *para* position of the aromatic rings (eq 1; M = alkali metals; X = OM, OR, NR₂, alkyl);¹⁻⁵ however, neither the dianionic species nor the enolates have been well characterized.



On the other hand, the reduction of diaryl ketones by alkali metals⁶ in liquid ammonia or by lanthanide metals in THF/HMPA⁷ or DME⁸ has been well known to afford the cor-

responding ketone dianions. Extensive studies have so far shown that these ketone dianions always receive electrophilic attacks at the carbonyl group to give diaryl alcohol derivatives. Hydrogenation of the aromatic rings has not been reported to date. The first X-ray structure of metal ketone dianion complexes, [Yb(μ - η^1, η^2 -OCPh₂)(HMPA)₂]₂, has been recently determined in this laboratory.⁹ Protonation of this complex with ArOH (Ar = 2,6-^tBu₂-4-Me-C₆H₂)^{9a} or CpMo(CO)₃H¹⁰ also occurred at the carbonyl unit to release benzhydrol. In striking contrast to these results, when the analogous samarium benzophenone dianion species was allowed to react with ArOH, the protonation occurred at the aromatic ring to give the samarium(III) enolate complex Sm(OC(=CCH=CHCH₂-CH=CH)Ph)₂(OAr)(HMPA)₂ (**1a**). We report herein this new type of reaction and some of the reactivities of the enolate complex **1a**.

The reaction of samarium benzophenone dianion species with ArOH was carried out as in the case of Yb (Scheme 1).⁹⁻¹¹ The ¹H NMR spectrum of the yellow crystalline product **1a** suggested that two benzophenone-originated units remained in this molecule, together with one ArO and two HMPAs.¹² The intensities of the signals which appeared at the region from δ 3 to 7 showed that two of the four phenyl rings in the benzophenone units had lost their aromaticity. An X-ray crystallographic study revealed that this complex possessed a trigonal bipyramid structure with one ArO and two benzophenone moieties at the equatorial and two HMPA ligands at the apical vertices (Figure 1).¹³ Consistent with the ¹H NMR spectrum, one of the two phenyl rings in each benzophenone unit was protonated at the *para*-position and thus adopted a cyclohexadienylidene structure (see bond lengths and angles in Figure 1). Each benzophenone unit could therefore be regarded as an enolate. Reaction of the Sm-benzophenone mixture with ArOD

yielded the deuterated enolate Sm(OC(=CCH=CHCHD-

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(11) To a red-brown reaction mixture of Sm (1.503 g, 10 mmol, activated by 2% of ICH₂CH₂I) and benzophenone (1.822 g, 10 mmol) in THF (20 mL) and HMPA (8 mL) was added ArOH (Ar = 2,6-^tBu₂-4-Me-C₆H₂) (4.408 g, 20 mmol) in THF (15 mL) under Ar. The resulting light brown solution was then stirred for 3 h at room temperature. Evaporation of THF and addition of ether precipitated a yellow crystalline product which after recrystallization from THF gave yellow needle-like crystals of Sm(OC(=CCH=CHCH₂-CH=CH)Ph)₂(OAr)(HMPA)₂ (**1a**, 3.28 g, 60% yield based on benzophenone).

