The Chemistry of Manganese Alkyls and Aryls

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The formation of Mn^{II} alkyls by the interaction of manganous halides with alkylating reagents was first reported by Gilman, but the organometallic products were neither isolated nor characterized [1,2]. Later, Kochi, et. al. compared the rates of decomposition of manganese(II) alkyls prepared *in situ* by the action of Grignard reagents on manganese dichloride [3]. They obtained some of the first evidence that β-elimination followed by alkene dissociation was the principal decomposition route for alkyls that contain β-hydrogen atoms. Two β-stabilized tetra-alkyl manganates of stoichiometry $Li_2[MnR_4]$ (R = Me and CH_2SiMe_3) were subsequently prepared and characterized by EPR spectroscopy [4]. In contrast with the well-established organometallic chemistry of low-valent manganese, there are only five manganese alkyl complexes of oxidation state +3 or higher. Bower and Tennent reported the isolation of the tetravalent species $Mn(1\text{-norbornyl})_4$ [5], while Wilkinson prepared three other thermally unstable MnR_4 complexes (R = CH_2CMe_3, CH_2SiMe_3, and CH_2CMe_2Ph) and $MnMe_4(dmpe)$ (dmpe = 1,2-bis(dimethylphosphino)ethane [4,6]. Very recently, Jonas has reported the Mn^{III} bis-metallacycle $[K(py)_2][Mn(C_4H_8)_2(py)]$ [7].

The reaction of $MnCl_2$ with 4 equiv. of an organolithium reagent followed by the addition of N, N, N', N'-tetramethylethylenediamine (tmed) gives a series of tetraalkyl manganate(II) complexes of stoichiometry $[Li(tmed)]_2[MnR_4]$ (R = Me, Et, CH_2CH_2-t-Bu, n-Bu, CH_2SiMe_3, and Ph) in good yields [8]. The EPR spectra of these complexes are consistent with the presence of high-spin d^5 tetrahedral manganese centers which are rhombically distorted. The molecular structures of the methyl, ethyl, and neohexyl complexes are the first transition metal peralkyls which contain β-hydrogen atoms to be structurally characterized. The molecular structure of $[Li(tmed)]_2[MnEt_4]$ (Figure 1) is representative of the other two analogues.

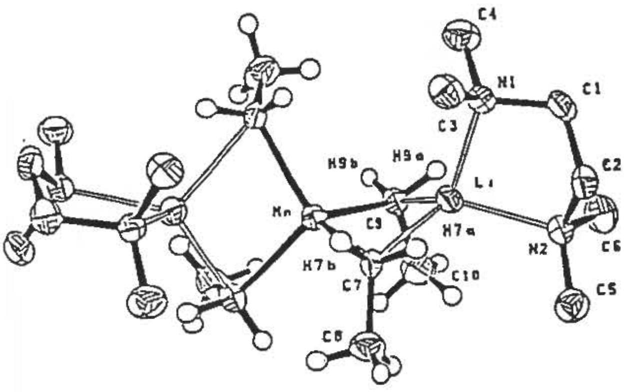

Figure 1

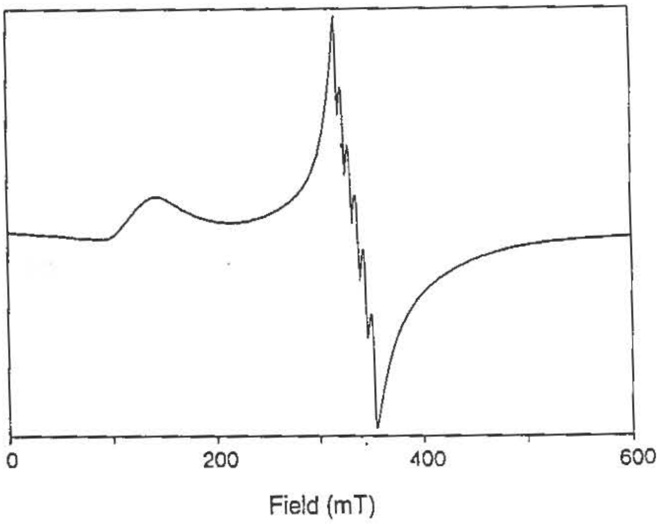

Figure 2

The addition of 2 equiv. of methyllithium to $MnMe_4(dmpe)$ [6] followed by treatment with tmed gives the first tetravalent peralkyl manganate, $[Li(tmed)]_2[MnMe_6]$, in good yield [9]. This high-spin d^3 species exhibits a slightly rhombically distorted EPR spectrum (Figure 2). The molecular structure of this organomanganese(IV) species reveals an octahedron of methyl groups around the manganese center with the Li(tmed) cations capping two opposing faces of the octahedron (Figure 3). This tetravalent species reacts with the divalent species $[Li(tmed)]_2[MnMe_4]$ in diethyl ether to give the trivalent permethyl manganate $[Li(tmed)]_2[MnMe_5]$ in a comproportionation reaction [9]. If the comproportionation is performed in toluene, the product is the tetramethyl manganate(III) species $[Li(tmed)_2][MnMe_4]$ [10]. The molecular structure of this species reveals a slightly distorted square-planar geometry around the manganese center.

