Dimeric μ-Dimethyl Lanthanide Complexes, a New Class of Electron-deficient Compound, and the Crystal and Molecular Structure of $[Yb(\eta\text{-}C_5H_5)_2Me]_2$

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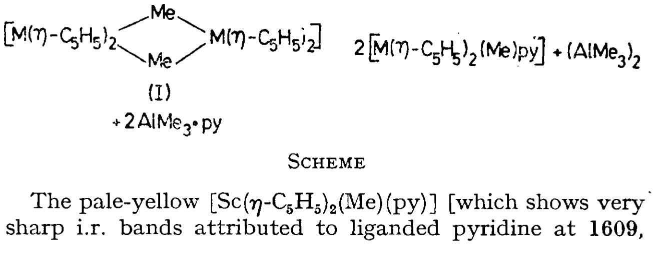
Summary The crystalline $[M(\eta\text{-}C_5H_5)_2Me]_2$ (M = Y, Dy, Ho, Er, or Yb) were obtained by equimolar reaction of $[M(\eta\text{-}C_5H_5)_2Me_2AlMe_2]$ and pyridine in toluene; the symmetrical MMe_2M double-methyl-bridge is established for the Y compound in solution from ^1H n.m.r. spectra, and for the solid Yb analogue from a single crystal *X*-ray analysis.

The occurrence of electron-deficient three-centre bonds between two transition metals and an alkyl-bridge is as yet extremely rare. In $[Cu(CH_2SiMe_3)]_4$ there are μ-monoalkyl bridges in the crystal (*X*-ray) and in solution,[1] whereas in $[Ni(\eta\text{-}R)Me]_2$ ($R = C_3H_5$, C_4H_7, or C_5H_9) ^1H n.m.r. data suggest a double methyl-bridge in solution[2] and in $[Zr(\eta\text{-}C_5H_5)_2Me]_2$ a similar structure has been inferred from the molecular weight in benzene.[3] We now show that this structure is also found for Y and some lanthanide methyls $[M(\eta\text{-}C_5H_5)_2Me]_2$ (M = Y, Dy, Ho, Er, and Yb), (I), both in solution (Y, ^1H n.m.r.) and in the crystal (Yb, *X*-ray).

Compounds (I) were prepared in high yield (*ca.* 70%) from the recently discovered $[M(\eta\text{-}C_5H_5)_2Me_2AlMe_2]$ (M = Y[4] or Ln[5]), (II), by reaction with pyridine in toluene [Scheme (a)], as air-sensitive crystalline materials soluble in CH_2Cl_2 or PhMe but insoluble in saturated hydrocarbons (see Table). The Yb and Er compounds have previously been reported.[6] They were prepared, as was the Gd analogue, from $[M(\eta\text{-}C_5H_5)_2Cl]_2$ and LiMe, but were not formulated as dimers.



Scheme

The pale-yellow $[Sc(\eta\text{-}C_5H_5)_2(Me)(py)]$ [which shows very sharp i.r. bands attributed to liganded pyridine at 1609, 1492, 1076, 1048, 767, and 710 cm^{-1}; Me deformations at 1365 (m) and 1224 (w) cm^{-1}; and η-C_5H_5 bands at 3100, 1020, and 800 cm^{-1}] readily lost pyridine *in vacuo*, but the metal product has not yet been identified. The different behaviour of the Sc complex (II) with pyridine [Scheme (b)] may be related to its non-fluxionality (in contrast to the Y analogue) at room temperature.[5]

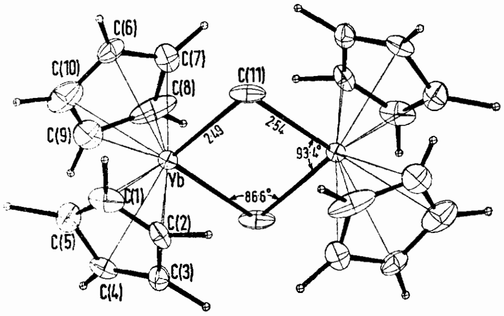


FIGURE. Structure of $[Yb(\eta\text{-}C_5H_5)_2Me]_2$.

