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Abstract

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CHLOROMETHYL- AND ALKOXYMETHYL-CYCLOPENTADIENYLMANGANESE TRICARBONYL

We have already reported that cyclopentadienylmanganese tricarbonyl reacts with paraformaldehyde and hydrogen chloride in the presence of anhydrous zinc chloride in carbon tetrachloride, with formation of chloromethylcyclopentadienylmanganese tricarbonyl ([1]). In the present work it is shown that, on interaction of cyclopentadienylmanganese tricarbonyl with chloromethyl ether in the presence of stannic chloride in a methylene chloride medium, chloromethyl- and bis-chloromethylcyclopentadienylmanganese tricarbonyl are formed; these are separated by distillation in vacuo and, on standing, are converted into crystalline substances, which had not previously been observed. These compounds dissolve well in organic solvents and are not hydrolyzed by water.

From monochloromethylcyclopentadienylmanganese tricarbonyl and sodium alcoholates, simple ethers were obtained: methoxy-, ethoxy-, propoxy-, butoxy-, allyloxy-, and benzyloxymethylcyclopentadienylmanganese tricarbonyl

$$\begin{array}{c}\text{(cyclopentadienyl ring)-Mn(CO)}_3\\ |\\ \text{CH}_2\text{Cl}\end{array} + \text{RONa} \longrightarrow \begin{array}{c}\text{(cyclopentadienyl ring)-Mn(CO)}_3\\ |\\ \text{CH}_2\text{OR}\end{array} + \text{NaCl}$$

The synthesized ethers are light-yellow liquids, soluble in organic solvents but insoluble in water; in the light they slowly decompose.

Infrared spectra were recorded for the compounds. In the spectra of this series of compounds, frequencies are observed that are characteristic of the spectrum of cyclopentadienylmanganese tricarbonyl: CH 3100–3120 cm^{-1}, $Mn(CO)_3$ 2017–2020 cm^{-1}, 1910–1925 cm^{-1}. In addition to these general vibrational frequencies, there are characteristic vibrational frequencies of the functional groups. Thus, for the simple ethers, intense bands occur in the region 1080–1130 cm^{-1}. In the spectrum of the methyl ether there is a band at 2830 cm^{-1}, characteristic of C–H bonds in the methoxy group. In the spectrum of the allyl ether there is a band at 1665 cm^{-1}.

Experimental Part

Chloromethyl- and bischloromethylcyclopentadienylmanganese tricarbonyl. To a mixture of 51 g (0.25 mole) of cyclopentadienylmanganese tricarbonyl, 34.2 g (0.42 mole) of chloromethyl ether (²), and 100 ml of methylene chloride, with cooling in an ice bath and stirring, 20.8 g (0.08 mole) of stannic chloride was added dropwise over 10 min. After 30 min the cooling was discontinued; the mixture was stirred for another 3-4 hours and left overnight. After removal of the cooling, over the course of an hour the temperature of the reaction mixture rose to 30° and then began to fall. The reaction mixture was washed with water, with a 3% solution of sodium bicarbonate, and again twice with water, and dried over $MgSO_4$. The methylene chloride was distilled off; the residue was distilled in vacuo twice. In the first distillation at 1.5×10^{-2} mm Hg, one fraction was collected, boiling in the range 39-52.5°, which was again distilled in vacuum. The following fractions were isolated at $1 \cdot 10^{-2}$ mm Hg:

Fraction 1, b.p. 35-36°; 34.6 g (54.7%), n_D^{20} 1.6095; the next day yellow crystals, m.p. 29-30°.

