

Neutral and Anionic Silylmethyl Complexes of the Group 3a and Lanthanoid Metals; the X-Ray Crystal and Molecular Structure of $[\text{Li}(\text{thf})_4][\text{Yb}\{\text{CH}(\text{SiMe}_3)_2\}_3\text{Cl}]$ (thf = Tetrahydrofuran)†

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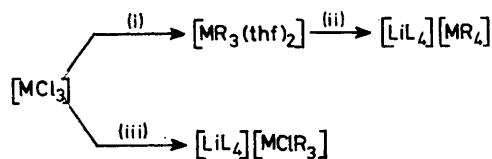
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Summary The neutral $[\text{M}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$ ($\text{M} = \text{Tb}, \text{Er},$ or Yb ; thf = tetrahydrofuran) and the ionic $[\text{Li}(\text{L})_4][\text{MR}_4]$ [$\text{R} = \text{Me}_3\text{SiCH}_2$; when $\text{M} = \text{Y}, \text{Er},$ or Yb , $\text{L}_2 = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ (tmed); when $\text{M} = \text{Y}$, $\text{L} = \text{thf}$], $[\text{Li}(\text{thf})_4][\text{M}(\text{Cl})\text{R}_3]$ [$\text{M} = \text{Er}$ or Yb , $\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$], and $[\text{LiL}_2][\text{M}(\eta\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Cl}_2]$ [$\text{L} = 0.5$ tmed or thf] are reported; their structures are deduced from i.r. and ^{13}C and ^1H n.m.r. ($\text{M} = \text{Y}$) spectra, conductivity, and in the case of $[\text{Li}(\text{thf})_4][\text{Yb}\{\text{CH}(\text{SiMe}_3)_2\}_3\text{Cl}]$, by a single crystal X-ray analysis [$d(\text{Yb}-\text{C})$ (av.) = 2.38 Å].

ALTHOUGH the organometallic chemistry of the Group 3a and lanthanoid metals is attracting increasing attention,¹ very few simple metal(III) alkyls are known. We have previously reported the neutral five-co-ordinate $[\text{MR}_3(\text{thf})_2]$ [$\text{M} = \text{Sc}$ or Y , $\text{R} = \text{Me}_3\text{SiCH}_2$,^{2a} Me_3CCH_2 ,^{2a} or $(\text{Me}_3\text{Si})_2\text{CH}$,^{2b} thf = tetrahydrofuran], and now extend this series to some of the lanthanoid metals. In addition, we describe the synthesis (see Scheme) and properties (see Table; the compounds are analytically pure and crystalline) of the first members of three important new classes of compound: $[\text{MR}_4]^-$ ($\text{R} = \text{Me}_3\text{SiCH}_2$), $[\text{M}(\text{Cl})\text{R}_3]^-$ [$\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$], and $[\text{MCP}_2\text{Cl}_2]^-$ ($\text{Cp} = \eta\text{-C}_5\text{H}_4\text{SiMe}_3$). Halogenohydrocarbyl-transition-metallates are rare, e.g., the unstable³ $[\text{Ti}(\text{Cl})\text{Me}_4]^-$ and the ill-characterised⁴ $[\text{Nb}(\eta\text{-C}_5\text{H}_5)_2(\text{Cl})\text{R}]^-$, but some main group metal analogues are well-established, particularly for aluminium.⁵ The low co-ordination numbers of four or five are unusual for elements the chemistry of which is dominated by the attainment of high co-ordination numbers.^{6,7} The crystal structure analysis of the title compound provides the first value of a Group 3a- or

lanthanoid-metal-C(*sp*³) bond length (cf. ref. 8 for a bridging alkyl in $[\{\text{Yb}(\eta\text{-C}_5\text{H}_5)_2\text{Me}\}_2]$).

The complexes $[\text{M}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$ ($\text{M} = \text{Tb}, \text{Er},$ or Yb) (Table) were obtained [Scheme, reaction (i)] from n-hexane, in which they are freely soluble. Although very air-sensitive in solution, they show remarkable stability in air as well-formed, undamaged crystals. The i.r. spectra are similar to those of the analogous Sc and Y complexes,² showing strong sharp bands at 1020–1023 cm^{-1} (co-ordinated thf). Values for μ_{eff} , obtained by the n.m.r. method of Evans in CH_2Cl_2 , are close to the theoretical value for the free ions.



SCHEME. (i), 3LiCH₂SiMe₃, thf; (ii), LiCH₂SiMe₃, 2thf or 2tmed; (iii), 3LiCH(SiMe₃)₂, thf.

