Carbon monoxide insertion reactions

III. Reactions of methylmanganese pentacarbonyl and acetylmanganese pentacarbonyl with nucleophiles*

Methylmanganese pentacarbonyl is known to react with uncharged nucleophilic reagents giving the carbonyl insertion reaction

$$CH_3Mn(CO)_5 + L \rightleftharpoons CH_3COMn(CO)_4L \qquad (1)$$

This reaction has been kinetically studied with L is carbon monoxide[1], triphenylphosphine[2,3] and amines[3].

The same products of the type $CH_3COMn(CO)_4L$ can be obtained from acetylmanganese pentacarbonyl with evolution of carbon monoxide:

$$CH_3COMn(CO)_5 + L \rightleftharpoons CH_3COMn(CO)_4L + CO \qquad (2)$$

Kinetic results for this latter reaction have been obtained with L is triphenylphosphine[2] and amines[4].

We now wish to report the results of a further extension of reactions (1) and (2) to charged nucleophiles, such as I^- in the form of lithium iodide. The anionic acetylmanganese tetracarbonyl complex $[CH_3COMnI(CO)_4]^-$ is thus obtained as the lithium salt.

$$CH_3Mn(CO)_5 + LiI \rightleftharpoons Li[CH_3COMnI(CO)_4] \qquad (3)$$

$$CH_3COMn(CO)_5 + LiI \rightleftharpoons Li[CH_3COMnI(CO)_4] + CO \qquad (4)$$

Methylmanganese pentacarbonyl (0.58 g, 2.76 mmoles) was dissolved in diethyl ether (2 ml) and added under nitrogen at room temperature to anhydrous lithium iodide (2.23 mmoles) dissolved in 3 ml of diethyl ether. The resulting solution became orange-red in a few minutes. After about 1 h the reaction was virtually finished and the solvent evaporated *in vacuo*. The solid residue was dried in high vacuum, washed with heptane, filtered and dried again (0.66 g, 86% yield based on the LiI employed). After crystallization from heptane–ether, the compound was obtained as orange-red crystals, which were maintained in high vacuum at room temperature for 6 h. (Found: C, 20.68, 21.50; H, 1.10, 1.24; I, 36.52. $C_6H_3ILiMnO_5$ calcd.: C, 20.96; H, 0.88; I, 36.90%.) If the compound was prepared similarly but without the final stage in high vacuum, the corresponding etherate $Li[CH_3COMnI(CO)_4]\cdot(C_2H_5)_2O$ was obtained. (Found: C, 28.25; H, 3.28; I, 30.79. $C_{10}H_{13}ILiMnO_6$ calcd.: C, 28.73; H, 3.13; I, 30.36%.) The presence of the ether was also established spectroscopically on CCl_4 solutions of the compound and after decomposition by air. Both compounds are hygroscopic and sensitive to air. They are very slightly soluble in heptane and carbon tetrachloride and very soluble in tetrahydrofuran and diethyl ether. They are readily decomposed by water to give $CH_3Mn(CO)_5$ and LiI. The infrared bands in tetrahydrofuran solution in the carbonyl stretching region, with relative intensities (optical densities) in parenthesis are: 2059 (29), 2007, doublet at 1975 and 1967 (100), 1920 (75), ~ 1590 (sh), 1566 (16) cm^{-1}. The band at 2007 cm^{-1} was shown to be due to some $CH_3Mn(CO)_5$ present in solution as the result of the reverse of reaction (3). By addition of an excess of LiI the equilibrium was shifted to the right and the band disappeared.

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* For Part II see Ref. 2.

The 1566 cm^{-1} band is attributed to the C–O stretching vibration of the acetyl group.

The infrared bands of the terminal CO groups of Li[$CH_3COMnI(CO)_4$] are not very far from those of the amine derivative $CH_3COMn(CO)_4NH_2C_6H_{11}$, for which bands at 2050, 2000, 1961 and 1927 cm^{-1} have been reported[3]. This suggests that in the complex described in this paper the negative charge is largely concentrated on the iodide ligand, the manganese atom being substantially in a zero oxidation state. Some transfer of negative charge must, however, take place and this is evidenced by the appearance of the more intense ketonic C–O stretching vibration at an unusually low wavenumber (1566 cm^{-1}). For the above mentioned cyclohexylamine compound this band appears at 1608 cm^{-1}, for $CH_3COMn(CO)_5$[5] at 1657 cm^{-1} and for $CF_3COMn(CO)_5$[5] at 1671 cm^{-1} (CCl_4 as solvent in all cases).

If reaction (3) is followed spectroscopically the new four bands reported above are observed, and no relevant changes of the spectrum occur at constant temperature even over long periods (one day) after completion of the reaction. This is also true at high ratios LiI/$CH_3Mn(CO)_5$, suggesting the absence of secondary reactions. Hence the system LiI/$CH_3Mn(CO)_5$ appears to be more simple and therefore more convenient to study than the similar reaction of $CH_3Mn(CO)_5$ with triphenylphosphine[2].

