# Neopentyl, Neophyl, and Trimethylsilylmethyl Compounds of Manganese. Manganese(II) Dialkyls; Manganese(II) Dialkyl Amine Adducts; Tetra-alkylmanganate(II) Ions and Lithium Salts; Manganese(IV) Tetra-alkyls †

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The interaction of manganese(II) chloride with Grignard or dialkylmagnesium reagents derived from $Me_3CCH_2Cl$, $Me_2PhCCH_2Cl$, and $Me_3SiCH_2Cl$ yields thermally stable dialkyl compounds of manganese(II). For the neophyl compound, $Mn_2(CH_2CMe_2Ph)_4$, a dimeric structure with a bridging alkyl group, the phenyl group of which lies over a manganese atom, has been confirmed by *X*-ray diffraction (to be reported separately). For the trimethylsilylmethyl compound, $\{Mn(CH_2SiMe_3)_2\}_n$, tetrahedral co-ordination of $Mn^{II}$ is achieved by polymerisation *via* alkyl bridges (*cf.* $BeMe_2$).

The dialkyl compounds interact with Lewis bases such as *NNN'N'*-tetramethylethylenediamine to give monomeric complexes of the type $MnR_2$·tmed and with lithium alkyls to give solvated dilithium tetra-alkylmanganate(II) complexes $Li_2[MnR_4]$. Salts where R = Me are also described and the existence of dimethyl- and diphenylmanganese is questioned.

The e.s.r. spectra of the manganese(II) species are described and assignments made. Oxidation of the dialkyl compounds in the presence of an excess of alkylating agent gives green solutions whose e.s.r. spectra are similar to that of tetranorbornylmanganese(IV) so that the solutions presumably contain unstable manganese(IV) alkyls.

THE comparative rates of decomposition of tetrahydrofuran solutions of what were considered to be manganese dialkyls,[1] made *in situ* by interaction of manganous chloride and Grignard reagents, provided some of the earlier evidence for the hydride transfer-alkene elimin-

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† No reprints available.

[1] M. Tamura and J. Kochi, *J. Organometallic Chem.*, 1971, **25**, 111; *Bull. Chem. Soc. Japan*, 1971, **44**, 3063.

ation route in the decomposition of transition-metal alkyls, and showed that alkyls such as the methyl, neopentyl, and benzyl, which could not decompose in this way, were much more stable thermally. It was stated however, that 'simple dialkylmanganese complexes which contain no π-bonding ligands are virtually unknown due to their thermal lability'. Materials said to be dimethylmanganese,[2] methylmanganese iodide,[3] diphenylmanganese,[2] and lithium salts [3] of stoicheiometry $LiMnR_3$ (R = Me, Et, Bu$^n$, and Ph, *etc.*) have been claimed but the characterisation was very poor and the analytical data, for manganese only, was commonly unsatisfactory.

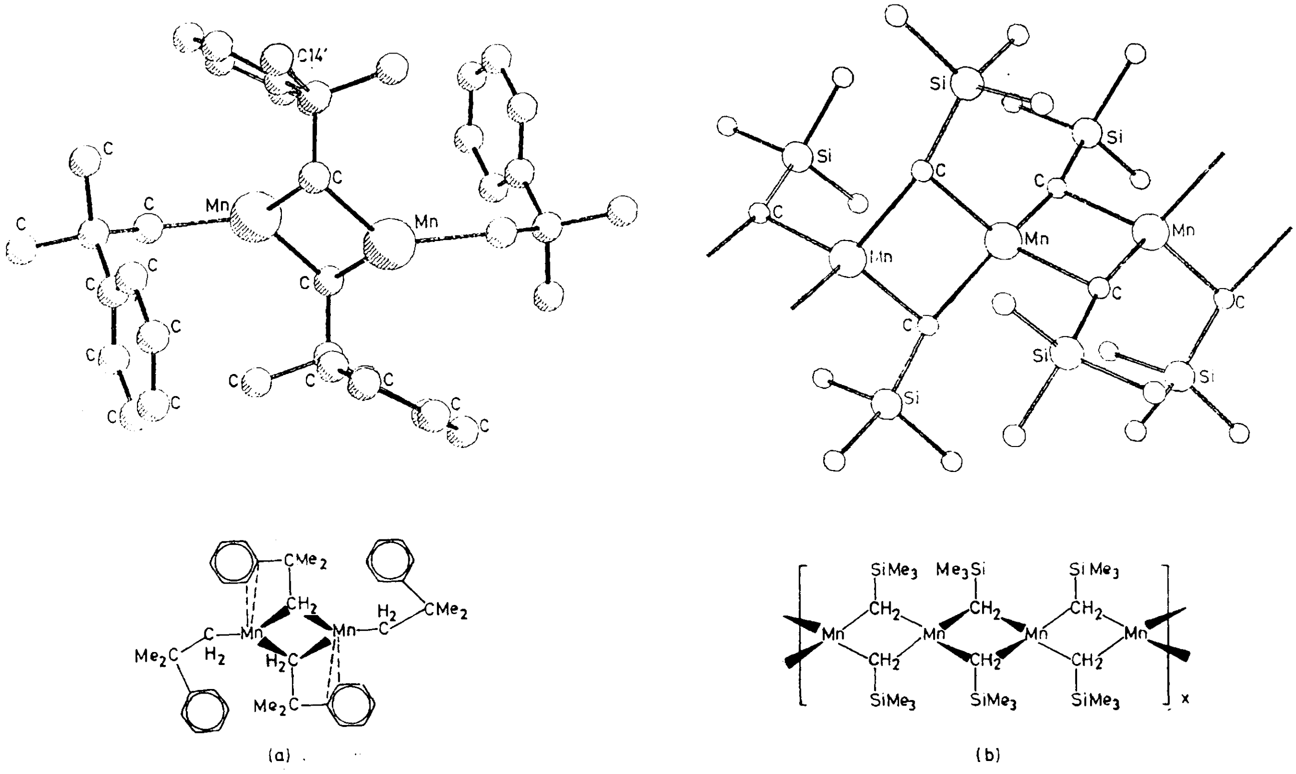

FIGURE 1 The structure of (a) dineophylmanganese(II) and (b) bis(trimethylsilylmethyl)manganese(II), according to an *X*-ray crystallographic study by M. B. Hursthouse and P. Raithby, Queen Mary College, London

In view of the isolation of β-elimination stabilised, transition-metal peralkyls [4] there seemed good reason to expect that similar alkyls of manganese(II) could be prepared; and also, because of the synthesis of the β-elimination stabilised tetranorbornylmanganese,[5] that other alkyls of manganese(IV) should be isolable.

