

**Novel Anionic Cages from 'Alkylmanganese Chloride' and 'Alkylcobalt Chloride' Solutions. Crystal and Molecular Structure of  $[\text{Li}(\text{thf})_4][\{(\text{Me}_3\text{Si})_3\text{C}\}_3\text{Mn}_3\text{Cl}_4(\text{thf})]$  (thf = tetrahydrofuran)**

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The reaction between tris(trimethylsilyl)methyl-lithium and manganese(II) or cobalt(II) chlorides yields lithium salts with chloride-bridged polynuclear anions; the manganese compound  $[\text{Li}(\text{thf})_4][\{(\text{Me}_3\text{Si})_3\text{C}\}_3\text{Mn}_3\text{Cl}_4(\text{thf})]$  (thf = tetrahydrofuran) has been characterised by an X-ray study.

Grignard or organolithium reagents react with manganese(II) halides to yield solutions of organomanganese compounds usually represented by the formula  $\text{RMnX}$ . Although the synthetic potential of these solutions was noted almost 50 years ago,<sup>1</sup> attempts to establish the structures of the species present were unsuccessful. In a few cases, it was possible, *e.g.*

after precipitating  $\text{MgCl}_2$  with dioxane, to obtain alkyls  $\text{R}_2\text{Mn}$ , which were studied in solution<sup>2,3</sup> or shown to be oligomeric, *e.g.*  $[\{\text{Mn}(\text{CH}_2\text{CMe}_2\text{Ph})_2\}_2]$ ,  $[\{\text{Mn}(\text{CH}_2\text{CMe}_3)_2\}_4]$ ,<sup>4</sup> and  $[\{\text{Mn}(\text{C}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\}_3]$ ,<sup>5</sup> or polymeric, *e.g.*  $[\{\text{Mn}(\text{CH}_2\text{SiMe}_3)_2\}_n]$ <sup>4</sup> in the solid state. In an attempt to characterise the tetramethylethylenediamine (tmeda) adduct

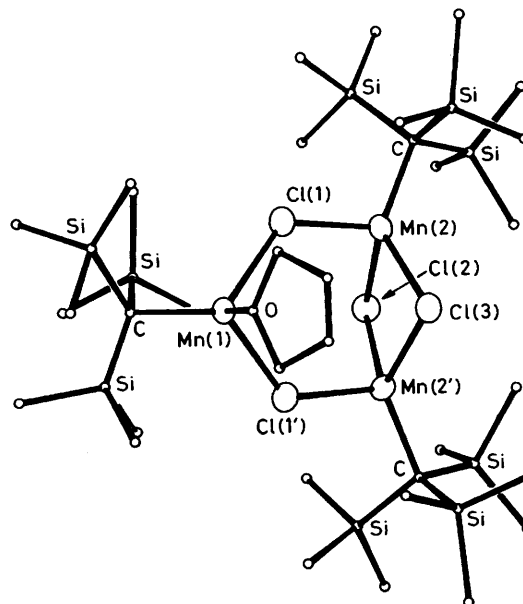
of  $(C_5H_5)_2MnCl$ , sublimation gave the halogen-free species  $(\eta^1-C_5H_5)(\eta^5-C_5H_5)Mn(tmeda)$ .<sup>6</sup> Since several unusual organometallic compounds having large alkyl groups, e.g.  $(Me_3Si)_3C-$  (Tsi) or  $(Me_2PhSi)_3C-$ ,<sup>7,8</sup> have recently been isolated, we treated manganese(II) chloride with TsiLi in tetrahydrofuran (thf); the product was the manganate(II) complex  $[Li(thf)_4][Tsi_3Mn_3Cl_4(thf)]$ . This is the first compound isolated from an 'alkylmanganese chloride' solution to be structurally characterised.

A solution of TsiLi<sup>7</sup> (0.22 mol) in thf (25 cm<sup>3</sup>) was added dropwise to a stirred suspension of anhydrous  $MnCl_2$  (0.22 mol) in thf at  $-78^\circ C$ . The pink suspension became orange-brown and on warming to  $20^\circ C$  a clear solution was obtained. After 12 h the solvent was removed; the residue was washed once with pentane and extracted into toluene. The toluene extract gave pale yellow air-sensitive crystals (60%), m.p.  $180-186^\circ C$ .

**Crystal data:**  $C_{50}H_{121}Cl_4LiMn_3O_5Si_9$ ,  $M = 1368.8$ , monoclinic, space group  $P2_1/m$ ,  $a = 14.445(3)$ ,  $b = 18.996(5)$ ,  $c = 14.892(4)$  Å,  $\beta = 95.72(2)^\circ$ ,  $U = 4065.6$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.19$  g cm<sup>-3</sup>. The structure was solved by routine heavy atom methods using Mo- $K_\alpha$  radiation and 3854 reflections ( $2 < \theta < 23^\circ$ ) with  $I > \sigma(I)$ . However, both the anion and cation had  $C_s$  symmetry: the  $(Me_3Si)_3C$  groups attached to Mn(1) (Figure 1) were therefore disordered. As in  $[Li(tmeda)_2][Li\{C(SiMe_3)_3\}_2]$ <sup>9</sup> the set of C sites has exact  $C_s$  symmetry and the Si atoms are disordered equally between two sets of sites related by the mirror plane. There was further disorder (a) in the  $(Me_3Si)_3C$  group attached to Mn(2) with unequal occupation of the two sets of three Si sites and (b) in the  $[Li(thf)_4]$  cation. Block diagonal least squares refinement (Mn and Cl atoms anisotropic) gave  $R = 0.156$ ,  $R' = 0.214$ .†