The presence of four bands in the terminal CO stretching region for the anion [$CH_3COMnI(CO)_4$]$^-$ would suggest that this has a *cis*-configuration for which four infrared active bands are expected. However, a more careful examination of the infrared spectrum reveals that at the end of reaction both *cis*- and *trans*-isomers are probably present in solution at temperatures between 10 and 50°. This is suggested by the fact that the relative intensities of the two bands at 1975 and 1967 cm^{-1} are not constant but vary either during the course of reaction (3), or by measuring the spectra of Li[$CH_3COMnI(CO)_4$] at different temperatures. Furthermore, a second ketonic C–O stretching vibration at about 1590 cm^{-1} is also observed as a shoulder in the infrared spectrum of [$CH_3COMnI(CO)_4$]$^-$ in addition to the main band at 1566 cm^{-1}. Furthermore, reaction (3) was run in polar deuterated solvents and the proton resonance spectra measured at room temperature, showing the presence of two sharp singlets of unequal intensities at 7.43 and 7.87 τ (in deuterated dimethyl sulphoxide) and at 7.21 and 7.81 τ (in deuterated acetone). Two sharp singlets of unequal intensities at 7.30 and 7.63 τ are also given by a $CDCl_3$ solution of $CH_3COMn \cdot (CO)_4P(C_6H_5)_3$ obtained by reaction (1) from $CH_3Mn(CO)_5$ and triphenylphosphine[2,3]. Weak proton resonances due to $CH_3Mn(CO)_5$ in equilibrium with the products were observed at about 10.1 τ. Since $CH_3COMn(CO)_5$ gives, as expected, only one single peak at 7.40 τ both in $CDCl_3$ and CD_3COCD_3, the previous results are consistent with the presence in solution of *cis*- and *trans*-species of the type [$CH_3COMnL(CO)_4$] with L = I$^-$ or $P(C_6H_5)_3$. All the reported chemical shifts are from TMS, the limit of accuracy being estimated to ± 0.03 τ.

Reaction (4) was also shown to take place. The kinetics of both reactions (3) and (4) have been studied and the results will be reported soon. Infrared evidence indicates that reactions similar to (3) also occur with other charged nucleophiles such as OCH_3^-, SCN^-, CN^-.

The present results open a new route to the preparation of anionic metal carbonyl complexes containing metal–carbon bonds. It is interesting to note that by a reaction which is probably, from a mechanistic point of view, strictly related to that presented in this paper, anionic alkylmetal carbonyls of the type [$W(CO)_5COR$]$^-$

were first obtained by treating $W(CO)_6$ with lithium alkyls[6]. The extension of reactions (1) and (2) initially using carbon monoxide, phosphines and amines, to other nucleophiles of completely different nature substantiates the generality of these reactions. The kinetic study of these new reactions should lead to a better understanding of the general problem of the carbon monoxide insertion reactions.

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The ^{7}Li nuclear quadrupole coupling constants of methyl- and ethyllithium

The structures of crystalline ethyllithium[1] and methyllithium[2] determined by X-ray crystallography show that the molecule is a tetramer in which, for the methyl compound, the lithium atoms lie at the apices of a regular tetrahedron and the four carbon atoms lie vertically above the center of each face. The structure of the ethyl compound is a distorted version of this in which one of the lithium–carbon distances is much longer than the other two while one of the lithium–lithium distances is much shorter.

In hydrocarbon solvents alkyllithiums are also associated, usually to tetramers and hexamers[3]. These molecules are thus electron-deficient and the electron distribution in them is of interest. In the hope that their ^{7}Li nuclear quadrupole coupling constants would be relevant to this problem the ^{7}Li nuclear magnetic resonance spectra of polycrystalline samples of these compounds have been measured and the results are reported here. The nuclear magnetic resonance spectrum of a polycrystalline sample of a compound in which the nucleus under study has a quadrupole coupling constant, eQq, is a central line flanked symmetrically by either two satellites whose separation in cycles/sec is approximately given by $\frac{1}{2}\, eQq$ when the field gradient at the nucleus has cylindrical symmetry or, when the field gradient has an asymmetry parameter η, by two pairs of satellites separated by $\frac{1}{2}\, eQq\ (1 - \eta)$ and $\frac{1}{2}\, eQq\ (1 + \eta)$ (ref. 4). The ^{7}Li nuclear magnetic resonance spectra of methyl- and ethyllithium at 14.7 kilogauss and 25° are shown in Figs. 1 (a) and (b) respectively.

The crystal structure of methyllithium shows that there is only one kind of lithium atom in the crystal and that the field gradient tensor is necessarily cylindrically symmetric. Its spectrum shows no visible structure so that either the coupling