We now report the synthesis of several neutral alkyls, $MnR_2$, the lithium salts $Li_2[MnR_4]$, and of unstable manganese(IV) species.

*Manganese Dialkyls.*—The interaction of manganous chloride with either neophylmagnesium chloride or, better, dineophylmagnesium in diethyl ether readily produces dineophylmanganese [systematic name bis(2-methyl-2-phenylpropyl)manganese(II)], $Mn_2(CH_2CMe_2Ph)_4$. The compound is readily soluble in petroleum and can be obtained as pale yellow needles. The solid, and even more so the solutions, are extremely sensitive to traces of oxygen, when they turn green; this sensitivity somewhat limits the study of physical properties such as molecular weights and i.r. spectra. However, an *X*-ray crystallographic study [6] has shown that the molecule is dimeric [Figure 1(a)] with each manganese(II) atom bound to a terminal alkyl group and to bridging carbon. The formally 3-co-ordinate manganese atom attempts to increase its co-ordination number by interaction with one of the double bonds in the phenyl ring of the bridged neophyl group where the Mn–C distances are *ca.* 2.7 Å. The Mn atoms have a distorted tetrahedral geometry but the Mn–Mn distance, 2.719 Å, is probably too long for any significant metal–metal bonding although magnetic and e.s.r. studies indicate magnetic interaction. The molecule is best described as electron deficient with three-centre two-electron (3c–2e) bridge bonds.

The *X*-ray structure reveals that the *ortho*-hydrogen atom of the phenyl group on the bridge ligand is close to the manganese atom. An intramolecular oxidative addition of this C–H bond to manganese could result in

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[2] C. Beerman and K. Clauss, *Angew. Chem.*, 1959, **71**, 627.

[3] R. Rienschneider, H.-G. Kassahn, and W. Schneider, *Z. Naturforsch.*, 1960, **15b**, 547.

[4] W. Mowat, A. J. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J.C.S. Dalton*, 1972, 533.

[5] B. K. Bower and H. G. Tennent, *J. Amer. Chem. Soc.*, 1972, **94**, 2512.

[6] Personal communication by M. D. Hursthouse and P. Raithby, Queen Mary College, London, E1 4NS.

an *ortho*-metallated species and also loss of t-butylbenzene from the non-bridged alkyl group. Indeed, when heated *in vacuo* at 80—100 °C, t-butylbenzene, identified by its mass spectrum and comparison with an authentic sample, is produced together with a toluene-soluble, red product. We have not succeeded in crystallising the latter but its i.r. spectrum has a new band at 775 $cm^{-1}$. This is in the accepted region for *ortho*-metallated complexes so that the red species could be formulated as $\{MnCH_2CMe_2(C_6H_4)_2\}_2$. Hydrolysis of $Mn_2(CH_2CMe_2Ph)_4$ with water also gave t-butylbenzene. Hydrolysis with $D_2O$ gave $PhCMe_2CH_2D$ virtually in quantitative yield.

The interaction of $MnCl_2$ and $Me_3SiCH_2MgCl$ or $(Me_3SiCH_2)_2Mg$ gives bis(trimethylsilylmethyl)manganese(II). This, unlike the corresponding neophyl compound, is very sparingly soluble in petroleum, although it can be crystallised from boiling toluene. Such behaviour taken together with the formation of long acicular crystals, suggested a different structre. *X*-Ray diffraction [6] has shown that in the crystal the compound is polymeric [Figure 1(b)] with alkyl bridges, each $Mn^{II}$ atom being four-co-ordinate. The structure is thus similar to the well known polymer $(BeMe_2)_n$. Hydrolysis with $D_2O$ gave mainly $[^2H_1]Me_4Si$ (93.6% $[^2H_1]$, 4.6% $[^2H_2]$, and 2.8% $[^2H_3]$). By contrast with the neophyl compound $Mn(Me_3SiCH_2)_2$ is thermally the most stable manganese(II) alkyl known and will sublime at 150 °C *in vacuo*. The mass spectrum does not give the molecular ion; a peak at *m*/*e* 371 can be attributed to the ion $Mn_2(CH_2SiMe_3)_3^+$. The i.r. spectrum of the compound shows strong absorption at 2 770 $cm^{-1}$, which is unusually low for C–H stretching frequencies. This suggests some type of interaction between the hydrogen atoms of methyl groups on silicon with a manganese atom in another chain.

Although the neopentyl compound $\{Mn(CH_2CMe_3)_2\}_4$ is similar to the trimethylsilylmethyl compound in its volatility and sublimes at 110 °C *in vacuo*, it resembles the neophyl compound in having high solubility in petroleum. Again the i.r. spectrum has a band at *ca.* 2 700 $cm^{-1}$. The structure by *X*-ray diffraction [6] shows the molecule to be a linear tetramer with bridging alkyl groups and the two end Mn atoms 3-co-ordinate with a terminal alkyl. Why the compound should be a tetramer rather than some other polymer is not clear but it is possible that this is a result of packing in the crystal lattice.

*'Dimethyl' and 'Diphenyl' Manganese*.—A yellow, ether-insoluble, thermally unstable material was claimed [2] to be $MnMe_2$. By contrast, the yellow tetrahydrofuran solution formed by interaction of the methyl Grignard reagent and $MnCl_2$ decomposed only during a period of days.[1] We have obtained a crystalline material from tetrahydrofuran but complete elemental analysis (except for oxygen) indicated a composition between $Me_2Mn{\cdot}MgCl_2{\cdot}C_4H_8O$ and $Me_2Mn{\cdot}MgCl_2{\cdot}2C_4H_8O$. Addition of tmed to the solution gave a white precipitate of $MgCl_2{\cdot}$tmed and crystallisation of the evaporated solution from toluene gave red-yellow crystals. Analysis showed only a trace of magnesium but the Mn : Cl ratio remained *ca.* 2.6 : 1. Recrystallisation did not improve the situation. Other attempts using trimethylaluminium to methylate manganous halides or manganese(III) acetylacetonate also failed to give a pure dialkyl.