$C_9H_{12}ClO_3Mn$.	Found, %: C 42.65, 42.50; H 2.49, 2.65; Cl 14.00, 14.20
	Calculated, %: C 42.80; H 2.40; Cl 14.04

IR spectrum* (ν, cm^{-1}) (paste in Vaseline oil):

455 (m), 490 (m), 583 (s), 605 (m), 635 (s), 685 (s), 705 (s), 740 (m), 764 (m), 775 (m), 842 (m), 903 (w), 925 (w), 935 (w), 1040 (m), 1048 (m), 1070 (w), 1135 (w), 1160 (w), 1210 (w), 1250 (m), 1273 (m), 1288 (m), 1382 (m), 1418 (w), 1420 (w), 1450 (m), 1468 (m), 1480 (w), 1490 (w), 1935 (s), 1952 (s), 2025 (s), 2027 (s), 2320 (w), 2322 (w), 2325 (w), 2330 (w), 2335 (w), 2345 (w), 2355 (w), 2360 (w), 2420 (w), 2455 (w), 2860 (m), 2930 (m), 2950 (m), 2960 (m), 3120 (w).

Fraction 2, b.p. 49-50°; 9.86 g (13.1%), n_D^{20} 1.6150; the next day light-yellow crystals, m.p. 45-46°.

$C_{10}H_7Cl_2O_3Mn$.	Found, %: C 40.04, 39.99; H 2.27; 2.29; Cl 23.72, 23.67
	Calculated, %: C 39.89; H 2.35; Cl 23.56

IR spectrum (ν, cm^{-1}) (paste in Vaseline oil):

418 (w), 475 (m), 490 (m), 535 (s), 583 (m), 613 (s), 635 (s), 676 (s), 707 (s), 750 (s), 758 (m), 763 (m), 842 (m), 852 (m), 857 (m), 860 (m), 895 (m), 903 (w), 912 (m), 920 (m), 950 (w), 952 (m), 982 (w), 1030 (m), 1047 (m), 1055 (m), 1097 (w), 1155 (m), 1247 (m), 1268 (s), 1275 (s), 1300 (m), 1318 (m), 1382

(m), 1443 (m), 1470 (s), 1900 (s), 1915 (s), 1925 (s), 1927 (s), 1937 (s), 1950 (s), 2005 (s), 2018 (s), 2028 (s), 2330 (m), 2350 (m), 2370 (m), 2380 (m), 2430 (m), 2440 (m), 2510 (m), 2520 (m), 2535 (m), 2560 (m), 2860 (s), 2865 (s), 2900 (s), 2930 (s), 2960 (s), 3020 (m), 3040 (m), 3110 (s), 3120 (m).

The residues after the first and second distillations are dark-brown in color and are viscous liquids that do not distill at the indicated reduced pressure and decompose when the temperature of the glycerin bath is raised (in this case the vacuum in the system sharply deteriorates).

Methoxymethylcyclopentadienylmanganese tricarbonyl. To a solution of sodium methylate (1.5 g of sodium in 40 ml of anhydrous alcohol) was added a solution of 15.2 g (0.06 mole) of the chloride in 10 ml of methyl alcohol; the mixture, with stirring, was heated on a glycerin bath and kept at 70-80° for 1 h and left overnight. The mixture was poured into 200 ml of water and extracted with 200 ml of ether. The extracts were dried over $MgSO_4$, and the ether was distilled off. The residue was distilled in vacuum; 13 g (87.4%) of a yellow liquid was obtained, which darkens in the light and is stable when stored in the dark and below 0°.

B.p. 25-26° ($1 \cdot 10^{-2}$ mm Hg), n_D^{20} 1.5755, d_4^{20} 1.3816.

$C_{10}H_9O_4Mn$. Found, %: C 48.51, 48.35; H 3.72, 3.80; Mn 21.29, 21.65
Calculated, %: C 48.40; H 3.67; Mn 22.13

IR spectrum (ν, cm^{-1}):

430 (w), 494 (w), 540 (s), 634 (s), 682 (s), 705 (s), 720 (s), 774 (w), 842 (m), 910 (m), 935 (w), 958 (m), 970 (m), 1038 (m), 1068 (m), 1100 (s), 1118 (s), 1160 (w), 1182 (m), 1196 (m), 1218 (w), 1248 (w), 1286 (w), 1350 (w), 1370 (w), 1395 (m), 1418 (m), 1457 (m), 1468 (m), 1478 (m), 1928 (s), 2020 (s), 2430 (w), 2520 (w), 2575 (w), 2830 (m), 2885 (m), 2900 (m), 2935 (m), 2995 (w), 3115 (w).

