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Preliminary communication

Alkylmanganese pentacarbonyls

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Abstract

The new alkyl manganese pentacarbonyl complexes $RMn(CO)_5$ ($R = n\text{-}C_4H_9$ to $n\text{-}C_{18}H_{37}$) 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

$$CH_3Mn(CO)_5 + CO \rightarrow CH_3COMn(CO)_5 \qquad (1)$$

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 $RMn(CO)_5$ and decarbonylation for $RCOMn(CO)_5$, but these studies were limited to n-alkyl groups having no more than three carbon atoms [5]. Although $CH_3Mn(CO)_5$ is air and thermally stable, $C_2H_5Mn(CO)_5$ 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]; $n\text{-}C_3H_7Mn(CO)_5$ 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 $(CH_3)_3SiCH_2Mn(CO)_5$ is more stable than $C_2H_5Mn(CO)_5$ 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 alkylmanganese pentacarbonyls with medium and long chain alkyl groups. The new alkyl complexes were prepared by the two-step route:

$$\mathrm{NaMn(CO)_5 + RCOCl \xrightarrow{(i)} RCOMn(CO)_5 + NaCl} \qquad (2)$$

$$\mathrm{RCOMn(CO)_5 \xrightarrow{(ii)} RMn(CO)_5 + CO} \qquad (3)$$

((i) = room temperature in THF for 2 h; (ii) = reflux in hexane; R = n-C_4H_9 to n-$C_{18}H_{37}$)

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-$C_{18}H_{37}Mn(CO)_5$ 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 = C_2H_5 to n-$C_{18}H_{37}$) 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:

$$\mathrm{RMn(CO)_5 \xrightarrow{S} RCOMn(CO)_4S} \qquad (4)$$

$$\mathrm{RCOMn(CO)_4S \longrightarrow RMn(CO)_4S + CO} \qquad (5)$$

(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 $C_2H_5COMn(CO)_4S$ to give $C_2H_5COMn(CO)_5$, which is one of the decomposition products of $CH_3CH_2Mn(CO)_5$ [6]. We have measured the rates of the following reactions **:

$$\mathrm{RMn(CO)_5 + PPh_3 \xrightarrow{k_1}} \textit{cis}\text{-}\mathrm{RCOMn(CO)_4(PPh_3)} \qquad (6)$$

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* For example: n-$C_6H_{13}COMn(CO)_5$ 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}; ^{1}H NMR ($CDCl_3$) δ2.89t(Mn–C(O)CH_2), 1.45m (Mn–C(CO)CH_2CH_2) 1.22s (–$(CH_2)_2$–), 0.84s (–CH_3); ^{13}C NMR ($CDCl_3$) δ 210 (CO) 67.30 (C_1, *i.e.* Mn–C(O)CH_2) 31.53 (C_2) 28.50 (C_3) 24.28 (C_4) 22.38 (C_5) 13.86 (CH_3); 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-$C_9H_{19}Mn(CO)_5$ 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}; ^{1}H NMR ($CDCl_3$) δ 1.66 (Mn–CH_2), 1.27 (–$(CH_2)_7$–), 0.90 (–CH_3); ^{13}C NMR ($CDCl_3$) δ 210 (CO) δ 6.93 (C_1, *i.e.* Mn–CH_2) 37.21 (C_2) 35.60 (C_3) 31.74 (C_4) 29.55 (C_5) 29.25 (C_6) 29.12 (C_7) 22.56 (C_8) 13.89 (CH_3); 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, k_1 in eq. 6 for R = C_2H_5 is 3.26×10^{-4} sec^{-1} M^{-1} but for n-$C_{17}H_{35}$ it is 1.85×10^{-4} sec^{-1} M^{-1} at 32°C in hexane; k_2 in eq. 7 for R = C_2H_5 is 2.00×10^{-4} sec^{-1} but for R = n-$C_{17}H_{35}$ it is 0.70×10^{-4} sec^{-1} at 55.5°C in hexane.

$$RCOMn(CO)_5 \xrightarrow{k_2} RMn(CO)_5 + CO \qquad (7)$$

(for $R = CH_3$ to n-$C_{17}H_{35}$)

Indeed, we find that the rates of reactions 6 and 7 for $R = C_2H_5$ or n-C_3H_7 are faster than those for the same reactions with either the long chain complexes or for $R = CH_3$. We thus suggest that for the long chain alkyls and for $CH_3Mn(CO)_5$, 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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