Similarly we have been unable to isolate in a pure form the green, tetrahydrofuran-soluble, so-called [2] diphenylmanganese. Light green crystals from $Ph_2Mg$ and $MnCl_2$ always contain chloride, while dark green crystals from $Ph_2Mg$ and $MnBr_2$ have a ratio Mn : Mg : Br of 2 : 1 : 4.2 corresponding approximately to $Ph_2Mn{\cdot}MnBr_2{\cdot}MgBr_2{\cdot}4C_4H_8O$. Addition of pyridine removes $MnBr_2$ as $MnBr_2(py)_2$.

*Cleavage Reactions of the Dimeric Alkyls*.—The associated electron-deficient bridge alkyls should be cleaved by Lewis bases, L, to give monomeric tetrahedral compounds of stoicheiometry $MnR_2L_2$, and by lithium alkyls to give tetrahedral anionic species, $Li_2[MnR_4]$.

*Amine Complexes*.—Diethyl ether evidently does not cause bridge cleavage since the trimethylsilylmethylmanganese compound can be recovered ether free when crystallised from ether–petroleum mixtures. However, *NNN'N'*-tetramethylethylenediamine (tmed) readily gives $Mn(CH_2SiMe_3)_2{\cdot}$tmed which sublimes unchanged at 80 °C *in vacuo*. Similar tmed complexes of the corresponding neophyl and neopentyl compounds can be obtained; the neopentyl compound also gives a 1 : 1 complex with *NN'*-dimethylpiperazine and a 1 : 2 complex with pyridine.

*Tetra-alkylmanganate*(II) *Species*.—The interaction of the manganese dialkyl—or more directly manganous chloride—with lithium alkyls gives the co-ordinatively saturated light-sensitive tetra-alkyl anion, $[MnR_4]^{2-}$.

Interaction of methyl-lithium and $MnCl_2$ in diethyl ether yields an orange-red solution from which the compound $Li_2[MnMe_4]{\cdot}0.5Et_2O$ can be crystallised even when the Li : Mn molar ratio is varied from 2 : 1 to 8 : 1. Since $MnCl_2$ is insoluble in ether, methyl-lithium is always present in excess so that maximum alkylation is to be expected. At no time have we isolated a complex of stoicheiometry $LiMnMe_3$ as was said [2] to be obtained by interaction of $MnI_2$ and MeLi but no preparative details or analyses were given; if the formulation was based on C and H analyses we point out that the values for $LiMnMe_3$ and $Li_2[MnMe_4]{\cdot}0.5Et_2O$ are similar. We conclude that $MnMe_3^-$ species are not formed except as intermediates in solution (see below).

When the ether solvate is heated at 55 °C *in vacuo* for 24 h it leaves a thermally very stable yellow-brown powder $Li_2[MnMe_4]$ which will not redissolve in ether or tetrahydrofuran. Its colour suggests tetrahedral manganese(II). Polymerisation presumably occurs through some $Li^+{-}H_3C$ interaction, as is suggested by the i.r. spectrum. The absorptions at 2 860 and 2 780 $cm^{-1}$, assigned to the asymmetric and symmetric C–H stretches respectively, are much lower than is usual for methyl groups where no interaction occurs and this may be attributed to the type of interaction found in lithium alkyls. Thus $(MeLi)_4$ has absorptions at 2 840 and 2 780 $cm^{-1}$ and $(Bu^tLi)_4$ at 2 810 and 2 730 $cm^{-1}$ assigned in the former to inter-cluster and in the latter to intra-cluster

Li–H interactions.[7] This view has been verified by crystallographic study of $(C_6H_{11}Li)_6$.[8] A polymeric structure with lithium ions bridging $MnMe_4$ units through Li–H interactions may also account for the abnormally low magnetic moment, 2.2 B.M. (293 K), which could result from antiferromagnetic or other type of exchange interaction.

The interaction of MeLi and $MnCl_2$ in tetrahydrofuran (thf) gives the solvate $Li_2[MnMe_4]\cdot 2thf$ which also has i.r. bands at 2 780 and 2 700 indicating Li–H interactions. *NNN′N′*-Tetramethylethylenediamine will replace the tetrahydrofuran to yield the red, toluene-soluble complex $Li_2[MnMe_4]\cdot 2tmed$. Although the i.r. spectrum is complicated by tmed absorptions, again bands at 2 800 and 2 730 $cm^{-1}$ are discernible. It seems reasonable to assume that in these solvates there is a $[MnMe_4]^{2-}$ ion and a solvated $Li^+$ ion with additional $Li^+–H_3C–Mn$ interactions. Consistent with this idea, the e.s.r. spectra (see later) of frozen solutions of the solvates show only broad structureless resonances at $g \approx 2$. This is expected for a rather symmetrical $Mn^{II}$ anion with low zero-field splitting. For the crystalline tmed compound the magnetic moment is 5.5 B.M. (293 K) suggesting essentially high-spin $Mn^{II}$.

The other alkyls also give anionic species; thus the compound $Li_2[Mn(CH_2SiMe_3)_4]$ is readily soluble even in petroleum and can be crystallised on cooling as orange-brown crystals. Since the i.r. spectrum shows no lowered C–H stretches it is possible that the $Li^+$ atoms are sitting in the hydrophobic pocket created by the bulky alkyl group. We have been unable to measure the magnetic moment of this compound due to its extreme air-sensitivity but e.s.r data are discussed below; it also decomposes under $\gamma$-radiation.[6]

*Interaction with Alkynes.*—Dineophylmanganese cyclotrimerises both diphenylacetylene and but-2-yne in petroleum at room temperature, to hexaphenyl- and hexamethyl-benzene respectively. Phenylacetylene and hexafluorobut-2-yne yield red oily materials which we have been unable to purify. Tetracyanoethylene and olefins do not appear to react.

