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Preliminary communication

Alkylmanganese pentacarbonyls

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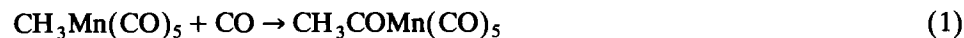
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Abstract

The new alkyl manganese pentacarbonyl complexes $\text{RMn}(\text{CO})_5$ ($\text{R} = \text{n-C}_4\text{H}_9$ to $\text{n-C}_{18}\text{H}_{37}$) have been prepared, and found to show relatively high air and thermal stability.

Methylmanganese pentacarbonyl was the first metal carbonyl alkyl complex to be prepared and characterised [1]. Its reaction with CO to give an acyl species is

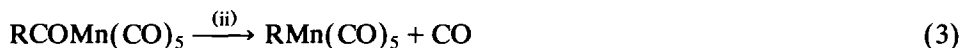
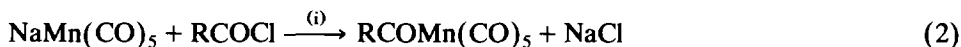


the classic example of a CO insertion/alkyl migration reaction. This reaction is of fundamental importance and is a key step in many catalytic reactions. The reaction shown in eq. 1 (and the reverse reaction, *i.e.* decarbonylation) has been much studied [2,3] and used as a model for alkyl migration reactions in general.

It is important to know how the nature of the alkyl group affects the alkyl migration reaction and its reverse. Berke and Hoffmann on the basis of a molecular orbital study, predicted that the alkyl migration will depend on the chain length of the alkyl group [4]. There are several reports of rate studies on alkyl migrations for $\text{RMn}(\text{CO})_5$ and decarbonylation for $\text{RCOMn}(\text{CO})_5$, but these studies were limited to *n*-alkyl groups having no more than three carbon atoms [5]. Although $\text{CH}_3\text{Mn}(\text{CO})_5$ is air and thermally stable, $\text{C}_2\text{H}_5\text{Mn}(\text{CO})_5$ has been reported to be "very unstable both thermally and to atmospheric oxidation . . . , pure samples decomposed slowly even when kept in the dark, in vacuum and at -10°C " [6]; $\text{n-C}_3\text{H}_7\text{Mn}(\text{CO})_5$ has been described as even less stable. The use of the trimethylsilylmethyl group has been reported to result in more stable alkyl complexes because the β -elimination reaction is effectively blocked; thus the observation that $(\text{CH}_3)_3\text{SiCH}_2\text{Mn}(\text{CO})_5$ is more stable than $\text{C}_2\text{H}_5\text{Mn}(\text{CO})_5$ was attributed to the lack of β -hydrogens in the former complex [7].

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We now describe the synthesis, characterisation and some properties of alkyl-manganese pentacarbonyls with medium and long chain alkyl groups. The new alkyl complexes were prepared by the two-step route:



((i) = room temperature in THF for 2 h; (ii) = reflux in hexane; R = n-C₄H₉ to n-C₁₈H₃₇)

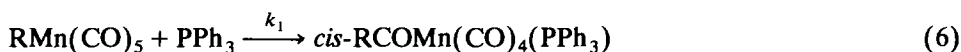
Full characterisation data have been obtained for selected acyl and alkyl complexes*.

The new alkylmanganese pentacarbonyls show surprisingly high air and thermal stability compared with their ethyl and propyl homologues (for example n-C₁₈H₃₇Mn(CO)₅ is an off-white crystalline solid, m.p. 42–44°C, that can be handled in air and kept for several months at 0°C without significant decomposition). Since all of the complexes RMn(CO)₅ (R = C₂H₅ to n-C₁₈H₃₇) contain β-hydrogens it appears unlikely that the β-elimination reaction is the main source of the instability of the short chain compounds. Instead, the instability of the ethyl and propyl complexes may be a consequence of the rates of alkyl migration and of the decarbonylation of the acyl intermediates:



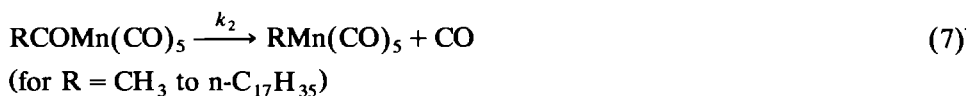
(where S is solvent or coordinating species)

Thus for the ethyl and propyl complexes, the rate of reaction 4 may be fast and 5 significant; CO can thus be produced, which reacts with C₂H₅COMn(CO)₄S to give C₂H₅COMn(CO)₅, which is one of the decomposition products of CH₃CH₂Mn(CO)₅ [6]. We have measured the rates of the following reactions**:



* For example: n-C₆H₁₃COMn(CO)₅ was obtained as colourless crystals in 40% yield; m.p. 28–30°C; %C, 47.3 (46.8), %H, 4.5 (4.3) (calc. values in parentheses); IR (hexane) ν(CO) 2112w, 2048w, 2006vs, 2000s, 1658 w cm⁻¹; ¹H NMR (CDCl₃) δ 2.89t(Mn–C(O)CH₂), 1.45m (Mn–C(CO)CH₂CH₂) 1.22s (–(CH₂)₂–), 0.84s (–CH₃); ¹³C NMR (CDCl₃) δ 210 (CO) 67.30 (C₁, i.e. Mn–C(O)CH₂) 31.53 (C₂) 28.50 (C₃) 24.28 (C₄) 22.38 (C₅) 13.86 (CH₃); the mass spectrum showed a parent molecular ion at m/e 308 with peaks corresponding to successive fragmentation of six carbonyl groups, followed by sequential loss of methylene fragments and n-C₆H₁₃Mn(CO)₅ was obtained as an almost colourless oil in 78% yield: %C, 52.3 (52.2), %H, 5.8 (5.9); IR (hexane) ν(CO) 2104w, 2006s, 1988m cm⁻¹; ¹H NMR (CDCl₃) δ 1.66 (Mn–CH₂), 1.27 (–(CH₂)₇–), 0.90 (–CH₃); ¹³C NMR (CDCl₃) δ 210 (CO) δ 6.93 (C₁, i.e. Mn–CH₂) 37.21 (C₂) 35.60 (C₃) 31.74 (C₄) 29.55 (C₅) 29.25 (C₆) 29.12 (C₇) 22.56 (C₈) 13.89 (CH₃); the mass spectrum showed a parent molecular ion at m/e 322 with peaks corresponding to successive fragmentation of five carbonyl groups followed by sequential loss of methylene fragments.

** For example, k₁ in eq. 6 for R = C₂H₅ is 3.26 × 10⁻⁴ sec⁻¹ M⁻¹ but for n-C₁₇H₃₅ it is 1.85 × 10⁻⁴ sec⁻¹ M⁻¹ at 32°C in hexane; k₂ in eq. 7 for R = C₂H₅ is 2.00 × 10⁻⁴ sec⁻¹ but for R = n-C₁₇H₃₅ it is 0.70 × 10⁻⁴ sec⁻¹ at 55.5°C in hexane.



Indeed, we find that the rates of reactions 6 and 7 for R = C₂H₅ or n-C₃H₇ are faster than those for the same reactions with either the long chain complexes or for R = CH₃. We thus suggest that for the long chain alkyls and for CH₃Mn(CO)₅, little CO is produced by decarbonylation and hence conversion of RMn(CO)₅ into RCOMn(CO)₅ is not observed under these conditions. In addition, we suggest that these and other long chain alkyl complexes such as CpM(CO)₂R (M = Fe or Ru) [8] are more stable because of the slowing down of any intermolecular process that may lead to decomposition.

We are at present investigating the properties and chemistry of these and other long chain alkyl complexes.

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