(12) ¹H NMR data (C₆D₆, 22 °C; assignments for **1a,b** were also confirmed by DEPT and H.C-COSY experiments): **1a**, δ 7.90 (d, *J* = 7.3 Hz, 4 H, Ph), 7.75 (s, 2 H, C₆H₂), 7.28 (t, *J* = 7.3 Hz, 4 H, Ph), 7.21 (t, *J* = 7.3 Hz, 2 H, Ph), 6.94 (br d, *J* = 8.9 Hz, 2 H, CH), 6.76 (br d, *J* = 8.9 Hz, 2 H, CH), 5.55–5.65 (br m, 2 H, CH), 5.28–5.40 (br m, 2 H, CH), 2.97 (br s, 4 H, CH₂), 2.67 (s, 3 H, Me), 2.11 (d, *J* = 9.6 Hz, 36 H, NMe), 1.35 (s, 18 H, ^tBu); **1b**, δ 7.95–7.85 (m, 6 H, Ph, C₆H₃), 7.35–7.10 (m, 7 H, Ph, C₆H₃), 6.90 (br d, *J* = 10.6 Hz, 2 H, CH), 6.77 (br d, *J* = 10.2 Hz, 2 H, CH), 5.55–5.65 (br m, 2 H, CH), 5.30–5.40 (br m, 2 H, CH), 2.96 (br s, 4 H, CH₂), 2.10 (d, *J* = 9.3 Hz, 36 H, NMe), 1.33 (s, 18 H, ^tBu); **2a**, δ 8.08 (d, *J* = 7.3 Hz, 8 H, Ph), 7.77 (s, 2 H, C₆H₂), 7.61 (br s, 2 H, CH), 7.33 (t, *J* = 7.3 Hz, 8 H, Ph), 7.20 (t, *J* = 7.3 Hz, 4 H, Ph), 2.71 (s, 3 H, Me), 2.01 (s, 18 H, ^tBu), 1.62 (d, *J* = 9.6 Hz, 36 H, NMe); **2b**, δ 8.07 (d, *J* = 7.3 Hz, 8 H, Ph), 7.93 (d, *J* = 7.9 Hz, 2 H, C₆H₃), 7.59 (br s, 2 H, CH), 7.36–7.15 (m, 13 H, Ph, C₆H₃), 1.99 (s, 18 H, ^tBu), 1.61 (d, *J* = 9.6 Hz, 36 H, NMe). Anal. Calcd for C₅₃H₈₁N₆O₅P₂Sm (**1a,2a**): C, 58.16; H, 7.46; N, 7.68. Found: C, 59.45; H, 7.62; N, 7.86 (**1a**); C, 58.19; H, 7.46; N, 7.61 (**2a**). Calcd for C₅₂H₇₉N₆O₅P₂Sm (**1b,2b**): C, 57.80; H, 7.37; N, 7.78. Found: **1b**: C, 57.20; H, 7.46; N, 7.74. **2b**: C, 57.73; H, 7.39; N, 7.70.

(13) **1a**: monoclinic, space group P2₁/n, *a* = 10.662(8), *b* = 33.827(4), and *c* = 16.205(2) Å, β = 96.61(2)°, *V* = 5806 Å³, *Z* = 4, *D_c* = 1.250 g cm⁻³, *R* = 0.0781 (*R_w* = 0.0892) for 5146 unique data with *F_o* > 5 σ (*F_o*) and 621 variables. **2b**: triclinic, space group P1, *a* = 10.637(2), *b* = 15.721(2), and *c* = 17.102(3) Å, α = 89.88(1)°, β = 101.72(2)°, γ = 95.40(2)°, *V* = 2788 Å³, *Z* = 2, *D_c* = 1.298 g cm⁻³, *R* = 0.0468 (*R_w* = 0.0580) for 10 355 unique data with *F_o* > 5 σ (*F_o*) and 696 variables.

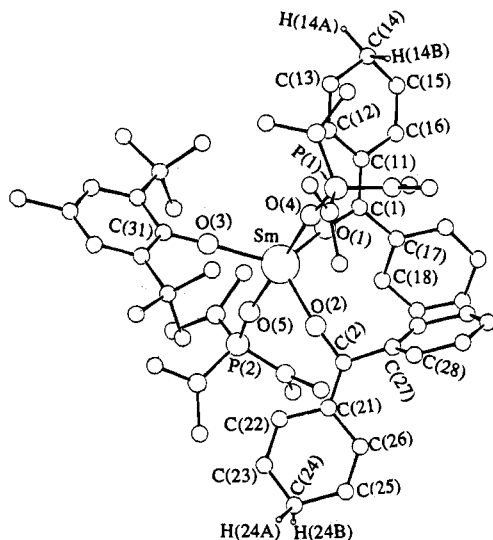
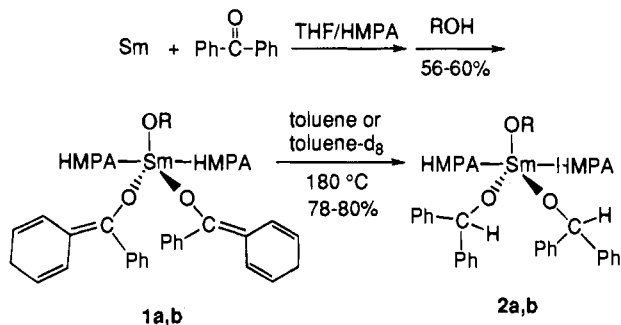
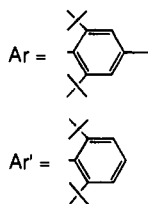