*Manganese*(IV) *Alkyls.*—It is by no means clear how and why the interaction of norbornyl-lithium and $MnCl_2$ in petroleum leads to the green volatile tetranorbornylmanganese(IV).[5] A disproportionation mechanism seems less likely than some type of radical chain oxidation; oxidation by traces of air has been shown to be necessary to get alkyls in high oxidation states in other cases.[4,9]

The neophylmanganese(II) complex readily turns green in the presence of traces of oxygen, hence we attempted to prepare the tetra-alkyl by introducing small amounts of dry oxygen into petroleum solutions of $Mn_2(CH_2CPhMe_2)_4$ and $Mg(CH_2CPhMe_2)_2$. Although the solution turned green, removal of the solvent left a deep green oil which would not crystallise. Attempts to chromatograph the compound or to purify it by distillation or sublimation led to decomposition. The e.s.r. spectrum of the green substance (see below) is, however, consistent with that expected for $Mn(CH_2CPhMe_2)_4$.

The trimethylsilylmethylmanganese(II) complex is less sensitive to oxidation than is the neophyl but again aerial oxidation of a petroleum solution in the presence of an excess of the Grignard reagent gives a deep green colour. Removal of solvent and vacuum sublimation from about room temperature to a liquid-nitrogen-cooled probe gave a dark green material which turned yellow rapidly on warming to room temperature. The green solutions and the green sublimate are also light sensitive and the operations must be carried out in the dark. When set aside even in the dark for *ca.* 12 h, the green solution becomes light yellow and $\{Mn(CH_2SiMe_3)_2\}_n$ can be isolated. Again the e.s.r. spectra are consistent with the presence of an unstable tetra-alkyl $Mn(CH_2SiMe_3)_4$.

*Electron Spin Resonance Spectra.*—In general the manganese alkyl solutions gave strong e.s.r. spectra, those at room temperature giving broad featureless lines centred on $g = 2$. The frozen solution spectra were more informative being spread over a very wide field range, but they were not easy to interpret since, except in certain cases, there were overlapping spectra from more than one species in solution. Since the compounds are very reactive, it was common to find minor spectral variations from one preparation to another, and with a change in solvent. There were also spectral variations with the temperature, indicating that molecular movements, especially in petroleum solutions, can take place at temperatures well below −100 °C. Measurements were hence made at −180 °C over the range 0—1 T; for the best samples, spectra were recorded up to the maximum field of 1.4 T. All the spectra were too complex and too widely spread to be interpreted as having $S = \frac{1}{2}$ so we may be sure that these are not low spin manganese(II) compounds. Since helium temperatures were never required for the spectra we also discount the fast-relaxing $S = 2$ state which could possibly arise from manganese(III). This leaves the only reasonable choice between $S = \frac{5}{2}$ from high-spin manganese(II) or $S = \frac{3}{2}$ from manganese(IV) to account for the observed spectra. A characteristic feature of all the spectra, apart from those of the anions, was the absence of manganese hyperfine structure. For the dimeric manganese dialkyls, this can be attributed to exchange by way of metal–metal interaction, presumably *via* the bridge carbon atoms, but in the other samples we reason that the zero field splitting is effectively modulated by small changes in molecular environment throughout the sample which would give rise to an inhomogeneous line broadening sufficient to remove the hyperfine structure. That the spectra are very sensitive to small changes in the environment is also evident from the strong solvent effects which will be mentioned later. The lack of hyperfine structure did not arise from intermolecular exchange resulting from too high a concentration since, although we were not able to

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[7] R. West and W. Glaze, *J. Amer. Chem. Soc.*, 1961, **83**, 3580; M. Weiner, G. Vogel, and R. West, *Inorg. Chem.*, 1962, **1**, 654.

[8] R. Zerger, W. Rhine, and G. D. Stucky, *J. Amer. Chem. Soc.*, 1974, **96**, 6048.

[9] K. Mertis, D. H. Williamson, and G. Wilkinson, *J.C.S. Dalton*, 1975, 607.

measure concentrations accurately, dilution of the sample did not improve the resolution. For the monomeric systems, the analysis is in terms of the spin Hamiltonian

$$\mathscr{H} = 2\beta BS + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2)$$

*The Manganese Dialkyls.*—The e.s.r. spectrum of a frozen petroleum solution of the neophyl, $Mn_2(CH_2CMe_2Ph)_4$, was a weak, broad line ($\Delta H$ = 40 mT, $g$ = 2.0). In some samples two resonances thought to be due to other species appeared in variable intensities, one near $g_{eff}$ = 4.0 and the other with features ranging from 0.05 to 0.82 T. Both were characteristic of high-spin monomeric manganese(II), and were accompanied by a green colour in the solution; they are thought to arise, in part, from oxidation products. The spectrum associated with $Mn_2(CH_2CMe_2Ph)_4$ is thus the weak line at $g_{eff}$ = 2.0. When pyridine is added the frozen solution spectrum changes to that of a monomeric species with $g_{eff} \approx 4.3$ and is much stronger. These spectra are compatible with the presence in solution of a dimeric species, being converted by pyridine into a monomeric species. The weak, featureless e.s.r. spectrum of the dimer is interpreted as arising from the partially occupied $S = 1$ state of a pair of manganous ions which couple antiferromagnetically to give a ground state with $S = 0$. Observation of a weak e.s.r. signal at *ca.* 100 K therefore means that the excited state responsible for the resonance must be occupied, which in turn requires an exchange interaction less than *ca.* 70 cm$^{-1}$.

A similar weak signal at $g_{eff}$ = 1.98 is found for a frozen toluene solution of $\{Mn(CH_2SiMe_3)_2\}_n$, but in mobile solution at room temperature a strong signal at $g$ = 2.0 is seen. This is compatible with increased occupation of the $S = 1$ state at the higher temperature, again supporting antiferromagnetic coupling with $J$ *ca.* 70 cm$^{-1}$, though we realise that an isotropic signal will always appear to be more intense than an anisotropic spectrum of the same number of spins. The magnetic moment of $\{Mn(CH_2SiMe_3)_2\}_n$ measured in benzene solution by the Evans n.m.r. method was *ca.* 3.0 B.M., in keeping with the proposed antiferromagnetic ground state with $S = 0$. The moment is lower than expected for manganese(II) with $S = \frac{5}{2}$ which would be expected if there were no interaction and indicates partial occupancy of the proposed $S = 1$ state at room temperature.

