Use of the Bis(trimethylsilyl)cyclopentadienyl Ligand for stabilising Early (f^0—f^3) Lanthanocene Chlorides; *X*-Ray Structure of $[(Pr\{\eta\text{-}[C_5H_3(SiMe_3)_2]\}_2Cl)_2]$ and of Isoleptic Scandium and Ytterbium Complexes†

By Michael F. Lappert and Anirudh Singh
(*School of Chemistry and Molecular Sciences, University of Sussex, Brighton,* BN1 9QJ)

and Jerry L. Atwood and William E. Hunter
(*Department of Chemistry, University of Alabama, University, Alabama* 35486)

Summary Reaction of the appropriate MCl_3 and $2Li[C_5H_3(SiMe_3)_2]$ in tetrahydrofuran affords $[(M\{\eta\text{-}[C_5H_3(SiMe_3)_2]\}_2Cl)_2]$ (M = Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu); the *X*-ray structure of the first early lanthanocene chloride $[(Pr\{\eta\text{-}[C_5H_3(SiMe_3)_2]\}_2Cl)_2]$ (the Sc and Yb complexes are isostructural) shows the Pr atoms to be in a distorted tetrahedral environment, and important molecular parameters include $Pr\text{–}Cl_{av.}$ 2·81, $Pr\text{–}C(\eta\text{-})_{av.}$ 2·76 Å, Pr . . . Pr′ 4·372(1) Å, Cl–Pr–Cl′ 78, and Pr–Cl–Pr′ 102°.

We draw attention to the potential of the trimethylsilylcyclopentadienyl ligands $[C_5H_{5-n}(SiMe_3)_n]^-$ (n = 1, 2, or 3), for organometallic chemistry, the availability of which will allow appropriate selection to be made to meet particular synthetic targets. Introduction of the $SiMe_3$ group provides a means of increasing the solubility of a derived complex in an aprotic medium (and hence the opportunity of obtaining *X*-ray quality crystals), and often also its volatility, doubtless because of a corresponding increase in covalent character. The strategy of using bulky cyclopentadienyls to develop novel aspects of organometallic chemistry is not new, being particularly well established for $C_5Me_5^-$.[1] However, the results of the present study convince us that the $[C_5H_{5-n}(SiMe_3)_n]$ (n = 1—3) series offers distinct and complementary features to $C_5Me_5^-$.

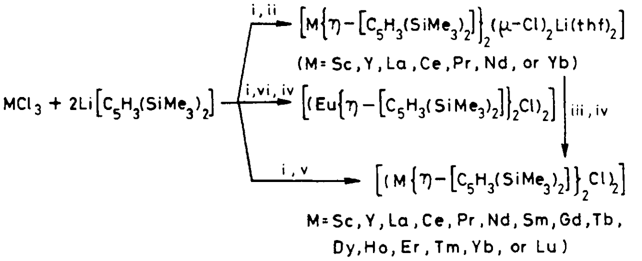
In this paper we restrict the scope to the case of $[C_5H_3(SiMe_3)_2]^-$ and its role in providing access to a hitherto elusive class of compounds, the early (f^0—f^3) lanthanocene chlorides $[(Ln\{\eta\text{-}[C_5H_3(SiMe_3)_2]\}_2Cl)_2]$ [Ln = La, Ce, Pr (also its *X*-ray structure), or Nd] (an alternative approach, by linking two cyclopentadienyl ligands, has yielded [La or $Ce\{\eta\text{-}C_5H_4[CH_2]_3C_5H_4\text{-}\eta\}Cl]_x$.[2]) These, by substitution of Cl^-, will surely prove to be key intermediates to a wealth of interesting compounds, as has previously been established for the f^5—f^{14} analogues $[\{Ln(\eta\text{-}C_5H_5)_2Cl\}_2]$ (Ln = Sm to Lu)[3] as well as offering the opportunity of opening up the as yet unexplored organometallic chemistry of Ln^{IV}. By contrast, use of (i) $MCl_3 + 2LiC_5H_5$, yields $[Ln(\eta\text{-}C_5H_5)_3]$;[3] and (ii) $C_5Me_5^-$ affords not $[\{Nd(\eta\text{-}C_5Me_5)_2Cl\}_x]$ but $[Nd(\eta\text{-}C_5Me_5)_2(\mu\text{-}Cl)_2Li(thf)_2]$ (thf = tetrahydrofuran);[4] the latter is a member of the series[5] $[LnL'_2(\mu\text{-}Cl)_2LiL_2]$ which for Ln = an f^5—f^{14} metal and L′ = C_5H_5 is on the synthetic pathway to the lanthanocene chloride.[6]

The lanthanocene chlorides were obtained as shown in the Scheme.‡ Single crystals of $[(Pr\{\eta\text{-}[C_5H_3(SiMe_3)_2]\}_2Cl)_2]$ were obtained from toluene.

---

† No reprints available.

