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Preliminary communication

Tris(tetracarbonylcobalt)tetrakis(tetrahydrofuran)erbium

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There has been some interest in the organometallic chemistry of the lanthanides as evidenced by the preparation and characterization of compounds such as $Ln(C_5H_5)_3$ [1] (Ln = lanthanide metal), $(C_5H_5)_3UF \cdot Yb(C_5H_5)_3$ [2] and more recently $[Ln(C_8H_8)Cl \cdot 2THF]_2$ [3,4]. To date, metal—metal bonded compounds involving the lanthanides have not been reported. Bennett *et al.*,[5] recently reported the first uranium-transition metal bonded compound and we would like to communicate our preliminary results on $Er[Co(CO)_4]_3 \cdot 4THF$, which we believe represents the first example of a lanthanide-transition metal, metal—metal bonded compound.

All reactions were carried out under a nitrogen atmosphere with solvents that had been previously dried and deoxygenated. A 1% w/w, erbium (1.0 g, 6.58 mmoles—mercury (110 g) mixture was stirred vigorously with bis(tetracarbonylcobalt)mercury, $Hg[Co(CO)_4]_2$ [6] (4.0g, 7.38 mmoles), prepared as reported by King[7], in tetrahydrofuran (THF) (125 ml) under nitrogen for approximately two hours at room temperature. After reaction the flask was transferred to an inert atmosphere box where the deep red THF solution was filtered and reduced to a volume of 25 ml. Upon addition of n-pentane a red oil separated. The oil was washed three times with approximately 20 ml portions of n-pentane. It was then evacuated to give a dark red, air and water sensitive solid which was washed with n-pentane and stored in the box. The product, $Er[Co(CO)_4]_3 \cdot 4THF$ was obtained in high yield (3.5 g, 75%), decompn. 138—140° (Found: mmoles Co/mmoles Er, 2.97; C, 31.43; H, 3.54; Er, 17.37; Co, 18.20. $C_{28}H_8Co_3ErO_{16}$ calcd.: mmoles Co/mmoles Er, 3.00; C, 34.74; H, 3.33; Er, 17.28; Co, 18.26%.) Several preparations of the compound showed, at most, trace amounts of mercury when treated with thioacetamide in aqueous acid solution.

The IR spectrum of the compound in THF solution [0.1mm NaCl matched cells and 0.1mm IRTRAN-2 (ZnS) *vs.* 0.1 mm NaCl] and as a nujol and fluorolube mull showed several absorptions in the $\nu(CO)$ region. The solution spectra were run in an IRTRAN-2 cell in order to ascertain if the compound was interacting with the NaCl cell. The spectra in the two cells were virtually identical. The THF and nujol results are given in Table 1. Some difficulty was encountered in obtaining the IR spectra since the compound is so air and water sensitive. Decomposition peaks have been omitted where they could be definitely identified by observing the IR spectrum as a function of time. It was noted that the decomposition spectrum agreed well with the spectrum reported for $Co_2(CO)_8$ [8].

TABLE 1

CARBONYL ABSORPTION FREQUENCIES FOR $Er[Co(CO)_4]_3 \cdot 4THF$[a]

THF solution (cm^{-1})	Nujol mull (cm^{-1})
2065 m	2068 w
2053 m	2030 vs
2032 s	1999 s, sp
1998 m (sh)	$\left.\begin{matrix}1965\\1930\end{matrix}\right\}$ vs, (br) d
1966 s (br)	
$\left.\begin{matrix}1898\\1888\end{matrix}\right\}$ vs, (br) d	

[a] IR spectra were obtained using a Perkin-Elmer model 621 grating spectrophotometer. vs, very strong; s, strong; m, medium; w, weak; br, broad; sp, sharp; d, doublet; sh, shoulder.

The observed absorptions attributable to the compound are consistent with similar examples of $Co(CO)_4$ bound to a metal via a metal–metal bond[9]. In particular the ν(CO) absorptions between 2100–2000 cm^{-1} would seem to indicate a fairly strong metal–metal interaction. It should also be noted that the $Co(CO)_4^-$ anion only shows a single IR absorption in this region, at 1883 cm^{-1} [10]. The appearance of seven bands in the ν(CO) region would indicate a compound of low symmetry. The absorptions at 1888 and 1898 cm^{-1} may be due to the appearance of $CoCO_4^-$ from either decomposition or partial ionization of the compound in THF. Although these absorptions appear in the initial spectrum with appreciable intensity they do increase in intensity with time.

Although the analyses agreed well for the compound as formulated and the fluorolube IR indicated the presence of THF, additional evidence to support the formulation of the compound was sought. A sample of the compound was evacuated and then heated to approximately 100°. The mass spectrum of the volatile components was recorded with a Varian Ion Cyclotron Resonance Spectrometer Model ICR-9. After re-evacuating, the residue was reheated to approximately 150° and the mass spectrum of the volatile components again recorded. In both cases the mass spectrum indicated the presence of only THF and CO; the former by its fragmentation pattern[11] and the latter by its appearance potential (Obs. 13.99 eV, Lit.[12] 14.02 eV). The relative amount of THF was greater after the second heating indicating that some of the THF is fairly tightly bound. Since the thermal decomposition of the compound is not known to be quantitative the mass spectral data could not be used to establish the CO/THF ratio accurately although a determination of this ratio was in reasonable agreement with the expected value of 3/1.

Therefore, based on our preliminary results we tentatively formulate the compound as $Er[Co(CO)_4]_3 \cdot 4THF$ with an Er – Co metal–metal bond.

We are continuing with the characterization of the above compound and are investigating additional reactions that should lead to other compounds containing Er–transition metal bonds.

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