Similar experiments with toluene solutions of $[Mn(CH_2CMe_3)_2]_n$ gave inconclusive results. The low-temperature spectra were strong and could be analysed by the $D$–$B$ plot method [10] as arising from monomeric high-spin manganese(II) having $D = 0.12$, $\lambda = E/D = 0.267$, but a weak line in the $g = 2$ region in frozen solution spectra and a strong line at $g = 2.0$ at room temperature were also compatible with the antiferromagnetically coupled system proposed for the other two compounds. The magnetic susceptibility, 3.9 B.M., again suggests antiferromagnetic coupling.

*The Dialkyl Compounds plus Donor Ligand.*—The e.s.r. spectra of the dialkyls in pyridine, 1,2-dimethoxyethane, or diethyl ether, in the presence of tetramethylethylenediamine (tmed), are strong and wide ranging at −180 °C. Figure 2 shows the spectra of the tmed adducts of the neophyl, trimethylsilylmethyl, and neopentyl. The magnetic susceptibilities of these compounds in solution are all close to 5.7 B.M., typical of high-spin manganese(II). The principal features of the e.s.r. spectra which may be observed up to fields of 1.1 T, have been analysed using the $D$–$B$ plot method, for fields along the principal directions of the zero-field-splitting tensor. A common feature is the intense band at *ca.* 150 mT, the $g_{eff} \approx 4.3$ region. Such a feature commonly arises in the so-called 'rhombic' symmetry for high-spin $d^5$ complexes which are characterised by $D$ values greater than *ca.* 0.23 cm$^{-1}$ and $\lambda$ values ($=E/D$) close to 1/3. Griffith [11] has shown that a tetrahedral ion of the type $MA_2B_2$ should give this type of spectrum and such spectra have been observed in near-tetrahedral manganese compounds.[12]

The spectra are not of the pure rhombic type and this is anticipated for $MnR_2{\cdot}tmed$ in which the symmetry cannot be as high as in 'tetrahedral' $MA_2B_2$. The spectra for $MnR_2{\cdot}tmed$ ($R = CH_3SiMe_3$ and $CH_2CMe_3$) are assigned Hamiltonian parameters $D = 0.47$, $\lambda = 0.27$ and $D = 0.42$, $\lambda = 0.23$ respectively. The parameters for $Mn(CH_2CMe_2Ph)_2{\cdot}tmed$ are also of this order but the spectrum shown in Figure 2(c) must be that of a mixture because the features near $g_{eff}$ = 2.0 are incompatible with those near the $g_{eff}$ = 4.3 region for a single species; consequently, our assignment cannot be precise.

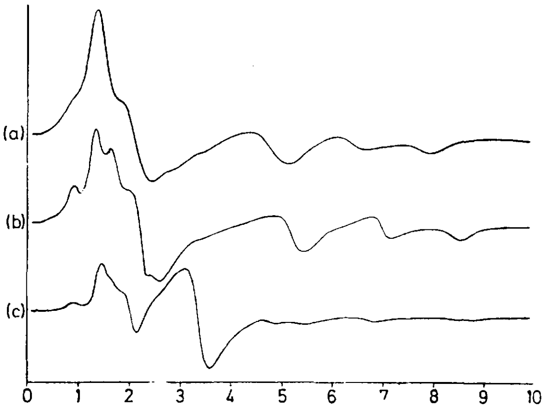

FIGURE 2 *X*-Band e.s.r. spectra of frozen solutions of the tetramethylethylenediamine adducts: (a) $Mn(CH_2SiMe_3)_2{\cdot}tmed$, (b) $Mn(CH_2CMe_3)_2{\cdot}tmed$, and (c) $Mn(neophyl)_2{\cdot}tmed$ in benzene. Temperature = −180 °C; frequency = 9.16 GHz

A strong asymmetric feature in the $g_{eff}$ = 4.3 region is characteristic for the complexes in the presence of pyridine or oxygen donor solvents so these donors cleave the dimers giving four-co-ordinate $Mn^{II}$ species although on crystallisation only dimers are obtained. However, other species also may be present which, as judged by the

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[10] R. D. Dowsing and J. F. Gibson, *J. Chem. Phys.*, 1969, **50**, 294.

[11] J. S. Griffith, *Mol. Phys.*, 1964, **8**, 213, 217.

[12] R. D. Dowsing, J. F. Gibson, D. M. L. Goodgame, M. Goodgame, and P. J. Hayward, *J. Chem. Soc.* (*A*), 1969, 1242.

broad line near $g_{eff} = 2.0$ in Figure 2(c) (*ca.* 0.33 T) which is characteristic of low $D$ values, are probably more symmetric and may be four- or six-co-ordinate.

*The* $[MnR_4]_2^-$ *Anions*.—When $LiCH_2SiMe_3$ is added to $\{Mn(CH_2SiMe_3)_2\}_n$ in petroleum as many as four different e.s.r. spectra may be seen [Figure 3(a) and (b)]. Three of these, A, B, and C, are broad featured and spread over the range 50—700 mT; they will not be discussed further. The fourth, D, however is a well-resolved hyperfine sextet centred on $g = 2.0$. This spectrum is that of a highly symmetric high-spin manganese(II) species with $D = E = 0.0$, *i.e.*, with cubic symmetry. The most reasonable assignment is to the species $[Mn(CH_2SiMe_3)_4]^{2-}$, but since this anion is in a non-co-ordinating petroleum solution it is presumably ion-compensated with two nearby lithium ions. The following equilibria, with monomeric or aggregate species, are proposed to account for the presence of this anion.

