

## Novel Crystal Structure of Ytterbium(II)–Benzophenone Dianion Complex and its Reaction with 2,6-Di-*tert*-butyl-4-methylphenol

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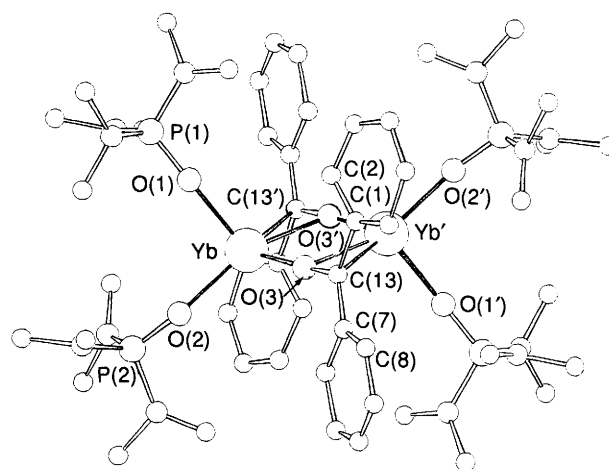
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Treatment of 1 equiv. of Yb metal with benzophenone in tetrahydrofuran–hexamethylphosphoramide (hmpa) gives a Yb<sup>II</sup>–benzophenone dianion complex, [ $\{Yb(OCPh_2)(hmpa)_2\}_2$ ] **1** which on treatment with 2,6-di-*tert*-butyl-4-methylphenol produces  $[Yb(OC_6H_2Bu^t_2-2,6-Me-4)_2(hmpa)_2]$  **2**; both **1** and **2** are structurally characterized by X-ray crystallography.

The formation of the benzophenone dianion *via* the reaction of benzophenone with alkali metals was known as early as 1911.<sup>1</sup> Reaction of active titanium metal with diaryl ketones was also reported to result in the formation of the corresponding diaryl ketone dianions.<sup>2</sup> However, none of these dianion compounds has been structurally characterized. To the best of our knowledge, the only structurally characterized metal benzophenone complex in the literature, which is directly formed *via* the reaction with benzophenone, is  $[W(OCH_2Bu^t)_4(py)(\eta^2-OCPh_2)]$  (py = pyridine),<sup>3</sup> although the structure of  $[\{(C_5H_5)_2Zr(\eta^2-OCPh_2)\}_2]$ , which was obtained from the reaction of diphenylzirconocene with carbon monoxide, is also known.<sup>4</sup> Recently, it was reported that reaction of lanthanoid metals with diaryl ketones produced the corresponding dianions, but their structures are still unknown.<sup>5–8</sup> Considering the potential uses of the lanthanoid diaryl ketone complexes in synthetic chemistry,<sup>5–7,9</sup> their structural characterization should be of great importance and interest in understanding their reactivities. We have now succeeded in isolating and structurally characterizing the ytterbium(II)–benzophenone dianion complex, [ $\{Yb(OCPh_2)(hmpa)_2\}_2$ ] **1** (hmpa = hexamethylphosphoramide). In this communication, we report its X-ray crystal structure and its reaction with 2,6-di-*tert*-butyl-4-methylphenol to give  $[Yb(OC_6H_2Bu^t_2-2,6-Me-4)_2(hmpa)_2]$  **2**. The structure of complex **2** is also described.

