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Preliminary communication

Preparation of cationic dimethylmanganese(III) complexes having 1,2-bis(dimethylphosphino)ethane ligands. α-Hydrogen elimination

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Abstract

The stable paramagnetic dimethylbis(1,2-bis(dimethylphosphino)ethane)manganese(III) tetramethylaluminate (**1**) has been prepared by the reaction of tris(2,4-pentanedionato)manganese(III) with trimethylaluminum in the presence of 1,2-bis(dimethylphosphino)ethane ligand. Ion exchange reaction of **1** with sodium tetraphenylborate gives the corresponding dimethylmanganese(III) cation (**2**). α-Hydrogen elimination in the thermolysis is proposed.

Although tertiary phosphine ligands are well known as stabilizing ligands for transition metal alkyls, up to now, only a few examples of alkylmanganese complexes containing tertiary phosphine ligands have been described [1]. Thus, homoleptic dialkyl- or diaryl-manganese(II) species are trapped as MnR_2L_n, were L represents a tertiary phosphine ligand such as tricyclohexylphosphine [2] and 1,2-bis(dimethylphoshphino)ethane (dmpe) [3]. So far, most of the isolated organomanganese complexes such as above and organomanganese carbonyls generally have relatively low oxidation states such as I and II. In contrast, high valence organomanganese complexes, which are of interest for their possible unusual reactivities, are scarce except for $Mn^{IV}Me_4$(dmpe) [4] and $Mn^{IV}(nor)_4$ [5]. Alkylation of manganese(III) with MeLi is reported to give a mixture of manganese(II) and manganese(IV) species [4] and no organomanganese(III) complexes have been isolated, except for $Mn^{III}Br_2(C_6H_2Me_3)(PMe_3)_2$ [6] described very recently. We now report the isolation of novel dimethylmanganese(III) cationic complexes having dmpe ligands by the reaction of $Mn(acac)_3$ with trimethylaluminum in the presence of dmpe ligand.

Treatment of tris(2,4-pentanedionato)manganese(III) with an excess of trimethylaluminum in the presence of 2 equivalents of dmpe in ether at −40 °C gave a red precipitate, **1**, which was recrystallized from THF/ether as deep-red prisms. Com-

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plex **1** was characterized as dimethylbis(1,2-bis(dimethylphosphino)ethane)manganese(III) tetramethylaluminate by IR, magnetic susceptibility and elemental analysis as well as by chemical reactions. Yield 45%. M.p. 195 °C (dec.). Anal. Found: C, 45.41; H, 11.06; Mn, 12.5. $C_{18}H_{50}AlP_4Mn$ calcd.: C, 45.76; H, 10.67; Mn, 11.6%.

$$\mathrm{Mn(acac)_3} + \underset{\text{excess}}{\mathrm{AlMe_3}} + \mathrm{2dmpe} \rightarrow \underset{(\mathbf{1})}{[\mathrm{MnMe_2(dmpe)_2}]^+\ [\mathrm{AlMe_4}]^-}$$

Ion exchange reaction of **1** with $NaBPh_4$ in THF readily gave $[MnMe_2(dmpe)_2]^+$ BPh_4^- (**2**), which was purified by recrystallization from acetone as red prisms, thus supporting the cationic structure of **1**. Yield 46%. M.p. 173 °C (dec.). Anal. Found: C, 64.05; H, 8.25; Mn, 8.12. $C_{38}H_{58}BP_4Mn$ calcd.: C, 64.78; H, 8.30; Mn, 7.80%.

$$\mathbf{1} + \mathrm{NaBPh_4} \rightarrow \underset{(\mathbf{4})}{[\mathrm{MnMe_2(dmpe)_2}]^+\ \mathrm{BPh_4}^-}$$

The IR spectrum of **1** shows characteristic strong bands due to $AlMe_4^-$ at 693 and 542 cm^{-1} and a band attributable to ν(Mn–Me) at 455 cm^{-1}. In the IR spectrum of **2** peaks due to aluminate anion disappeared, whereas the peak at 455 cm^{-1} remains. The large molar electric conductivities of **1** and **2** in dry THF (18 and 45 S cm^2 mol^{-1} for **1** and **2**, respectively) supports their ionic structure. Magnetic susceptibilities of Mn in **1** and **2** were 3.15 and 3.02 BM, respectively. The values correspond to two unpaired electrons in Mn, which suggests that both complexes have low spin octahedral structure.

The formation of the dimethylmanganese(III) complex, which has tetramethylaluminate anion, in the present reaction is interpreted in terms of methyl back transfer from possible trimethylmanganese(III) species to trimethylaluminium. Similar transfer of methyl group from transition metal to aluminum moiety has been seen in the case of cobalt [7], and iron complexes [8].

$$\begin{tikzcd}
\mathrm{Mn(acac)_3} + \mathrm{AlMe_3} + \mathrm{dmpe} \arrow[r] & {[\mathrm{MnMe_3(dmpe)}_n]} \arrow[d, "+\ \mathrm{AlMe_3}"] \\
 & {[\mathrm{MnMe_2(dmpe)_2}]^+\,[\mathrm{AlMe_4}]^-}
\end{tikzcd}$$

Some chemical reactions of **1** and **2** are listed in Table 1. Acidolysis of **1** and **2** with concentrated sulfuric acid liberated methane and ethane. Iodolysis gave iodomethane in both cases. The amounts generated also support the stoichiometry of **1** and **2**. Thermolysis of **2** in DMSO at 80 °C liberated methane and ethylene and a small amount of ethane. The generation of ethylene and methane in a 1/2 ratio in the thermolysis of **2** is noteworthy. The gases evolved during thermolysis of **2** in DMSO-d_6 contained no deuterium. The results are best interpreted on the assump-

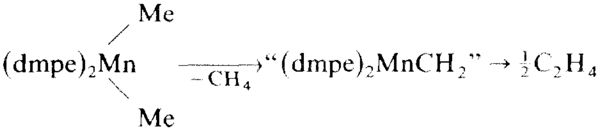
Table 1

Acidolysis, iodolysis and thermolysis of **1** and **2** (Values indicate the amount per mol of Mn)

	Acidolysis [a]		Iodolysis [b]		Thermolysis [c]		
	CH_4	C_2H_6	CH_3I	CH_4	CH_4	C_2H_4	C_2H_6
1	4.91	0.31	4.67	0.86	3.95	0.16	0.05
2	1.05	0.20	1.84	0.07	1.05	0.45	0.08

[a] In concentrated H_2SO_4. [b] In THF. [c] **1**: in solid state at 195 °C. **2**: in DMSO at 80 °C.

tion that intramolecular α-hydrogen elimination from one of the methyl groups attached to manganese(III) by another methyl group takes places to give methane and carbene species which spontaneously give ethylene. Similar α-hydrogen elimination reactions have been reported during the thermolysis of dimethyliron(II) complex [9].



$$(\text{dmpe})_2\underset{\text{Me}}{\overset{\text{Me}}{\text{Mn}}} \xrightarrow[-\text{CH}_4]{} \text{“}(\text{dmpe})_2\text{MnCH}_2\text{”} \rightarrow \tfrac{1}{2}\text{C}_2\text{H}_4$$

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