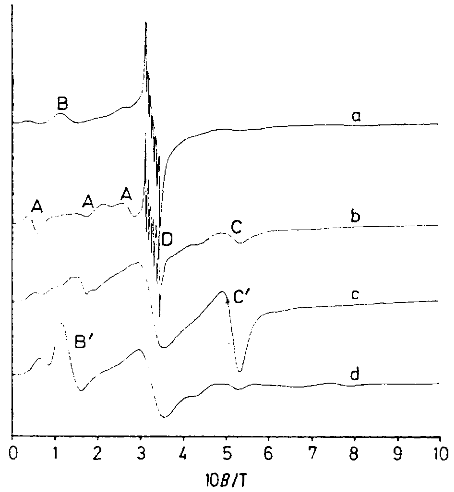

FIGURE 3 $X$-Band e.s.r. spectra of solutions of $Li_2[Mn(CH_2SiMe_3)_4]$. Temperature = −180 °C; frequency = 9.15 GHz. (a) Petroleum, (b) petroleum but about ten times more dilute than in (a) and with increased gain, (c) diethyl ether, (d) 1,2-dimethoxyethane

$$[MnR_2]_n + nLiR \rightleftharpoons nLiMnR_3$$

$$nLiMnR_3 + nLiR \rightleftharpoons nLi_2[MnR_4]$$

In diethyl ether the colour is red-brown at room temperature changing to yellow-orange at −180 °C, and the e.s.r. spectrum [see Figure 3(c)] is quite different, in that the highly symmetric species is absent. A broad line with just a hint of manganese hyperfine structure takes the place of spectrum D. This could come from a four- or a six-co-ordinate species with a small but finite $D$ value. The spectrum is similar to that of $[Mn(H_2O)_6]^{2+}$ and presumably represents the completely solvated cation.

In 1,2-dimethoxyethane [Figure 3(d)] the e.s.r. spectrum is different again. The highly symmetric $[Mn(CH_2SiMe_3)_4]^{2-}$ ion is absent and, as for the ether solution, a broad line at $g_{eff} = 2.0$ is present, indicating the presence of solvated manganese(II). However, a very strong feature C′ at 500 mT in the ether solution is replaced by a strong $g_{eff} = 4.3$ feature B′ in the 1,2-dimethoxyethane. The latter could be assigned to a complex of the $MA_2B_2$ type, *i.e.* $Mn(CH_2SiMe_3)_2(MeOCH_2CH_2OMe)$ as described in the previous section; this could result from the chelating ability of this ether affecting the LiR–$MnR_2$ equilibria.

Samples containing $Li_2[MnMe_4]$ in tetrahydrofuran gave weak spectra consistent with high-spin manganese(II) with a small zero-field splitting. In the presence of tmed or diethyl ether the spectrum was stronger and sharper but with practically no sign of manganese hyperfine structure. Since almost the same spectrum is seen with both these donors, it is likely that $[MnMe_4]^{2-}$ is present in solution, probably very weakly solvated so as to lower the symmetry to below that found for the highly symmetric and sterically protected tetrakis(trimethylsilylmethyl) anion. This would account for the absence of a highly resolved spectrum similar to D of Figure 3(a).

*Oxidation of Manganese*(II) *Alkyls*.—On addition of dry air to solutions of the reaction mixture $MnR_2$ (R = $CH_2SiMe_3$ or $CH_2CMe_3$) with an excess of Grignard reagent in toluene or petroleum, a deep bottle green colour is first formed. With more air the colour becomes red-brown and finally a dark gelatinous precipitate appears.

The green solution gave an e.s.r. spectra comprising a smooth asymmetric line with effective values of $g_\perp \simeq 4.0$ and $g_\parallel = 2.0$ [Figure 4(a) and 4(b)], though the $g_{eff} = 2.0$ region was partially obscured due to the spectrum of the red-brown species. The shape and position of the spectrum of the green species is typical of a complex with $S = \frac{3}{2}$ and with a large axial zero-field splitting. This spin state is rather rare for manganese compounds but is known[5] for $Mn(norbornyl)_4$ [Figure 4(c)]. Thus we assign these spectra to $MnR_4$. The situation for the neophyl compound was less straightforward since although a line at $g_{eff} = 4.0$ was seen, it was not asymmetric and no simple spectrum representative of the $S = \frac{3}{2}$ state

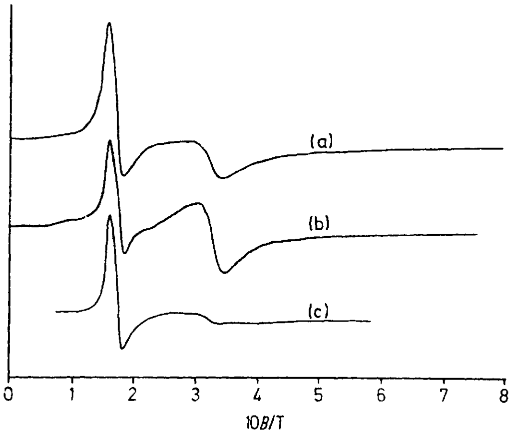

FIGURE 4 $X$-Band e.s.r. spectra of solutions of $MnR_2$ plus RMgX (X = halide) after admission of oxygen to give a deep green colour. Temperature = −180 °C; frequency = 9.15 GHz. (a) R = $CH_2SiMe_3$ in toluene; (b) R = $CH_2CMe_3$ in toluene and some petroleum; (c) e.s.r. spectrum of $Mn(norbornyl)_4$ in benzene at −196 °C, by permission of B. K. Bower and H. G. Tennent, Hercules Incorporated could be found. The complex $Mn(CH_2CMe_2Ph)_4$ presumably is present, however, since the dark green colour seems to be characteristic.

## EXPERIMENTAL

Microanalyses were by Butterworth Microanalytical Consultancy Limited, Middlesex, and in one instance by Pascher Microanalytical Laboratory, Bonn. Metal analyses were done by Mr. John Gulton using a plasma arc atomic absorption technique or by Mr. David Hickman using conventional atomic absorption methods. Magnetic moments on solid samples were measured on a magnetic balance constructed by Dr. D. F. Evans. The solution moments were measured by a modification of a n.m.r. method.[13] The concentration was determined by hydrolysing a 1 cm$^3$ aliquot with dilute hydrochloric acid and then diluting it to 10 cm$^3$; the manganese concentration was then measured by atomic absorption. E.s.r. spectra were obtained at *X*-band using a Varian E12 spectrometer. Solutions were prepared by standard vacuum-line techniques in quartz e.s.r. tubes.

The dialkylmagnesium or dialkylmagnesium–alkylmagnesium chloride mixtures were prepared by the method similar to that used for $Bu^t{}_2Mg$.[14] The concentration was estimated by acid titration of a hydrolysed aliquot. Anhydrous $MnCl_2$ was prepared by action of $SOCl_2$ on the hydrate and pumping at 200 °C *in vacuo*.

The light petroleum used had b.p. 30—40 °C unless otherwise stated.

The yields of the three manganese alkyls were essentially quantitative.

Analytical data for the compounds are given in the Table.

