## Synthesis and Properties of the Benzenetricarbonylchromium Derivatives of Divalent Samarium, Europium, and Ytterbium

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The title compounds,  $Ln[PhCr(CO)_3]_2 \cdot n$ (tetrahydrofuran) Ln = Sm, Eu, Yb, representing a new tye of organometallic derivative of divalent lanthanides, were produced by the reaction of Hg[PhCr(CO)\_3]\_2 with an excess of Ln<sup>0</sup> filings in tetrahydrofuran.

The organic derivatives of divalent lanthanides  $R_2Ln$  (Ln = Sm, Eu, Yb) produced to date, are confined to compounds containing relatively strong electron withdrawing R groups (*e.g.* cyclopentadienyl,<sup>1</sup> C-carbaboranyl,<sup>2</sup> C<sub>6</sub>F<sub>5</sub>, PhC=C,<sup>3</sup> with the pK<sub>a</sub>'s of the corresponding CH acids being 15-23<sup>4</sup>).

Recently, *trans*-(ClHC=CH)<sub>2</sub>Hg (p $K_a$  of CH acid 31.5<sup>5</sup>) and metallocene derivatives [C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>4</sub>]<sub>2</sub>Yb and [(OC)<sub>3</sub>MnC<sub>5</sub>H<sub>4</sub>]<sub>2</sub>Yb have been produced and characterized by their <sup>1</sup>H n.m.r. spectra.<sup>6</sup> An attempt to obtain Ph<sub>2</sub>Yb in the reaction of Ph<sub>2</sub>Hg with Yb failed,<sup>3</sup> however according to the <sup>1</sup>H n.m.r. data Ph<sub>2</sub>Yb·*n*THF (THF = tetrahydrofuran) is formed (in 30–35% yield) in this reaction with the precipitation of Yb–Hg, after 48 h. This was proved by measuring the yield of benzene after hydrolysis of the reaction mixture. In order to stabilize phenyl derivatives of lanthanides we used the (CO)<sub>3</sub>Cr group and carried out the reaction of Hg[PhCr(CO)<sub>3</sub>]<sub>2</sub> with Ln<sup>0</sup>, which yielded 68–73% of Ln[PhCr(CO)<sub>3</sub>]<sub>2</sub>.

$$[(OC)_{3}CrPh]_{2}Hg + mLn^{0} \xrightarrow{THF, 4 h} (m - 1)Ln (m = 5-7)$$
(1)
$$+ Hg + [(OC)_{3}CrPh]_{2}Ln \cdot nTHF$$
(1)
(2) Ln = Sm, n = 2
(3) Ln = Eu, n = 1
(4) Ln = Yb, n = 2

Compounds (2)—(4) were isolated at low temperatures  $(-40 \text{ to } -70 \,^{\circ}\text{C})$  as tetrahydrofuran adducts by deposition with hexane from THF. Attempts to remove the THF molecules from these complexes led to their decomposition. They are quite soluble in polar solvents, but only slightly in aliphatic hydrocarbons. Compounds (2)—(4) are instantly oxidized and hydrolysed; the hydrolysis products are benzene-tricarbonylchromium (5) and the respective lanthanide hydroxides (6)—(8), equation (2).

(2)--(4) 
$$\xrightarrow{H_2O} 2C_6H_6Cr(CO)_3 + [Ln(OH)_2]$$
 (2)  
(5) (6)--(8)

Complexes (2)—(4) have no precise melting points. Their i.r. spectra (Perkin-Elmer 850, CaF<sub>2</sub> cell, inert gas atmosphere) show v(CO) absorptions at 1800—2000 cm<sup>-1</sup> and at 1600—1800 cm<sup>-1</sup>. We ascribe the lower carbonyl stretching frequences to CO→Ln co-ordination (of intra- or intermolecular type). The lanthanide elements in (2)—(4) were detected by an X-ray fluorescence technique with 'VRA-2'. The Cr/Ln ratio for all complexes was ca. 2. A good <sup>1</sup>H n.m.r. spectrum (Bruker WP-200-SY, 200.13 MHz, [<sup>2</sup>H<sub>8</sub>]THF, SiMe<sub>4</sub> internal standard) was registered only for complex (4). Compounds (2) and (3) are paramagnetic, (4) is diamagnetic. The ytterbium complex (4) was obtained in an inert gas atmosphere, starting from (1) (0.25 g) and Yb metal filings (0.43 g) in THF (25 ml). Initially the reaction mixture was stirred at room temperature for 40—60 min, and then at -20 °C for 4 h. The light-cherry coloured solution was separated from the precipitated Hg and excess of Yb by decantation, then cooled n-hexane (50 ml) was added to the filtrate. The precipitated complex (4) was separated by filtration from the solution (75% yield) [0.32 g, m.p. 95 °C (decomp.); found: C 40.0, H 3.3, Cr 15.8, calc. for  $C_{26}H_{26}Cr_2YbO_8$ : C 42.0, H 3.5, Cr 14.0; i.r. (in light petroleum) v(CO) 1965, 1890, 1695, 1650, v(THF) 890, 1075 cm<sup>-1</sup>; <sup>1</sup>H n.m.r.  $\delta(C_6H_5)$  5.645,  $J(^{171}Yb^{-1}H)$  80 Hz,  $\delta(THF)$  1.71 and 3.62].

Similarly, using Eu (0.35g) in THF (25 ml) compound (3) was obtained in 73% yield [m.p. 55 °C (decomp.); found: C 39.45, H 3.3, Cr 18.0, calc. for  $C_{22}H_{18}Cr_2EuO_7$ : C 40.6, H 2.8, Cr 16.0; i.r. (in THF) v(CO) 1958, 1880, 1780, 1725 cm<sup>-1</sup>]. Compound (2) was produced in 68% yield [m.p. 62 °C (decomp.); found: C 44.1, H 3.7, Cr 16.9, calc. for

C<sub>26</sub>H<sub>26</sub>Cr<sub>2</sub>SmO<sub>8</sub>: C 43.3, H 3.6, Cr 14.4; i.r. (in THF) v(CO) 1960, 1882, 1750, 1715 cm<sup>-1</sup>].

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