In spite of the uncertainties in the Tsi and thf fragments, the anion  $[(Tsi)_3Mn_3Cl_4(thf)]^-$  (Figure 1) is well defined, and we are aware of no analogous structure in the literature.<sup>10,11</sup> The compounds  $MnR_2$  which have been characterised have linear arrays of Mn atoms, but Mn triangles are observed in  $H_3Mn_3(CO)_{12}$  or  $(\eta^5-C_5H_5)_3Mn_3(NO_3)_4$  and Re triangles in the Cl-bridged species  $[Re_3Cl_{12}]^{3-}$  and  $Re_3(CH_2SiMe_3)_6Cl_3$ , in which the Re is formally in oxidation state 3 and six-co-ordinate. As expected, the Mn-Cl(1) bonds are significantly shorter than the Mn-Cl(2) bonds (Figure 1). All the Mn-Cl bonds appear to be shorter than those in  $\alpha$ -(254.9 pm) and  $\beta$ -(258.3 pm)  $RbMnCl_3$ , where the two polymorphs have respectively  $\mu$ -Cl and  $(\mu-Cl)_2$  bridges.<sup>12</sup> The co-ordination number of Mn atoms bearing the large Tsi groups is 4 rather than 6: for Mn(1) which is bound to only two Cl atoms there is enough room for co-ordination of a molecule of thf. The Mn(2)-Mn(2') distance is shorter than that in the  $(\mu-Cl)_2$  bridged  $\beta$ - $RbMnCl_3$  (377.4 pm) but much longer than that in the metal (269-273 pm), or in  $Mn_2(CO)_{10}$  (293 pm),  $Mn(C_6H_2Me_3-2,4,6)_2$  (285 pm), or  $H_3Mn_3(CO)_{12}$  (311 pm), indicating that there is little metal-metal bonding. Some interaction between the Mn atoms is, however, indicated by the mean magnetic moment ( $3.8 \mu_B$ ) which was found by Evans' method<sup>13</sup> using the signals from benzene to measure the paramagnetic shift. The value is similar to that in  $Mn(C_6H_2Me_3-2,4,6)_2$  ( $3.65 \mu_B$ ) but considerably lower than the (spin-only) values, 5.8-5.95  $\mu_B$ , found for  $MnCl_4^{2-}$ .<sup>14</sup>

The reaction between TsiLi and  $CoCl_2$  gave a bottle-green solution from which green crystals, m.p.  $160^\circ C$ , were



**Figure 1.** The structure of the anion  $[(Tsi)_3Mn_3Cl_4(thf)]^-$ , with hydrogen atoms omitted. Selected mean dimensions (standard deviations in parentheses): Mn-Cl(1) 241.2(4), Mn(2)-Cl(2) 246.8(4), Mn(2)-Cl(3) 249.5(4), Mn-C 217(2), Mn-O 221(2), C-SiMe<sub>3</sub> 188(8), Si-Me 196(11), Mn(1) ··· Mn(2) 427, Mn(2) ··· Mn(2') 348 pm. Cl(1)-Mn(1)-Cl(1') 103.9(2), Cl(2)-Mn(2)-Cl(3) 88.5(1), Mn(1)-Cl(1)-Mn(2) 124.2(2), Mn(2)-Cl(2)-Mn(2') 89.8(2), Mn(2)-Cl(3)-Mn(2') 88.6(2), Mn-C-Si 106(2), Si-C-Si 113(4), Me-Si-Me 106(4)°.

isolated. Attempts to determine the structure by X-ray diffraction were hampered by extensive disorder<sup>9</sup> but the data were consistent with a structure containing an anion like  $[(Tsi)_3Mn_3Cl_4(thf)]^-$  with Mn replaced by Co. The magnetic moment ( $2.48 \mu_B$ ) is considerably smaller than that for  $[CoCl_4]^{2-}$  ( $4.6 \mu_B$ ).

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## References

- H. Gilman and J. C. Bailie, *J. Org. Chem.*, 1937, **2**, 84; H. Gilman and R. H. Kirby, *J. Am. Chem. Soc.*, 1941, **63**, 2046.
- H. Tamura and J. Kochi, *J. Organomet. Chem.*, 1971, **29**, 111; E. J. Corey and G. H. Posner, *Tetrahedron Lett.*, 1970, 315.
- K. Jacob and K.-H. Thiele, *Z. Anorg. Allg. Chem.*, 1979, **455**, 3.
- R. A. Andersen, E. Carmona-Guzman, J. F. Gibson, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1976, 2204.
- S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1983, 1128.
- J. Heck, W. Massa, and P. Weinig, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 722.
- C. Eaborn, P. B. Hitchcock, J. D. Smith, and A. C. Sullivan, *J. Chem. Soc., Chem. Commun.*, 1983, 827 and 1390; 1984, 870.
- C. Eaborn, M. N. A. El-Kheli, P. B. Hitchcock, and J. D. Smith, *J. Chem. Soc., Chem. Commun.*, 1984, 1673.
- P. B. Hitchcock, unpublished results.
- P. R. Raithby in 'Transition Metal Clusters,' ed. B. F. G. Johnson, Wiley, Chichester, 1980, p. 7.
- R. E. McCarley, *Philos. Trans. R. Soc. London, Ser. A*, 1982, **308**, 141.
- S. J. Jensen, *Acta. Chem. Scand.*, 1967, **21**, 889.
- D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
- R. Colton and J. H. Canterford, 'Halides of the First Row Transition Metals,' Wiley, Chichester, 1969, p. 212.

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