A mixture of 40-mesh Yb metal (173 mg, 1 mmol) and benzophenone (182 mg, 1 mmol) in tetrahydrofuran (thf)–hmpa (6:1)<sup>5–7</sup> was stirred at room temperature in a Schlenk flask for 1 h and then filtered into another Schlenk flask.† Fine

crystals were formed after reducing the volume under vacuum and leaving it to stand at room temperature overnight. The supernatant was carefully removed using a syringe and the crystals were washed with toluene and dried under vacuum. Finally fine red–black crystals of [ $\{Yb(OCPh_2)(hmpa)_2\}_2$ ] **1**



**Fig. 1** X-Ray structure of **1** and selected bond lengths (Å) and angles (°). Yb...Yb': 3.508(4), Yb–O(1): 2.27(3), Yb–O(2): 2.28(2), Yb–O(3): 2.11(3), Yb–O(3'): 2.39(2), Yb–C(13'): 2.59(5), C(13)–O(3): 1.39(6); O(1)–Yb–O(2): 93(1), O(2)–Yb–O(3): 105(1), O(1)–Yb–O(3): 110(1), O(1)–Yb–C(13'): 99(1), O(2)–Yb–C(13'): 134(1), O(3)–Yb–C(13'): 110(1), C(13)–O(3)–Yb: 172(3), Yb–O(3)–Yb': 102(1), C(13)–O(3)–Yb': 82(2), O(3)–C(13)–C(1): 117(3), O(3)–C(13)–C(7): 118(4), C(1)–(13)–C(7): 123(4).

† The complexes reported in this paper are extremely air- and moisture-sensitive and must be manipulated using Schlenk techniques under a very pure argon atmosphere.

(303 mg, 42%)<sup>‡</sup> were obtained. The <sup>1</sup>H NMR spectrum<sup>‡</sup> of complex **1** showed a large upfield shift for the signals of the benzophenone phenyl groups, showing a doublet and two triplets at δ 7.04, 6.59 and 5.63, respectively. This upfield shift is consistent with the large electron density increase in the benzophenone ligand of complex **1**.

Complex **1** could be recrystallized from thf–toluene to give red–black needle crystals, from which a crystal of X-ray quality was obtained. Its X-ray structure and selected bond lengths and angles are shown in Fig. 1. § Two benzophenone dianions bridge two Yb atoms, to each of which two hmpa ligands are coordinated to form a distorted tetrahedron around each Yb atom. The bridge is built in such a manner that a benzophenone dianion uses its O<sup>−</sup> to make a Yb–O bond with one Yb<sup>II</sup> ion and its C<sup>−</sup> to form a Yb–C bond with the other Yb<sup>II</sup> ion to which the lone electron pair of the oxygen atom is also donated. This makes the structure unique. It is different both from the usual metal–ketone complexes<sup>3,4,12</sup> in that the coordination form of the CO group of benzophenone is not a simple η<sup>2</sup> pattern, and from common bimetallic alkoxides<sup>13</sup> in that the oxygen bridge is unsymmetrical. The bond distance of Yb–O(3) [2.11(3) Å] is comparable with that of a Yb–O ion bond (*cf.* Yb<sup>II</sup>–OAr: 2.14–2.22 Å),<sup>14</sup> and the Yb–O(3') bond [2.39(2) Å] is similar to a Yb–O coordinate bond [*cf.* Yb<sup>II</sup>–O(thf): 2.37–2.51<sup>14</sup> and 2.412(5) Å].<sup>15</sup> The bond length of Yb–C(13') is 2.59(5) Å, which is comparable with the Yb–(μ–Me) distances in [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Yb(μ–Me)<sub>2</sub>AlMe<sub>2</sub>] [2.562(18) and 2.609(23) Å],<sup>16</sup> but longer than the Yb–CH<sub>3</sub>(terminal) distance in [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Yb(Me)(thf)] [2.362(11) Å].<sup>17</sup> The C–O bond distance of the benzophenone in **1** [1.39(6) Å] is comparable with those reported for [W(OCH<sub>2</sub>–Bu<sup>t</sup>)<sub>4</sub>(py)(η<sup>2</sup>–OCPh<sub>2</sub>)] [1.397(11) Å]<sup>3</sup> and [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Zr(η<sup>2</sup>–OCPh<sub>2</sub>)<sub>2</sub>] [1.419(4) and 1.425(4) Å],<sup>4</sup> and longer than that of free benzophenone (1.23 Å).<sup>18</sup> The average bond distance of Yb–O(hmpa) (2.28 Å) is longer than those in [Yb(H<sub>2</sub>O)<sub>5</sub>(hmpa)<sub>2</sub>]Cl<sub>3</sub>·H<sub>2</sub>O·hmpa (2.178 Å) and YbCl<sub>3</sub>(hmpa)<sub>3</sub> (2.224 Å), possibly owing to the lower electrophilicity of Yb<sup>II</sup> compared to Yb<sup>III</sup>.<sup>19</sup> It is also noteworthy that in complex **1** the complexation of the CO group with Yb does not destroy the original planarity of the ligand.<sup>18</sup> The sum of the angles formed by O(3), C(1) and C(7) around C(13) is 358°, which is in contrast to those for the W (344°)<sup>3</sup> and the Zr (336 and 341°)<sup>4</sup> benzophenone complexes. This suggests that