Analytical data for manganese alkyls [a]

| Compound | Found (%) C | H | N | M | Required (%) C | H | N | M |
|---|---|---|---|---|---|---|---|---|
| $Mn_2(CH_2CMe_2Ph)_4$ | 74.0 | 8.1 | | 16.3 (Mn) | 74.8 | 8.1 | | 17.1 (Mn) |
| $Mn(CH_2CMe_2Ph)_2\cdot$tmed | 70.9 | 9.4 | 6.3 | | 71.4 | 9.6 | 6.3 | |
| $\{Mn(CH_2SiMe_3)_2\}_n$ | 40.2 | 9.5 | | *b* | 41.9 | 9.4 | | |
| $Mn(CH_2SiMe_3)_2\cdot$tmed | 48.6 | 11.3 | 7.7 | | 48.7 | 11.0 | 8.1 | |
| $\{Mn(CH_2CMe_3)_2\}_n$ | 58.3 | 10.8 | | | 60.9 | 11.2 | | |
| $Mn(CH_2CMe_3)_2\cdot$tmed | 62.8 | 11.4 | 8.9 | | 61.4 | 12.1 | 8.9 | |
| $Mn(CH_2CMe_3)_2\cdot$dmp | 61.5 | 11.5 | 8.1 | | 16.8 | 11.6 | 9.0 | |
| $Mn(CH_2CMe_3)_2\cdot$2py | 67.4 | 8.9 | 7.5 | | 67.6 | 9.0 | 7.8 | |
| $Li_2[MnMe_4]\cdot 0.5Et_2O$ | 44.8 | 9.4 | | | 43.4 | 10.2 | | |
| $Li_2[MnMe_4]$ | 36.6 | 9.2 | | *c* | 37.2 | 9.3 | | |
| $Li_2[MnMe_4]\cdot$2thf | 51.4 | 10.1 | | 5.7 (Li) | 52.8 | 10.3 | | 5.1 (Li) |
| $Li_2[MnMe_4]\cdot$2tmed | 51.7 | 11.6 | 13.7 | 14.6 (Mn) | 53.2 | 12.2 | 15.5 | 15.2 (Mn) |
| $Li_2[Mn(CH_2SiMe_3)_4]$ | 44.9 | 10.3 | | 13.6 (Mn) | 46.1 | 10.5 | | 13.2 (Mn) |

[a] tmed = *NNN'N'*-tetramethylethylenediamine, $Me_2N(CH_2)_2NMe_2$, dmp = *NN'*-dimethylpiperazine. [b] Si : Mn = 2.0 : 1.0. [c] Li : Mn = 2.1 : 1.0.

*Bis*(2-*methyl*-2-*phenylpropyl*)*manganese*(II).— Dineophylmagnesium (8 cm$^3$ of a 0.9M-diethyl ether solution, 0.007 2 mol) was added to a suspension of $MnCl_2$ (0.90 g, 0.007 2 mol) in diethyl ether (50 cm$^3$) at —70 °C. The yellow suspension was warmed to room temperature and was stirred for 30—48 h. The ether was removed *in vacuo* and the brown-orange oily residue was extracted with petroleum (2 × 50 cm$^3$). The green (light to deep coloured) extracts were combined and the volume reduced to *ca.* 25 ml. Cooling to −20 °C yielded pale yellow *needles* which were collected, washed with petroleum (3 × 1 ml), and dried *in vacuo* to give a brown-yellow solid, m.p. 78—80 °C (decomp).

*Bis*(*trimethylsilylmethyl*)*manganese*(II).—A 1 : 1 mixture of $(Me_3SiCH_2)_2Mg$ and $Me_3SiCH_2MgCl$ (10 cm$^3$ of a 0.9M-diethyl ether solution) was added to $MnCl_2$ (0.63 g, 0.0050 mol) suspended in ether (35 cm$^3$). The suspension was stirred for 3—4 h. The ether was removed *in vacuo* and the residue was extracted with toluene (150 cm$^3$) at 50—60 °C. The extract was allowed to cool slowly to room temperature to yield pale orange *needles*, m.p. 150 °C.

*Bis*(2,2-*dimethylpropyl*)*manganese*(II).—A 1 : 1 mixture of $(Bu^tCH_2)_2Mg$ and $Bu^tCH_2MgCl$ (10 cm$^3$ of a 0.9M-diethyl ether solution) was added to $MnCl_2$ (0.63 g, 0.005 0 mol) suspended in toluene (35 cm$^3$) and the suspension was stirred at 20 °C for 24 h. The volatile material was evaporated and the residual oil suspended in petroleum (30 cm$^3$). A white solid was allowed to settle for 6—10 h and the solution was filtered. The filtrate was evaporated to dryness. The solid was suspended in petroleum (20 cm$^3$), a white solid was allowed to settle (3—4 h), and the solution was filtered; cooling of the solution to −70 °C, afforded red-brown *needles*. The dialkyl was recrystallised twice from petroleum (−70 °C), m.p. 98 °C.

*Bis*(2-*methyl*-2-*phenylpropyl*)*manganese*–NNN'N'-*Tetramethylethylenediamine* (1/1).—To a solution of $(Me_2PhCCH_2)_2Mn$ in petroleum was added an excess of tmed. The resulting suspension was stirred for 30 min, after which the volatile material was removed *in vacuo*; the resulting solid crystallised as brown-red *prisms* from diethyl ether (−70 °C), m.p. 79–81 °C.

*Bis*(*trimethylsilylmethyl*)*manganese*–NNN'N'-*Tetramethylethylenediamine* (1/1).—An excess of tmed was added to a diethyl ether solution of $(Me_3SiCH_2)_2Mn$. After the mixture had been stirred for 15 min, the volatile material was removed *in vacuo*; the residue crystallised as colourless *crystals* from petroleum (−70 °C), m.p. 90 °C.

*Complexes of Bis*(2,2-*dimethylpropyl*)*manganese*.—*With* NNN'N'-*tetramethylethylenediamine*. The amine was added to a petroleum solution of $(Bu^tCH_2)_2Mn$ which was then stirred for 15 min. The solution was evaporated to dryness and the resulting solid crystallised as white *crystals* from petroleum at −70 °C, m.p. 110 °C.