The ^1H n.m.r. spectra of $[Y(\eta\text{-}C_5H_5)_2Me]_2$ are invariant between -40 and $+40$ °C and show a triplet at τ 10·81 [bridging Me, $J(^{89}Y\text{–}C^1H_3)$ 3·6 Hz] and a singlet at τ 3·79 (η-C_5H_5).

Crystals of $[Yb(\eta\text{-}C_5H_5)_2Me]_2$, suitable for *X*-ray analysis, were grown by slowly cooling a saturated toluene solution to -30 °C. The compound was found to be monoclinic, with $a = 10{\cdot}656(5)$, $b = 7{\cdot}535(4)$, $c = 13{\cdot}216(5)$ Å, $\beta = 112{\cdot}62(4)°$, $U = 979{\cdot}2$ Å^3, D_m not measured, $Z = 2$, $D_c = 2{\cdot}16$ g cm^{-3}, μ (Mo-K_α) = 99·7 cm^{-1}; space group $= P2_1/n$. Intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer using the ω–2θ scan technique. All reflections in one independent quadrant out to $2\theta = 50°$ were measured: 1435 reflections were considered having $I_{obs} \geqslant 2\sigma(I_{obs})$. The structure was solved by Patterson and difference Fourier techniques, and refined to $R = 0{\cdot}063$.

TABLE

M in $[M(\eta C_5H_5)_2Me]_2$[a]	Appearance and decomp. temp.
Y	Colourless, m.p. > 158 °C (decomp).
Dy	Pale-yellow, m.p. > 165 °C (decomp.)
Ho	Straw, m.p. > 160 °C (decomp.)
Er[b]	Pink, m.p. > 159 °C (decomp.)
Yb	Orange-red, m.p. > 165 °C (decomp.)

[a] All compounds are analytically pure; i.r. spectra show Me vibrations at 1368 (m) and *ca.* 1195 (s) cm^{-1}, and η-C_5H_5 vibrations at 3100, 1447, 1020, and 790 cm^{-1}, mass spectra show (parent − Me)$^+$ as the ion at highest *m/e*. [b] μ_{eff} = 9·50 B.M. (by ^1H n.m.r. spectroscopy).

The dimer, shown in the Figure, resides on a crystallographic centre of inversion, and is held together by electron-deficient methyl bridges. The cyclopentadienyl rings are symmetrically bound to the Yb atom at an average Yb–C(π) distance of 2·613(13) Å, a value in good agreement with the 2·585(8) Å average found in $[Yb(\eta\text{-}C_5H_5)_2Cl]_2$[7] and 2·66 Å in $[Yb(\eta\text{-}C_5H_5)_2Me_2AlMe_2]$.[5] The two independent Yb–C (methyl) lengths of 2·49 and 2·54 Å (average, 2·51 Å) are significantly shorter and may be compared with the 2·57 Å in $[Yb(\eta\text{-}C_5H_5)_2Me_2AlMe_2]$.[5] Unfortunately, there is no direct experimental value available for the Yb–C two-centre σ-bond, but a reasonable inference can be drawn from the structure of $[Li(C_4H_8O)_4][Lu(C_8H_9)_4]$.[8] The Lu–C ($\sigma$) average is 2·45 Å, and the Lu^{3+} radius is 0·85 Å,[9] while the Yb^{3+} radius is 0·86 Å; the calculated value for the Yb–C σ-bond distance is thus *ca.* 2·46 Å. This trend in bond lengths is quite similar to that found for organometallic complexes of magnesium. The π-distance in $[Mg(\eta\text{-}C_5H_5)_2]$ is known from electron diffraction data to be 2·34 Å,[10] the σ-bond length can be taken as 2·16 Å,[11] and for the electron-deficient methyl bridged $[MgMe_2]_\infty$, the separation is 2·24 Å.[12]

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