Organometallic Complexes of the Group 3A and Lanthanoid Metals containing $M(\mu\text{-}Cl)_2Li$ Bridging Units; the *X*-Ray Structure of $[Nd\{\eta\text{-}[C_5H_3(SiMe_3)_2]\}_2(\mu\text{-}Cl)_2Li(thf)_2]$ (thf = tetrahydrofuran)†

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Summary The following organometal(III) complexes have been prepared and characterised: (a) $[M\{\eta\text{-}[C_5H_3(SiMe_3)_2]\}_2(\mu\text{-}Cl)_2Li(L)_2]$ [M = Sc, Y, La, Ce, Pr, Nd, or Yb, and L = tetrahydrofuran (thf); or M = Y or La, and $L_2 = Me_2NCH_2CH_2NMe_2$ (tmeda); or M = Y or Nd, and $L_2 = MeOCH_2CH_2OMe$ (dme)], (b) $[MCl_{2-n}(OAr^{Me})_n$-

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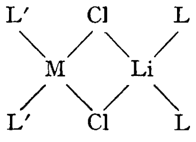
† No reprints available.

$(\mu\text{-Cl})_2Li(thf)_2]$ (OAr^{Me} = $OC_6H_2Bu^t_2$-2,6-Me-4, M = Y, La, Er, or Yb, and n = 1; or M = Y and n = 2), and (c) $[ErCl\{N(SiMe_3)_2\}(\mu\text{-Cl})_2Li(thf)_2]$; the *X*-ray structure of the title compound shows that both the Nd and Li atoms are in a distorted tetrahedral environment, and important molecular parameters include $Nd\text{–}Cl_{av.}$ 2·744, $Li\text{–}Cl_{av}$ 2·405, Nd . . . Li 3·63(3) Å, Cl–Nd–Cl′ 82·1, and Cl–Li–Cl′ 97·2(9)°.

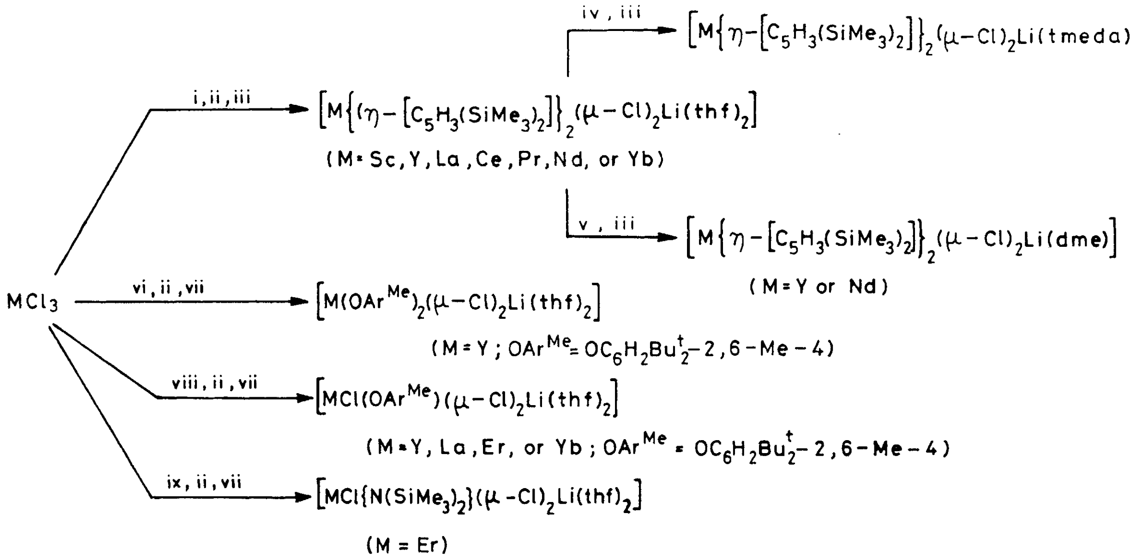
In 1978 we isolated complexes of composition $Y(\eta\text{-}C_5H_4SiMe_3)_2Cl.LiCl.(L)_2$ [L = tetrahydrofuran (thf) or 0·5 $Me_2NCH_2CH_2NMe_2$ (tmeda)] and suggested they contained a $Y(\mu\text{-Cl})_2Li$ bridge, but suitable *X*-ray quality crystals were not obtained.[1] Since then, using the $C_5Me_5^-$ ligand, similar complexes of Nd[2] and Yb[3] were reported, but again without structural data.

