Preparation and Molecular Structure of a σ-Bonded Lanthanide Phenyl

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Summary Tetrakis(tetrahydrofuran)lithium tetrakis(2,6-dimethylphenyl)lutetiate has been prepared; a single-crystal *X*-ray study has shown that the anion consists of four 2,6-dimethylphenyl groups in an approximately tetrahedral σ-bonded array about lutetium.

THE lanthanides and actinides form a number of *polyhapto*-aryl derivatives such as $Sm(C_5H_5)_3$ and $U(C_8H_8)_2$ whose structures have been established by *X*-ray diffraction.[1,2] There is however apparently no similarly proven example of a σ-bonded *f*-transition-metal alkyl or aryl. Thus, although $LiMPh_4$ (M = La, Pr) have been isolated in the solid state,[3] their microcrystalline and apparently polymeric character prevented detailed investigation of the nature of their metal–carbon bonds. Some lanthanide methyls have also been obtained,[3] but in an impure state. In solution, there is clear evidence for the existence of divalent lanthanide phenyls[4] and reactive solids may be obtained on evaporation. Apart from these instances, no other lanthanide or actinide phenyls or alkyls have apparently been isolated.

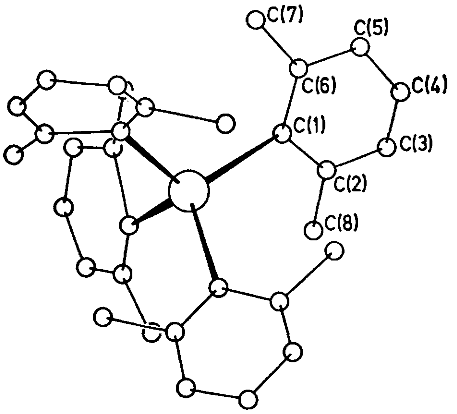

FIGURE. *The structure of the anion in* $[Li(C_4H_8O)_4][Lu(C_8H_9)_4]$.

The action of 2,6-dimethylphenyl-lithium on anhydrous lutetium chloride in tetrahydrofuran at −78° followed by repeated concentration, filtration, and re-dissolution in THF ultimately gave, on addition of benzene, colourless needles. *X*-ray analysis showed these to be $[Li(C_4H_8O)_4][Lu(C_8H_9)_4]$.

Crystal data: $[Li(C_4H_8O)_4][Lu(C_8H_9)_4]$, *M*, 890·98, orthorhombic, $a = 15{\cdot}093$, $b = 15{\cdot}265$, $c = 19{\cdot}959$ Å, $U = 4598$ Å^3 D_m not measured, $Z = 4$, $D_c = 1{\cdot}287$, $\mu(\text{Cu-}K_\alpha) = 43{\cdot}6$ cm^{-1}, space group $P2_12_12_1$. Intensity data were recorded on a G.E. XRD6 manual diffractometer using the stationary crystal-stationary counter technique and Cu-K_α radiation. Of a total of 2144 data recorded to a 2θ limit of 90°, 1859 were considered to have significant intensities. The structure was solved by Patterson and Fourier techniques and refined by least squares to a present *R* of 0·075. The structure of the anion is shown in the Figure.

The anion $[Lu(C_8H_9)_4]^-$ appears to be (a) the first crystallographically characterised example of a σ-bonded *f*-transition-metal organometallic and (b) the first example of a four-co-ordinated *f*-transition metal. The Lu–C bonding interatomic distances are 2·425 (15), 2·439 (16), 2·442(15), and 2·501(17) Å. The angle Lu–C(1)–C(4) and the three other analogous angles deviate somewhat from 180°, taking values from 175·6° to 167·7°. This deviation is understandable in terms of van der Waals repulsions between the eight methyl groups, as are deviations of a similar order of magnitude from strict tetrahedral co-ordination geometry (the six C–Lu–C inter-bond angles are 99·4, 101·2, 111·0, 112·4, 115·5, and 118·2°). Doubtless the highly hindered nature of the 2,6-dimethylphenyl ligand is responsible for the very low co-ordination number; the only other example of a co-ordination number lower than six in *f*-transition metal compounds is the 3-co-ordinate series $[M\{N(SiMe_3)_2\}_3]$ (M = a lanthanide) where the ligand is also very bulky.[5] The Lu–C bonding distances are to be compared with Sm–C = 2·76 Å in $Sm(C_5H_5)_3$;[1] thus, utilising the 0·11 Å difference in ionic radius between Lu^{3+} and Sm^{3+} as an approximate correction, the σ-bond is about 0·2 Å shorter than the *pentahapto* metal-carbon distance.

The analogous ytterbium compound has been similarly prepared and is isostructural; it smoulders instantly on exposure to air while the lutetium compound appears less readily affected. Our attempts to prepare analogous compounds of lighter lanthanides have so far failed.

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