<sup>‡</sup> M.p., 159–160 °C; <sup>1</sup>H NMR spectrum ([<sup>2</sup>H<sub>8</sub>]thf) δ 7.04 (d, *J* = 7.6 Hz, 4H, Ph), 6.59 (t, *J* = 7.6 Hz, 4H, Ph), 5.63 (t, *J* = 7.6 Hz, 2H, Ph), 2.54 (br s, 36H, NMe); IR (thf) ν<sub>CO</sub>: 1566 cm<sup>−1</sup>.

§ Crystal data for **1**: C<sub>25</sub>H<sub>46</sub>N<sub>6</sub>O<sub>3</sub>P<sub>2</sub>Yb, *M* = 713.62, triclinic, space group *P* $\bar{1}$  (No. 2), *a* = 12.897(3), *b* = 12.990(3), *c* = 10.480(2) Å, α = 109.80(2), β = 92.79(2), γ = 74.43(2)°, *U* = 1589.6 Å<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.491 g cm<sup>−3</sup>, μ(Cu–Kα) = 1.644 cm<sup>−1</sup>, *R* = 0.108 (*R<sub>w</sub>* = 0.129) for 1805 unique data with *F<sub>o</sub>* ≥ 6σ(*F<sub>o</sub>*). All attempts to obtain a better crystal were unsuccessful because of the extreme air- and moisture-sensitivity of the compound. For **2**: C<sub>42</sub>H<sub>82</sub>N<sub>6</sub>O<sub>4</sub>P<sub>2</sub>Yb, *M* = 970.08, hexagonal, space group *P*<sub>6</sub>22 (No. 178), *a* = *b* = 11.672(1), *c* = 65.664(10) Å, *U* = 7747.3 Å<sup>3</sup>, *Z* = 6, *D<sub>c</sub>* = 1.248 g cm<sup>−3</sup>, μ(Cu–Kα) = 1.193 cm<sup>−1</sup>, *R* = 0.052 (*R<sub>w</sub>* = 0.062) for 2161 unique data with *F<sub>o</sub>* ≥ 5σ(*F<sub>o</sub>*). Crystals were sealed in capillaries under Ar for crystallographic study. Data were collected on an Enraf–Nonius CAD4 diffractometer with a rotating anode (20 °C, Cu–Kα radiation, λ = 1.54184 Å, ω-scan, 2° ≤ θ ≤ 68°) and were corrected for X-ray absorption effects. The metal atoms were located by MULTAN,<sup>10</sup> and the remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. Refinements were performed by the block diagonal least-squares method for **1** and full-matrix least-squares method for **2**.<sup>11</sup> For **1** the structure analyses were in both *P*1 and *P* $\bar{1}$  space groups. The results indicate that a centre of symmetry exists at the centre of the Yb bridge, and so the space group was assigned as *P* $\bar{1}$ . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