The present study has the following objectives: (i) by varying the nature of the group 3A metal and the terminal ligands to show the widespread occurrence of the $M(\mu\text{-Cl})_2Li$ unit and (ii) to obtain structural verification.

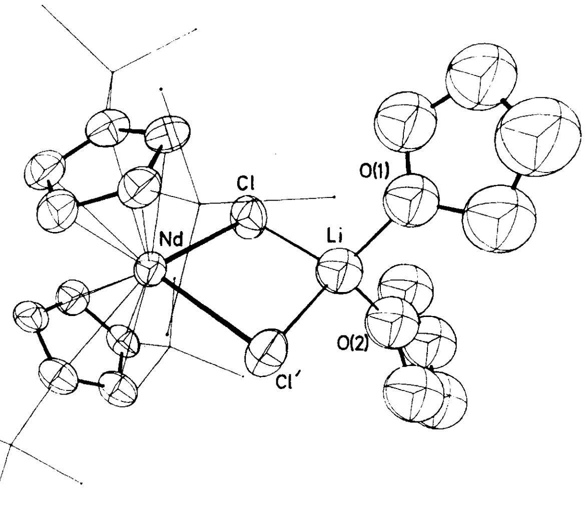
We now show that the $M(\mu\text{-Cl})_2Li$ unit is an important feature of group 3A and lanthanoid metal chemistry and occurs in complexes of the general formula (**1**). This has been achieved (see Scheme) by a wide variation in the nature of (a) the metal M and (b) the supporting ligands L′ and L attached to M and Li, respectively.‡ As for (b) and the L'_2M moiety, we sought to select both mono- and penta-hapto-ligands; our choice was further governed by the requirement that the ligands should confer on the appropriate complex (i) adequate steric protection to nucleophilic attack at M, (ii) good hydrocarbon solubility, and (iii) crystallisability from an aprotic, and preferably hydrocarbon, medium. The use of $^-N(SiMe_3)_2$[4] and $^-OC_6H_2Bu^t_2$-2,6-Me-4[5] (abbreviated as $^-OAr^{Me}$) has ample precedent. We believe the ligand $^-C_5H_3(SiMe_3)_2$ is especially noteworthy and may find a wider role in organometallic chemistry, comparable with and complementary to $^-C_5Me_5$; it imposes



(1)



Scheme. *Reagents and conditions:* i, $2Li[C_5H_3(SiMe_3)_2]$, thf, 0—20 °C, 48 h; ii, thf removed *in vacuo;* iii, crystallisation ($n\text{-}C_5H_{12}$, −10 to −30 °C); iv, tmeda, $n\text{-}C_5H_{12}$, 20 °C, 1 h; v, $MeOCH_2CH_2OMe$, $n\text{-}C_5H_{12}$, 20 °C, 1 h; vi, $[\{LiOAr^{Me}.OEt_2\}_2]$, thf, 0—20 °C, 24 h; vii, crystallisation (hot PhMe, *ca.* 20°C); viii, $\frac{1}{2}[\{LiOAr^{Me}.OEt_2\}_2]$, thf, 0—20 °C, 24 h; and ix, $\frac{1}{2}[\{LiN(SiMe_3)_2.OEt_2\}_2]$ 0—20 °C, 24 h.



Figure

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‡ All these complexes, obtained in > 50% yield, are crystalline, gave satisfactory microanalytical results, and melted with decomposition in the range 100—250 °C; the colourless Sc, Y, and La complexes provided reasonable ^1H and ^{13}C n.m.r. spectra in $CDCl_3$; the following complexes are coloured: Ce (yellow), Pr (pale green), Nd (blue), Er (pink), and Yb {orange for the $[C_5H_3(SiMe_3)_2]$ complex, or violet}.

similar steric contraints but offers far superior hydrocarbon solubility.[6]

The compound [Nd{η-[$C_5H_3(SiMe_3)_2$]}$_2$(μ-Cl)$_2$Li(thf)$_2$] precipitates from pentane at −10 °C as blue–green or blue–pink crystals depending on their size.

Crystal data: $C_{30}H_{58}LiCl_2NdO_2Si_4$, orthorhombic, space group *Pbca*, M = 785·2, a = 13·008(6), b = 20·280(7), c = 31·964(9) Å, U = 8432·2 Å^3, Z = 8, D_c = 1·24 g cm^{-3}, and μ(Mo-K_α) = 15·0 cm^{-1}. The structure was refined to a conventional R value of 0·041 for 2666 observed reflections.§

The molecular structure is illustrated in the Figure.

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

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