*With* NN'-*dimethylpiperazine*. The amine was added to a petroleum solution of the dialkyl and the solution was stirred for 15 min. After removal of volatile material the solid was crystallised from petroleum (−70 °C) as white *crystals*.

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[13] D. F. Evans, G. V. Fazakerley, and R. F. Phillips, *J. Chem. Soc.* (*A*), 1971, 1931.

[14] G. E. Coates and J. A. Helsop, *J. Chem. Soc.* (*A*), 1968, 514.

*With pyridine*. The amine was added to a petroleum solution of the dialkyl. After being stirred for 15 min, the solution was evaporated to dryness, and the solid crystallised from petroleum (−70 °C) as white *crystals*.

*Dilithium Tetramethylmanganate*(II)–*Diethyl Ether* (1/0.5).—Methyl-lithium (45 cm$^3$ of a 1.3M-diethyl ether solution, 0.060 mol) was added to $MnCl_2$ (1.6 g, 0.013 mol) suspended in diethyl ether (50 cm$^3$) at −70 °C. The orange-yellow suspension was warmed to room temperature and stirred for 8 h. The suspension was allowed to settle, the orange-brown supernatant filtered, the volume reduced to *ca*. 40 cm$^3$, and the solution cooled to −20 °C for 2 d. The small amount of methyl-lithium which crystallised was removed. The red-orange filtrate was used in subsequent reactions. Diethyl ether was removed *in vacuo* from a 5 cm$^3$ aliquot and solid was pumped for 24 h at $10^{-2}$ mmHg at room temperature.

*Dilithium Tetramethylmanganate*(II).—A 5 cm$^3$ aliquot of the above diethyl ether solution was exposed to vacuum for 5 h at room temperature; the solid was finely powdered and then heated (55 °C) *in vacuo* ($10^{-2}$ mmHg), for 24 h, yielding a brown-yellow *powder*.

*Dilithium Tetramethylmanganate*(II)–*Tetrahydrofuran* (1/2).—A 5 cm$^3$ aliquot of the diethyl ether complex was dissolved in tetrahydrofuran and the solution was evaporated to dryness; the resulting yellow solid crystallised as orange-yellow *plates* from tetrahydrofuran (−70 °C).

*Dilithium Tetramethylmanganate*(II)–NNN′N′-*Tetramethylethylenediamine* (1/2).—To a 5 cm$^3$ aliquot of the diethyl ether solution was added tmed and the red solution was stirred for 15 min. The solution was evaporated to dryness and the brown-red solid crystallised as red *needles* from a dilute solution in toluene at −20 °C. When heated in a sealed capillary it melted at 110—120 °C and turned black at 160—165 °C.

*Dilithium Tetra(trimethylsilylmethyl)manganate*(II).—Trimethylsilylmethyl-lithium (10 cm$^3$ of a 0.90M-solution, 0.009 0 mol) was added to a diethyl ether (50 cm$^3$) suspension of $MnCl_2$ (0.34 g, 0.002 7 mol) at −70 °C. After addition the suspension was warmed to room temperature and stirred for five days. The colour was initially yellow and after *ca*. 4 d was deep brown-red. The volatile material was removed *in vacuo*, the brown-red oil was stirred with petroleum (50 cm$^3$), and the insoluble material was allowed to settle. The mixture was filtered and the filtrate concentrated to *ca*. 5 ml; it was then cooled to −20 °C. The light brown-red *prisms* were collected, washed with chilled petroleum (2 × 1 cm$^3$), and then dried *in vacuo*.

*Reaction of Dimethylmagnesium and Manganese*(II) *Chloride*.—Dimethylmagnesium (5.4 cm$^3$ of a 0.90M-diethyl ether solution, 0.004 9 mol) was added to $MnCl_2$ (0.6 g, 0.004 8 mol) suspended in diethyl ether (50 cm$^3$) at −70 °C. The resulting yellow suspension was stirred for 24 h at room temperature. The solid was then collected and washed with diethyl ether (5 × 50 cm$^3$). The dark brown residue was extracted by stirring the suspension with tetrahydrofuran (30 cm$^3$). After filtration, the orange-yellow solution was concentrated to *ca*. 20 cm$^3$ and cooled to −15 °C, to give bright yellow *prisms*. These were collected, washed with a small amount of tetrahydrofuran, and kept *in vacuo* for 16 h at room temperature (Found: C, 34.2; H, 6.2; Cl, 27.4; Mg, 7.5; Mn, 19.2%).

A portion of the above solid was suspended in toluene (10 cm$^3$) and an excess of *NNN′N′*-tetramethylethylenediamine was added to it. The red suspension was stirred for 30 min, allowed to settle, and was then filtered. The filtrate was evaporated to dryness to give a yellow solid. This was twice crystallised from a small quantity of toluene to give a yellow *solid* (Found: C, 39.3; H, 9.0; Cl, 7.4; Mg, 1.0; Mn, 30.0; N, 12.6%).

*Reaction of Diphenylmagnesium and Manganese*(II) *Bromide*.—Diphenylmagnesium (8.5 cm$^3$ of a 0.5M-diethyl ether solution, 0.013 mol) was added to manganese(II) bromide (1.8 g, 0.0084 mol) suspended in diethyl ether (100 cm$^3$). The yellow-green suspension turned slowly to brown-yellow after being stirred for 1 d. The diethyl ether was removed *in vacuo* and the green-brown solid was washed with diethyl ether (4 × 50 cm$^3$) and then tetrahydrofuran (4 × 50 cm$^3$). The green tetrahydrofuran washings were combined and cooled to −20 °C. The green *solid* that slowly formed was collected, washed with a small amount of tetrahydrofuran, and pumped *in vacuo* for 2 h (Found: C, 35.2; H, 3.6; Br, 35.4; Mg, 2.5; Mn, 11.7%).

A portion of the green solid was suspended in toluene (5 cm$^3$) and pyridine (10 cm$^3$) was added to it. The red solution was boiled, filtered, and cooled slowly to room temperature to yield light coloured *needles* shown to be $MnBr_2(py)_2$ by analysis (Found: C, 32.7; H, 2.7; Br, 43.6; N, 7.1%. $C_{10}H_{10}Br_2MnN_2$ requires C, 32.2; H, 2.7; Br, 42.9; N, 7.5%).

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