The metallates $[\text{M}(\text{CH}_2\text{SiMe}_3)_4]^-$ ($\text{M} = \text{Y}, \text{Er},$ or Yb) [see Scheme, reaction (ii)] were conveniently isolated as lithium salts, using either tetramethylethylenediamine (tmed) or thf for solvating the cation. (Interestingly, for ytterbium there is a colour change from deep-red to yellow between the neutral and anionic complexes). They are insoluble in non-polar solvents (oils were produced with toluene) but are readily soluble in tetrahydrofuran or ether. Vigorous reaction occurred with halogenated solvents (the neutral

† No reprints are available.

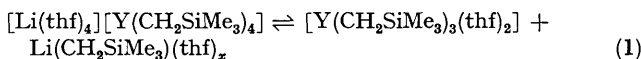
TABLE

New organo-yttrium or -lanthanoid metal complexes

Type	M	Appearance	M.p. (°C)
[M(CH ₂ SiMe ₃) ₃ (thf) ₂]	Tb ^a	Colourless	50—54
	Er ^b	Pink	49—51
	Yb ^c	Red	53—54
[LiL ₄][M(CH ₂ SiMe ₃) ₄]	Y (L = thf)	Colourless	85—89
	Y (L ₂ = tmed)	Colourless	123—124
	Er (L ₂ = tmed)	Pink	122—124
	Yb (L ₂ = tmed)	Yellow	136—138
[Li(thf) ₄][M{CH(SiMe ₃) ₂ Cl}]	Er	Pink	122—123 (decomp.)
	Yb	Red	123—124 (decomp.)
[LiL ₂][M(η-C ₅ H ₄ SiMe ₃) ₂ Cl ₂]	Y (L = thf)	Colourless	—
	Y (L ₂ = tmed)	Colourless	—

^a $\mu_{\text{eff}} = 9.12$ BM. ^b $\mu_{\text{eff}} = 9.82$ BM. ^c $\mu_{\text{eff}} = 4.64$ BM.

complexes are stable in CH₂Cl₂). In the i.r. spectra, the band assigned to co-ordinated thf occurs at higher frequency (1040—1045 cm⁻¹), as also in the complexes below. The molar conductivity of [Li(tmed)₂][Yb(CH₂SiMe₃)₄] in tetrahydrofuran (6.14 × 10⁻³ mmol cm⁻³) at 2.5 °C is 21.2 Ω⁻¹ cm² mol⁻¹. This is similar to the values obtained for some titanium(IV) species, e.g. [TiMe₅]⁻,^{3b} and establishes the ionic formulation. The ¹³C and ¹H n.m.r. spectra of [Li(thf)₄][Y(CH₂SiMe₃)₄] in OEt₂ at room temperature are consistent with this formulation, although yttrium-carbon or yttrium-hydrogen coupling was not observed; ¹³C chemical shifts (rel. to SiMe₄) are at 68.0 (thf), 34.6 (YCH₂Si), 25.2 (thf), and 3.74 (SiMe₃) p.p.m.; ¹H chemical shifts are at τ ca. 6.24 (thf), ca. 7.85 (thf), 10.09 (SiMe₃), and 10.82 (YCH₂Si). On cooling to -80 °C, the methylene resonance in the ¹³C n.m.r. spectrum appears as a weak doublet, ¹J(⁸⁹Y-¹³C) = 28 Hz, which suggests that a rapid dissociation-recombination reaction is occurring at room temperature; the equilibrium (1) lies well to the left in the system.



The reaction of anhydrous chlorides [MCl₃] with LiCH(SiMe₃)₂ in ether-tetrahydrofuran took a different course [Scheme, reaction (iii)]. The chlorotrialkylmetallate complexes [Li(thf)₄][M{CH(SiMe₃)₂Cl}] (M = Er or Yb) are moderately soluble in n-hexane and very soluble in many polar solvents. (Similar complexes may well be implicated as intermediates in halide-alkyl exchange reactions.) Upon heating a solution of [Li(thf)₄][Er{CH(SiMe₃)₂Cl}] in n-hexane, a white solid, possibly Li[ErCl₄], was deposited, leaving a pink solid which contained the homoleptic [Er{CH(SiMe₃)₂Cl}]⁻ as its lithium salt. This could not be prepared independently *via* chloride-alkyl exchange from [Li(thf)₄][Er(Cl)R₃] and LiR.

A single crystal of [Li(thf)₄][Yb{CH(SiMe₃)₂Cl}] was obtained by crystallisation from tetrahydrofuran-n-hexane at -30 °C.