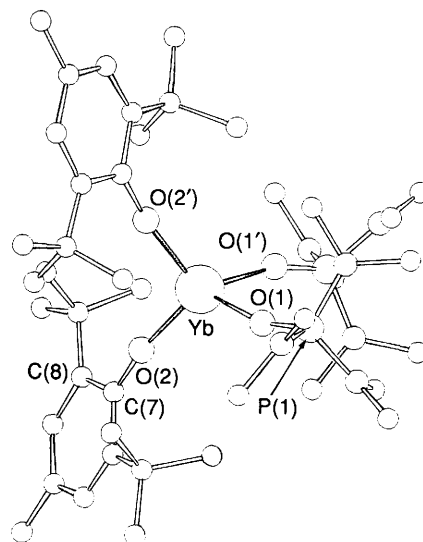


Fig. 2 X-Ray structure of **2** and selected bond lengths (Å) and angles (°). Yb–O(1): 2.298(7), Yb–O(2): 2.179(9), P(1)–O(1): 1.481(8), C(7)–O(2): 1.303(15); O(1)–Yb–O(2): 122.1(3), O(1)–Yb–O(1'): 97.0(3), O(2)–Yb–O(2'): 110.3(3), O(2)–Yb–O(1'): 103.1(3), C(7)–O(2)–Yb: 171.3(6).

C(13) is still sp<sup>2</sup>-hybridized and compound **1** should be a true ketone dianion metal complex, which is consistent with the fact that complex **1** is formed *via* two-electron transfer from Yb metal to benzophenone, whereas for W and Zr the formation of the η<sup>2</sup>-ketone metal complexes could be explained by the donation and back-donation theory as for metal–alkene complexes.<sup>20</sup>

Complex **1** showed the same reactivity as reported for the *in situ* formed ytterbium–benzophenone intermediate.<sup>5–7</sup> For example, when treated with D<sub>2</sub>O it gave Ph<sub>2</sub>CDOD and with cyclohexanone gave the corresponding cross-coupling product in almost quantitative yields. In addition, it reacted in thf with 4 equiv of 2,6-di-*tert*-butyl-4-methylphenol to give [Yb(OC<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup>-2,6-Me-4)<sub>2</sub>(hmpa)<sub>2</sub>] **2** in 80% yield. ¶ Complex **2** could be recrystallized from thf or thf–toluene to give orange crystals. The molecular structure has twofold symmetry as shown in Fig. 2. § The central Yb atom is coordinated by two ArO<sup>−</sup> groups (Ar = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup>-2,6-Me-4) and two hmpa ligands in a distorted tetrahedral geometry. The Yb–O(2) distance [2.179(9) Å] is slightly longer than that in [Yb(OAr)<sub>2</sub>(thf)<sub>2</sub>] [2.139(10) and 2.135(9) Å, Ar = C<sub>6</sub>H<sub>2</sub>Bu<sup>t</sup>-2,6-Me-4],<sup>14</sup> possibly because **2** is more sterically crowded. The Yb–O(hmpa) distance [2.298(7) Å] is again longer than Yb<sup>III</sup>–O(hmpa),<sup>19</sup> but comparable with those in complex **1**.

The easy formation of **2** from **1** shows that the reactions of lanthanoid diaryl ketone dianion complexes with aryl or alkyl alcohols could constitute a convenient alternative for the synthesis of the corresponding lanthanoid aryl oxides or alkoxides, a class of compounds which is of current interest. ¶<sup>14</sup>

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¶ For the synthesis of **2**, isolation of **1** is not necessary. Reaction of the mixture of Yb metal and benzophenone in thf–hmpa with 2,6-di-*tert*-butyl-4-methylphenol gave similar results. <sup>1</sup>H NMR data for **2** (in [<sup>2</sup>H<sub>8</sub>]thf): δ 6.64 (s, 4H, Ph), 2.61 (d, *J*<sub>P–H</sub> = 9.3 Hz, 36H, NMe), 2.07 (s, 6H, Me), 1.44 (s, 36H, Bu<sup>t</sup>).

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