Synthesis and Characterisation of Stable Anionic Group 3a Dichlorometallocene(III) Complexes and the *X*-Ray Structure of $[AsPh_4][Nd\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2Cl_2]$†

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A new class of group 3a organometallic compounds, containing the dichlorometallocene(III) anion $[Ln(cp'')_2Cl_2]^-$ is reported, obtained most conveniently by Cl^- addition to $[\{Ln(cp'')_2Cl\}_2]$ $[cp'' = \eta\text{-}C_5H_3(SiMe_3)_2]$; the *X*-ray structure of $[AsPh_4][Nd(cp'')_2Cl_2]$ shows $Nd\text{–}Cl_{av.}$ 2.668(4) Å and Cl–Nd–Cl 99.3(1)°.

The metallocene(III) chlorides of Sc, Y, and the lanthanoid elements are key intermediates to many of the organometallic compounds of the group 3a metals. They fall into two classes: (a) homometallic complexes of formula $[\{Ln(\eta\text{-}cp^*)_2(\mu\text{-}Cl)\}_2]$[1] and (b) the heterometallic compounds $[Ln(\eta\text{-}cp^*)_2(\mu\text{-}Cl)_2LiL_2]$[2] [Ln = a group 3a metal; η-cp* denotes a general substituted or unsubstituted 1—5η-cyclopentadienyl ligand, cp specifically C_5H_5 and cp'' $C_5H_3(SiMe_3)_2$; L = tetrahydrofuran (thf) or L_2 = tetramethylethylenediamine (tmeda)].

$$\begin{tikzcd}
 & \tfrac{1}{2}[\{Ln(cp'')_2Cl\}_2] + [M]Cl \arrow[d, "i"] \\
2\,Li(cp'') + LnCl_3 \arrow[r, "ii"] & {[M][Ln(cp'')_2Cl_2]}
\end{tikzcd}$$

Scheme 1. *Reagents and conditions:* (i) CH_2Cl_2, 20 °C, 16 h; then concentration, OEt_2 addition, filtration, and crystallisation at −10 to −30 °C. (ii) [M] = $[Li(thf)_4]$, Ln = La, thf-n-C_6H_{14}, 20 °C, 24 h; then successively heating under reflux for 18 h, removing solvent *in vacuo*, OEt_2 addition, filtration, and crystallisation at −30 °C.

We now describe the synthesis (Scheme 1), characterisation,‡ and molecular structure (see Figure 1 for the title Nd complex) of a third class, (c), $[Ln(\eta\text{-}cp^*)_2Cl_2]^-$ in which cp* = cp'' which should prove useful as precursors to anionic metallocene(III) complexes such as hydrides and alkyls. Similar chlorometallates have previously been postulated as unstable intermediates and indeed an unpurified 'ate' complex containing $[Y(\eta\text{-}C_5Me_4Et)_2Cl_2]^-$ has been tentatively identified.[3] Unlike compounds of classes (a) and (b), we find that the salts having the $[Ln(cp'')_2Cl_2]^-$ anions‡ are relatively stable in air. The presence of the cp''^- ligands also provides for good solubility in diethyl ether.

Of the two methods of preparation, (i) and (ii) in Scheme 1, the former is the more general and preferred procedure. It is likely that this belongs to a wider group of reactions of the neutral homometallic metallocene chlorides (a), whereby $(\mu\text{-}Cl)_2$-bridge-splitting by an anionic nucleophile Y^- may provide

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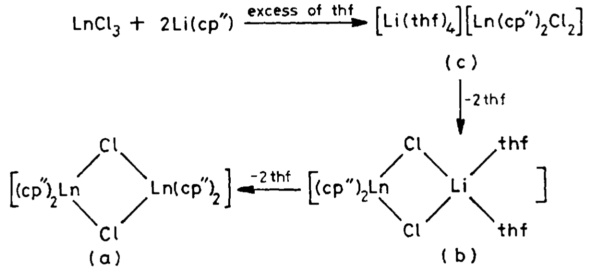
† No reprints available.

‡ The following compounds were obtained in 75—82% yield: $[N(PPh_3)_2][Y(cp'')_2Cl_2]$, $[Li(thf)_4][La(cp'')_2Cl_2]$, $[PPh_4][Pr(cp'')_2Cl_2]$, $[AsPh_4][Nd(cp'')_2Cl_2]$, $[P(CH_2Ph)Ph_3][Nd(cp'')_2Cl_2]$, $[P(CH_2Ph)Ph_3][Dy(cp'')_2Cl_2]$, and $[PPh_4][Tm(cp'')_2Cl_2]$. These are crystalline and decompose on melting at *ca.* 165—175 °C; they gave satisfactory microanalytical results and, for the Y and La salts, also ^1H n.m.r. spectra. They are usually white, except for the violet Nd salts.



Scheme 2

a range of 'ate' complexes of type $[M][Ln(cp'')_2(Cl)Y]$ exemplified here by the dichlorides (c). The stability of the latter may be due to the use of the large cation $[M]^+$ as well as the choice of $^-C_5H_3(SiMe_3)_2$ as the cyclopentadienyl ligand. Particularly noteworthy are the complexes of the early lanthanoid metals, the f^0 La^{III}, f^2 Pr^{III}, and f^3 Nd^{III}. The formation of the neutral metallocene(III) chlorides (a) from $LnCl_3$ and Li(cp″) in thf is now established as involving the intermediates of types (b) and (c), Scheme 2.