Crystal data M 982.0, orthorhombic, *a* = 12.751(5), *b* = 19.280(7), *c* = 23.210(8) Å, *U* = 5705.9 Å³, *Z* = 4, *D*_c = 1.12 g cm⁻³, $\mu(\text{Mo-K}\alpha) = 84.4$ cm⁻¹, space group *P*2₁2₁2₁. Intensity data were recorded on a Enraf-Nonius CAD-4 diffractometer using the ω -2 θ scan technique. All reflections in one independent octant out to 2 θ = 50° were measured; 3356 reflections were considered observed [*I* > 3 σ (*I*)]. The structure was solved by Patterson and

difference Fourier techniques, and refined to a conventional *R* value of 0.060. The molecular arrangement around the yttrium atom is shown in the Figure. The three Yb-C σ bond lengths, 2.372(16), 2.373(24), and 2.391(20) Å, are shorter than might be expected on the basis of the Lu-C σ bond length average of 2.45 Å in [Li(thf)₄][Lu(C₆H₃Me₂)₄].⁷ The Yb-Cl terminal distance, 2.486(6) Å, is much shorter than the Yb-Cl bridge length, 2.64(1) Å in [Yb(η-C₅H₅)₂Cl]₂,⁹ but agrees well with the 2.56(2) Å U-Cl terminal length in [U(η-C₅H₅)₂Cl],¹⁰ after a correction of 0.07 Å for the difference in ionic radii of Yb³⁺ and U⁴⁺ ‡

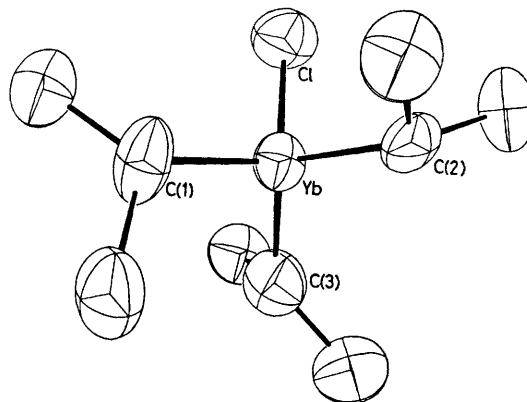
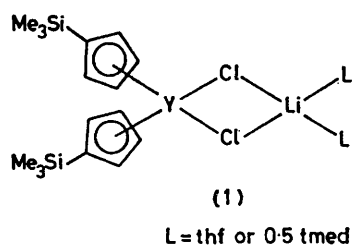


FIGURE. The structure of the anion [Yb{CH(SiMe₃)₂Cl}]⁻; bond lengths (Å) and angles (°): Yb-C(1), 2.373(24); Yb-C(2), 2.372(16); Yb-C(3), 2.391(20); Yb-Cl, 2.486(6); ∠C(1)YbC(2), 115.9(7); ∠C(2)YbC(3), 107.6(8); ∠C(1)YbC(3), 107.1(6); ∠C(2)YbCl, 110.3(5); ∠C(1)YbCl, 104.0(5); and ∠C(1)YbCl, 112.0(6).

It is likely that a similar extensive chemistry (formation of 'ate' complexes) occurs for various cyclopentadienylmetal complexes. From reaction of LiC₅H₄SiMe₃ (2 mol) with [YCl₃] (1 mol) in tetrahydrofuran, [Li(thf)₂][Y(η-C₅H₄SiMe₃)₂Cl₂] was obtained as colourless crystals from n-hexane, in which it is moderately soluble. Further reaction with tmed gave the microcrystalline [Li(tmed)][Y(η-C₅H₄SiMe₃)₂Cl₂]; ¹H n.m.r. (C₆D₆) τ 3.7 and 3.3 (Cp); 7.9 (NMe₂), 8.2 (NCH₂CH₂N) and 9.4 (SiMe₃). Such a complex is unusual, in that in the ionic formulation the lithium ion is incompletely solvated. It is likely, therefore, that the novel

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



chloride-bridged formulation (1) better describes its structure. On heating the thf-solvate complex to *ca.* 250 °C *in vacuo*, the crystalline $[\{Y(\eta-C_5H_4SiMe_3)_2Cl\}_2]$ was obtained as sublimate. We have also obtained the as yet unpurified 'ate' complex $[Y(\eta-C_5Me_4Et)_2Cl_2]^-$, as its lithium salt.

These observations enable us to provide an explanation for the unexpected formation of $[\{Sc(\eta-C_5H_5)_2Cl\}_2]$ and $[Sc(\eta-C_5H_5)_2Cl(thf)]$ *via* reaction of $[ScCl_3]$ with NaC_5H_5 ¹¹ or $Mg(C_5H_5)_2$ ¹² and TiC_5H_5 ,¹³ respectively. Thus, we suggest that intermediate complexes $[M(thf)_x][Sc(\eta-C_5H_5)_2Cl_2]$ of differing stability are produced which are transformed *via* two alternative paths; for the case of $M = Na$ or 0.5 Mg loss of thf occurs on heating *in vacuo* either before or concurrent with elimination of $NaCl$ or $MgCl_2$, whereas for $M = Ti$, loss of $TiCl$ takes place in tetrahydrofuran solution, giving the stable tetrahydrofuran adduct.

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