Figure 1. ORTEP drawing of **1a** and selected bond lengths (Å) and angles (deg): Sm—O(1), 2.189(13); Sm—O(2), 2.170(11); Sm—O(3), 2.187(8); Sm—O(4), 2.331(10); Sm—O(5), 2.335(10); C(1)—O(1), 1.32(2); C(2)—O(2), 1.34(2); C(1)—C(11), 1.36(2); C(1)—C(17), 1.49(2); C(11)—C(12), 1.46(3); C(12)—C(13), 1.31(3); C(13)—C(14), 1.57(4); C(14)—C(15), 1.45(4); C(15)—C(16), 1.36(3); C(11)—C(16), 1.47(3); C(2)—C(21), 1.36(2); C(2)—C(27), 1.50(2); C(21)—C(22), 1.47(2); C(22)—C(23), 1.38(3); C(23)—C(24), 1.47(3); C(24)—C(25), 1.51(3); C(25)—C(26), 1.34(3); C(21)—C(26), 1.44(3); C(1)—O(1)—Sm, 167(1); C(2)—O(2)—Sm, 169(1); C(3)—O(3)—Sm, 179(1); C(13)—C(14)—C(15), 114(2); C(23)—C(24)—C(25), 113(2).

Scheme 1



a: R = Ar, b: R = Ar'

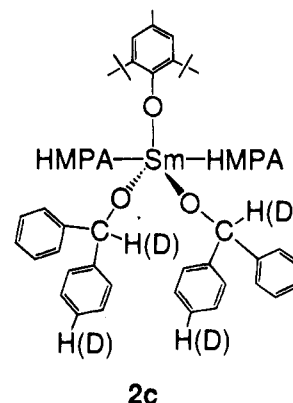


CH=CH)Ph)₂(OAr)(HMPA)₂ (**1c**), which confirmed that the formation of **1a** was *via* the direct protonation by ArOH.

Reaction of **1a** with alcohol Ar'OH (Ar' = 2,6-Bu₂-C₆H₃) afforded quantitatively the aryloxy exchange product **1b**.¹² No protonation occurred at either carbon or oxygen atoms of the enolate parts, even when 2 equiv of Ar'OH was added, which is in contrast to the case of Birch reductions, where protonation of the enolate intermediates usually gives the 1,4-dihydro derivatives.¹⁻⁵ These results imply that the enolate anions in **1a** are even less basic than the aryloxy one, which might be caused by the electron-withdrawing property of the phenyl groups in the enolate units.¹⁴

When heated in toluene at 180 °C overnight, **1a,b** isomerized into colorless Sm(OC(H)Ph)₂(OR)(HMPA)₂ (**2a,b**; **2a**, R = Ar;

2b, R = Ar'),¹² respectively (Scheme 1). No deuterium was incorporated into **2a** when **1a** was thermolyzed in toluene-*d*₈, indicating the hydrogen shift was an intramolecular process. This was further confirmed by the thermolysis of the deuterated enolate **1c** in toluene, which yielded **2c** as identified by comparison of its ¹H NMR spectrum with that of **2a**.



An X-ray analysis of **2b** shows that the geometry around the central Sm atom is very similar to that in **1a**.¹³ However, reflecting the loss of conjugation of the diphenylmethoxy anions in **2b**, the average bond distance (2.143(5) Å) of Sm—O(diphenylmethoxy) in **2b** is shorter than that (2.18(1) Å) of Sm—O(enolate) in **1a**, and the C—O(diphenylmethoxy) bonds (av 1.387(8) Å) in **2b** are longer than the C—O(enolate) bonds (av 1.33(2) Å) in **1a**.

The difference observed in the protonation of Sm(II) and Yb(II) benzophenone dianion species may result from the difference in the two divalent metal ions. Since Sm(II) ion is bigger in radius and softer than Yb(II), the negative charges in the Sm(II) benzophenone dianion species must be more delocalized into its phenyl rings, which probably causes the protonation to occur more easily at the aromatic part.¹⁵ The results presented here and in previous papers^{9,10} represent a good example that reactivity can be finely tuned simply by changing the metals in the lanthanide series. Further studies on metal effects in these reactions are in progress.

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Supplementary Material Available: Listings of atomic coordinates, thermal parameters, bond distances and angles for **1a** and **2b** (15 pages); listing of observed and calculated structure factors (39 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(14) Although the possibility of metal dependence could not be ruled out, the difference in reactivity toward a proton between **1a** and the enolate intermediates in the Birch reductions probably arises from the difference in the substituents in these two types of enolates: in the case of Birch reductions, the substituents are all electron-donating groups (eq 1, X = OM, OR, NR₂, alkyl),¹⁻⁵ while in **1a** (X = Ph), the substituent Ph is an electron-withdrawing one.

(15) The mechanism for the enolate formation is under investigation and will be discussed in a forthcoming full paper. Although the samarium benzophenone species has not been isolated yet, we believe it possesses a dimeric structure similar to that of the ytterbium benzophenone complex.⁹ For an example of oxidation of Yb(II) species into Yb(III) by a proton, see ref 10.