Metal Carbonyl Derivatives of Divalent Lanthanoids. Bis(tetracarbonylcobalt)-samarium, -europium, and -ytterbium

Gul'Mamed Z. Suleimanov,* Vladimir N. Khandozhko, Leila T. Abdullaeva, Rozalia R. Shifrina, Khalil S. Khalilov, Nadegda E. Kolobova, and Irina P. Beletskaya

Karpov Institute of Physical Chemistry, 10 Ulitza Obukha, 107120 Moscow, U.S.S.R.

The first metal carbonyl derivatives, $Ln[Co(CO)_4]_2{\cdot}(THF)_n$ (THF = tetrahydrofuran; $n = 3, 4$), of divalent lanthanoids Ln (Ln = Sm, Eu, Yb) were prepared by treating $Hg[Co(CO)_4]_2$ with an excess of Sm, Eu, or Yb in THF at room temperature; the title complexes were also formed in high yields from the reaction of stoicheiometric amounts of the appropriate LnI_2 compounds and $TlCo(CO)_4$.

The first reported metal carbonyl derivative of the lanthanoids with a metal carbonyl bond was a trivalent erbium compound formed by treating $Hg[Co(CO)_4]_2$ with Er/Hg.[1] Using this result, we found that similar complexes were formed for most of the lanthanoids by the interaction of binuclear metal carbonyls (of Co, Mn, and Re) with the amalgamized lanthanoid.[2] However, until now, compounds of divalent lanthanoids with metal carbonyl substituents were unknown, even though some of these lanthanoids may form quite stable organic[3] and divalent derivatives.[4]

We have investigated the reaction of the mercury derivative of cobalt carbonyl[5] with the lanthanoids Ln^0 (Ln = Sm, Eu, Yb) in tetrahydrofuran (THF) and herein report our results. The cobalt carbonyl derivatives (**1**)—(**3**) of the corresponding divalent lanthanoids separated from solution at 20 °C in the form of tetrahydrofuran solvates and in high yields [Equation (1); $m = 4(5)$].

$$Hg[Co(CO)_4]_2 + mLn^0 \xrightarrow{\text{THF, 20 °C}} Ln[Co(CO)_4]_2{\cdot}(THF)_n + Ln/Hg \quad (1)$$

(**1**) Ln = Sm, $n = 4$
(**2**) Ln = Eu, $n = 4$
(**3**) Ln = Yb, $n = 3$

On drying, (**1**)—(**3**) gradually lost THF molecules to form the monosolvates. Attempts to remove THF entirely resulted in decomposition. Compounds (**1**)—(**3**) were also formed as the THF solvates in the stoicheiometric reaction of the corresponding divalent iodides LnI_2 (Ln = Sm, Eu, or Yb) with thallium(tetracarbonylcobalt)[6] in THF at temperatures ranging from −70 to 20 °C [Equation (2)].

The yields of complexes (**1**)—(**3**) obtained by both methods are nearly quantitative. The complexes are coloured crystalline substances, highly sensitive to air and moisture, which dissolve readily in THF and acetone but poorly in aliphatic solvents. The compounds were characterized by elemental

$$2\,TlCo(CO)_4 + LnI_2 \xrightarrow{\text{THF, −70 to 20 °C}} (\mathbf{1})\text{—}(\mathbf{3}) + 2\,TlI \quad (2)$$

analysis and by i.r. spectroscopy.† The presence of the lanthanoid and cobalt as well as the ratio between them in the complexes (**1**)—(**3**) (Co : Ln = 2 : 1) were confirmed by *X*-ray fluorescence analysis.‡

Received, 19th September 1983; Com. 1238

---

† (**1**), 78% yield; m.p. 65 °C (decomp.), i.r., ν_{CO} 2010, 1925, 1760 cm^{-1}; (**2**), 84% yield; m.p. 80 °C (decomp.); i.r., ν_{CO} 2025, 2000, 1960, 1910, 1800 cm^{-1}; (**3**), 81% yield; m.p. 105 °C (decomp.); i.r., ν_{CO} 2020, 1915, 1805 cm^{-1}. The i.r. spectra for (**1**)—(**3**) were measured on a Perkin–Elmer 580 spectrometer in a CaF_2 cell. The i.r. bands given here are the most intense in the range 1500—2200 cm^{-1}. More detailed i.r. spectral data for these complexes will be discussed in a future paper.

‡ The *X*-ray fluorescence analyses were made on a VRA-2 spectrometer on the complexes in the form of a tablet.

References

1 R. S. Marianelli and M. T. Durney, *J. Organomet. Chem.*, 1971, **32**, C41.

2 G. Z. Suleimanov, L. F. Rybakova, L. T. Abdullaeva, A. A. Pasynskii, and I. P. Beletskaya, *Dokl. Akad. Nauk SSSR*, 1983, 272.

3 H. Schumann, 'Organometallic Chemistry of the f Elements,' eds. T. J. Marks and R. D. Fischer, Proc. N.A.T.O., Adv. Study Inst. Sogesta Urbino, 1978; Reidel, Dordrecht, 1979, pp. 81–112.

4 G. Z. Suleimanov, L. F. Rybakova, Ya. A. N. Nuriev, T. Kh. Kurbanov, and I. P. Beletskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 190.

5 W. Hiber, E. O. Ficher, and E. Böckly, *Z. Anorg. Allg. Chem.*, 1952, **269**, 308.

6 J. M. Burlotch and T. W. Theyson, *J. Chem. Soc., Dalton Trans.*, 1974, 828.