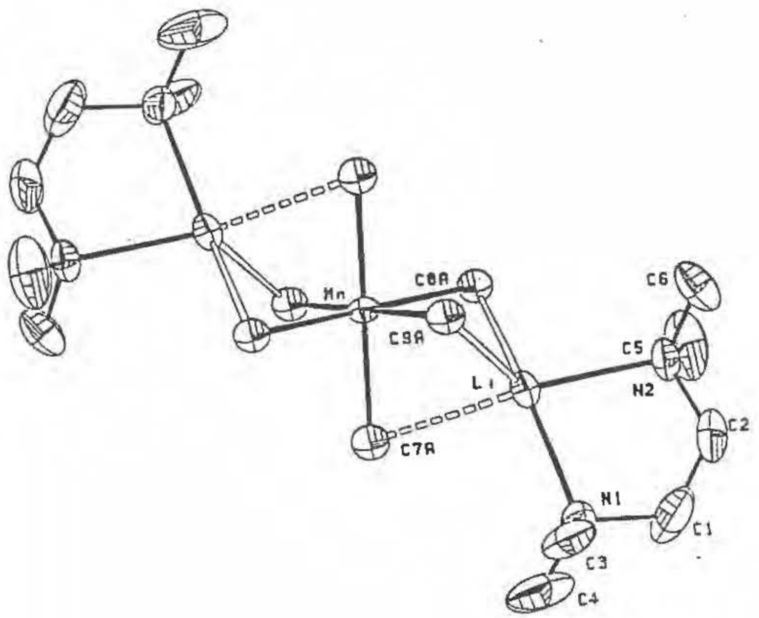

Figure 3

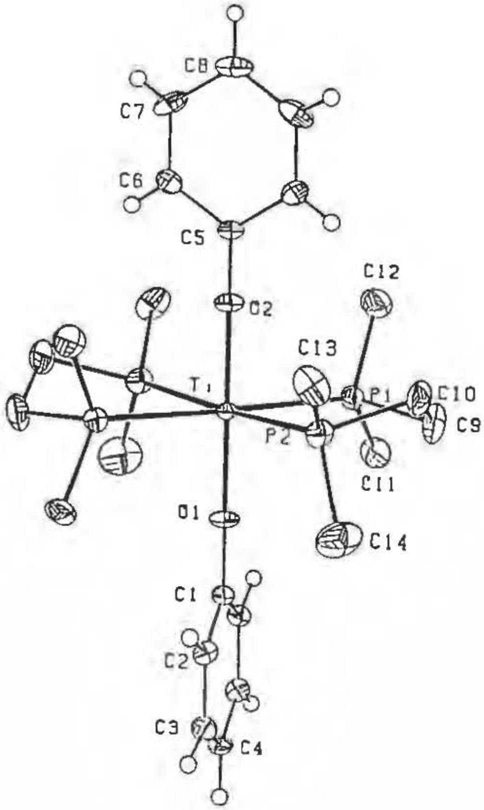

Figure 4

The interaction of manganous halides with 1/2 equiv. of the diarylmagnesium reagent $MgMes_2(thf)_2$ and 2 equiv. of trimethylphosphine in diethyl ether followed the addition of dry dioxygen leads to the isolation of a series of trivalent arylmanganese(III) species of stoichiometry $Mn(Mes)X_2(PMe_3)_2$ (X = Cl, Br, and I) [10,11]. The molecular structure of $Mn(Mes)Br_2(PMe_3)_2$ is a slightly distorted trigonal bipyramid with the phosphine ligands occupying the axial positions. These complexes are the only known manganese(III) aryls. Treatment of $Mn(acac)_3$ with 5 equiv. of LiMe leads to the isolation of the first oxo-alkyl of manganese which has the stoichiometry $\{Li_2[MnOMe_3]\cdot 2Li_2(OCMe{=}CHCMe_2O)\cdot tmed\}_2$ [12]. The molecular geometry around the Mn^{III} center is also a slightly distorted square-plane.

Treatment of Ti$(BH_4)_2$(dmpe)$_2$ with 2 equiv. of sodium phenoxide in tetrahydrofuran gives Ti(OPh)$_2$(dmpe)$_2$ which is the first divalent titanium aryloxide or alkoxide of any kind. The molecular structure of this complex is an octahedron where the trans phenoxide ligands are mutually orthogonal (Figure 4). Similarly, the monophenoxide species Ti(OPh)Cl(dmpe)$_2$ can be prepared from $TiCl_2$(dmpe)$_2$ and sodium phenoxide. Along with $TiMe_2$(dmpe)$_2$, these three compounds are the only octahedral d^2 metal centers of the first-row transition series to exhibit spin-pairing within the t_{2g} manifold; the complexes are *diamagnetic*. The spin-pairing of the two d-electrons in $TiMe_2$(dmpe)$_2$ is the result of π-donation from the reduced titanium center to the trialkylphosphines; the spin-pairing in the phenoxide complexes is due to π-donation from the phenoxide groups [13].

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