The anion $[Nd(cp'')_2Cl_2]^-$ is the first of its type of a group 3a element to be subjected to an *X*-ray structural analysis. However, some revealing comparison can already be made. Firstly, the title compound affords an indirect measure of the strength of the interaction of the Li ion with the chlorides in $[Nd(cp'')_2(\mu\text{-}Cl)_2Li(thf)_2]$.[2] In the former Nd–Cl is 2.668(4) Å and ∠Cl–Nd–Cl is 99.3(1)°, while in the latter the corresponding values are 2.744 Å and 82.1°. The average Nd–C(η-cyclopentadienyl) distance in $[Nd(cp'')_2Cl_2]^-$ of 2.78 Å shows the effect of the wider Cl–Nd–Cl angle compared with $[Nd(cp'')_2(\mu\text{-}Cl)_2Li(thf)_2]$ where the corresponding average Nd–C distance is 2.76 Å. Secondly, since the Pr^{3+} radius is only 0.02 Å longer than that of Nd^{3+},[4] the title compound can be compared to $[\{Pr(cp'')_2(\mu\text{-}Cl)\}_2]$,[1] where the Pr–Cl distance, 2.81 Å, has been lengthened by the bridging nature of the chlorides. Finally, the most direct geometrical analogue of $[Nd(cp'')_2Cl_2]^-$ is the isoleptic $[U(cp'')_2Cl_2]$.[5] The radius of Nd^{3+} is 0.06 Å larger than that of U^{4+},[4] and the U–Cl distance is 0.09 Å shorter at 2.579 Å. The Cl–U–Cl angle is 95.3°.

Crystal data: $C_{46}H_{62}AsCl_2NdSi_4$, triclinic, space group $P\bar{1}$, $M = 1017.46$, $a = 12.334(4)$, $b = 13.924(4)$, $c = 15.844(5)$ Å, $\alpha = 91.60(3)$, $\beta = 97.96(3)$, $\gamma = 104.35(3)°$, $U = 2605.2$ Å^3, $Z = 2$, $D_c = 1.30$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 18.86$ cm^{-1}. The structure was refined to $R = 0.027$, $R_w = 0.032$, based on 2273 observed reflections, using an Enraf–Nonius CAD4 diffractometer.§

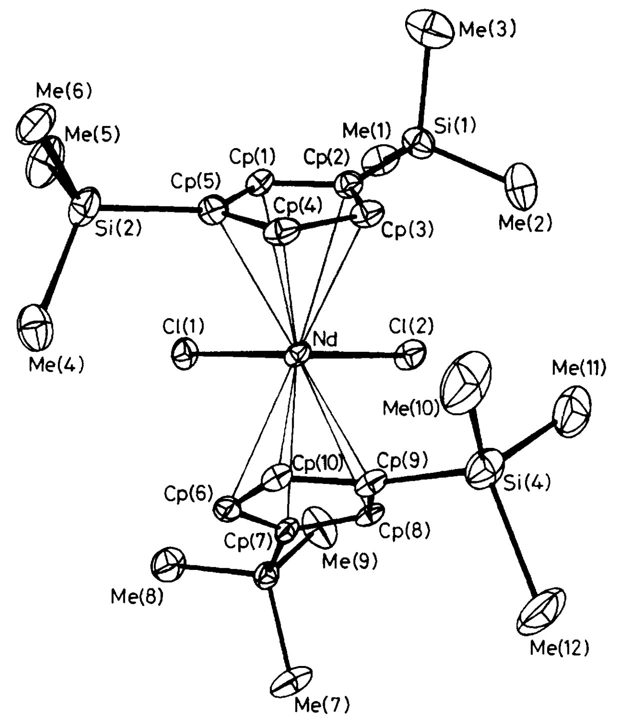


Figure 1. Molecular structure of the anion of $[AsPh_4][Nd\{\eta\text{-}C_5H_3(SiMe_3)_2\}_2Cl_2]$; the hydrogen atoms are omitted. Some important bond lengths and angles: Nd–Cl(1) 2.669(3), Nd–Cl(2) 2.667(3), Nd–Cp(1) 2.81(1), Nd–Cp(2) 2.80(1), Nd–Cp(3) 2.76(1), Nd–Cp(4) 2.75(1), Nd–Cp(5) 2.78(1), Nd–$Cp_{av.}$ 2.78 Å; Cl(1)–Nd–Cl(2) 99.3(1), Cent–Nd–Cent′ 126.3°.

The molecular structure consists of discrete monomers and that of the anion is illustrated in Figure 1.

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4 *Cf.* F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley, New York, 4th edn., 1980, pp. 982, 1006.
5 Unpublished work: (a) synthesis, M. F. Lappert, A. Singh, and R. G. Taylor; (b) *X*-ray analysis, J. L. Atwood and W. E. Hunter.

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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.