‡ All these complexes, obtained in > 40% yield, are crystalline and high melting (normally in the range 280—335 °C, but the Eu complex decomposes at 115—120 °C), gave satisfactory microanalytical results, showed the highest peak in the mass spectrum at m/e corresponding to $[M\{C_5H_3(SiMe_3)_2\}_2Cl]^+$; the diamagnetic colourless Sc, Y, La, or Lu complexes provided reasonable ^1H and ^{13}C n.m.r. spectra in $CDCl_3$; the Gd, Tb, Dy, and Ho complexes are colourless, but the following are coloured: Ce, Pr, Sm, and Tm (yellow), Nd (blue), Er (pink), Eu (violet), and Yb (red).



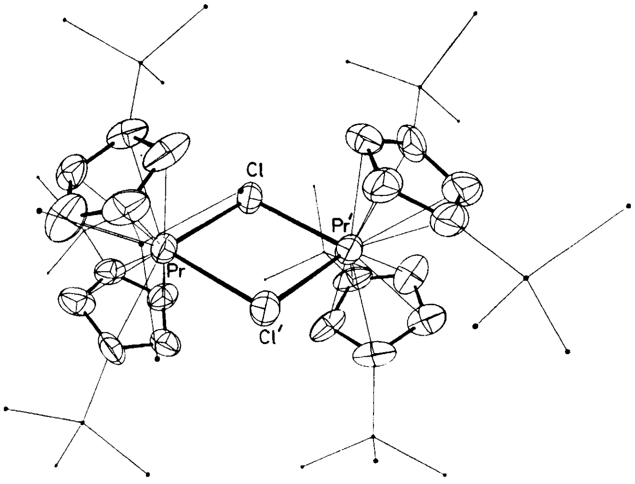
Scheme. *Reagents and conditions:* i, thf, 0—20 °C, 48 h, then thf removed *in vacuo*; ii, crystallisation (n-C_5H_{12}, −10 to −30 °C; iii, 140—150 °C, *ca.* 4 h; iv, crystallisation (PhMe, −30 °C); v, sublimation, at *ca.* 250—280 °C/10^{-3} Torr; vi, 60—80 °C, *ca.* 2 h.

Crystal data: $C_{44}H_{84}Cl_2Pr_2Si_4$, triclinic, space group $P\bar{1}$, $M = 1188{\cdot}9$, $a = 10{\cdot}630(5)$, $b = 11{\cdot}817(5)$, $c = 13{\cdot}293(5)$ Å, $\alpha = 109{\cdot}30(4)$, $\beta = 99{\cdot}42(4)$, $\gamma = 86{\cdot}66(4)°$, $U = 1533{\cdot}6$ Å^3, $Z = 1$ dimer, $D_c = 1{\cdot}28$ g cm^{-3}, and μ(Mo-K_α) = 18·1 cm^{-1}. The structure was refined to a conventional R value of 0·033 based on 1831 observed reflections.§

The molecular structure consists of discrete dimers with centre of inversion site symmetry. There is one dimer per unit cell. The molecular structure is illustrated in the Figure.

Table. Comparison of structural parameters for [(M{η-[$C_5H_3(SiMe_3)_2$]$_2$}Cl)$_2$] complexes.

M	Pr	Yb§	Sc§
M^{3+} radius (Å)	1·01	0·86	0·68
(M–Cl) (Å)	2·81	2·65	2·58
[M–C(η-)] (Å)	2·76	2·62	2·51
Cl–M–Cl′ (°)	78	80	79
M–Cl–M′ (°)	102	100	101
Cent–M–Cent′ (°)	130	130	131



Figure

Some parameters and comparisons with isostructural complexes of Sc and Yb are shown in the Table.¶ The bond distances correlate well with the changes in the M^{3+} radius. The [$C_5H_3(SiMe_3)_2$]$^-$ ligand is sufficiently bulky to fill the area about the metal ion, but the overall effect on the bonding parameters at the metal is not large, as is evident by noting that in [(Sc{η-[$C_5H_3(SiMe_3)_2$]}$_2$Cl)$_2$] and [{Sc(η-C_5H_5)$_2$Cl}$_2$][7] the Sc–Cl lengths are identical, and Sc–C(η-) distances are only 0·05 Å longer for the former complex.

We thank S.R.C. and the U.S.N.S.F. (to J. L. A.) for their support and the University of Rajasthan, Jaipur (India), for providing A. S. with study leave.

(*Received, 7th August* 1981; *Com.* 952.)

§ 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.

¶ Full X-ray data on [(M{η-[$C_5H_3(SiMe_3)_2$]}$_2$Cl)$_2$] (M = Sc or Yb) will be provided in the full paper.

[1] *Cf.* for C_5Me_5H preparation: R. S. Threlkel and J. E. Bercaw, *J. Organomet. Chem.*, 1977, **136**, 1.

[2] J. N. John and M. Tsutsui, *Inorg. Chem.*, 1981, **20**, 1602.

[3] *Cf.* T. J. Marks, *Progr. Inorg. Chem.*, 1978, **24**, 52.

[4] A. L. Wayda and W. J. Evans, *Inorg. Chem.*, 1980, **19**, 2190.

[5] M. F. Lappert, A. Singh, J. L. Atwood, and W. E. Hunter, following communication.

[6] J. L. Atwood, W. E. Hunter, R. D. Rogers, J. Holton, J. McMeeking, R. Pearce, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1978, 140.

[7] J. L. Atwood and K. D. Smith, *J. Chem. Soc., Dalton Trans.*, 1973, 2487.