Ethoxymethylcyclopentadienylmanganese tricarbonyl. From 15.2 g (0.06 mole) of the chloride and 1.5 g of sodium in 40 ml of ethyl alcohol, 7.94 g (50.4%) was obtained as described above. A yellow liquid, less stable on storage than methoxymethylcyclopentadienylmanganese tricarbonyl. B.p. 29-30° ($1 \cdot 10^{-2}$ mm Hg), n_D^{20} 1.5625, d_4^{20} 1.3248.

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* The IR spectra were measured by Yu. P. Sheinker and G. G. Dvoryantseva, to whom the authors express their gratitude.

Found, %: C 50.61, 50.82; H 4.32, 4.35; Mn 20.39, 20.17
$C_{11}H_{11}O_4Mn$. Calculated, %: C 50.40; H 4.24; Mn 20.95

IR spectrum (ν, cm^{-1}):
427 (w), 429 (w), 434 (w), 485 (w), 494 (w), 541 (s), 635 (s), 688 (s), 705 (s),

720 (s), 722 (s), 767 (w), 772 (w), 774 (w), 820 (w), 840 (m), 848 (m), 850 (m), 879 (w), 888 (w), 894 (w), 912 (w), 936 (w), 1010 (m), 1025 (m), 1027 (m), 1048 (m), 1098 (s), 1112 (s), 1122 (s), 1160 (m), 1162 (m), 1165 (m), 1173 (m), 1177 (m), 1210 (w), 1219 (w), 1247 (w), 1272 (w), 1278 (w), 1342 (m), 1388 (m), 1417 (w), 1450 (m), 1468 (w), 1494 (w), 1928 (s), 2020 (s), 2370 (w), 2430 (w), 2515 (w), 2575 (w), 2870 (m), 2930 (m), 2985 (m), 3120 (w).

n-Propoxymethylcyclopentadienylmanganese tricarbonyl. To a solution of sodium propylate (1.5 g of sodium in 40 ml of anhydrous alcohol) was added a solution of 15.2 g (0.06 mole) of the chloride in 10 ml of propyl alcohol. The mixture was heated with stirring to 100°, and after cooling was poured into 200 ml of water and extracted with 200 ml of ether. The ether extracts were dried over $MgSO_4$, the ether was distilled off, and the residue, consisting of propyl alcohol and the ether obtained, was distilled in vacuo. The propyl alcohol, if the condenser of the apparatus is not cooled, collects in the trap. Yield: 14.28 g (86.1%) of a yellow liquid. B.p. 34-35° ($1 \cdot 10^{-2}$ mm Hg), n_D^{20} 1.5520, d_4^{20} 1.2807.

Found, %: C 52.10, 52.19; H 4.73, 4.74; Mn 20.00, 19.86
$C_{12}H_{13}O_4Mn$. Calculated, %: C 52.19; H 4.75; Mn 19.89

IR spectrum (ν, cm^{-1}):
430 (w), 475 (w), 495 (w), 540 (s), 635 (s), 688 (s), 722 (s), 773 (w), 842 (m), 853 (m), 910 (w), 915 (w), 935 (w), 962 (m), 990 (w), 1045 (m), 1050 (m), 1100 (s), 1103 (s), 1159 (w), 1220 (w), 1246 (w), 1345 (m), 1350 (w), 1388 (m), 1422 (w), 1447 (w), 1468 (m), 1482 (w), 1915 (s), 2017 (s), 2440 (w), 2490 (w), 2520 (w), 2570 (w), 2590 (w), 2620 (w), 2665 (w), 2750 (w), 2870 (m), 2880 (m), 2945 (m), 2970 (m), 3100 (w), 3125 (w).

n-Butoxymethylcyclopentadienylmanganese tricarbonyl. To a solution of sodium butylate (1.5 g of sodium in 40 ml of anhydrous alcohol) was added a solution of 15.2 g (0.06 mole) of the chloride in 10 ml of butyl alcohol. The mixture was heated and kept at 120° for 20 min and then stirred for another 30 min. Subsequent treatment of the mixture was as in the preparation of the preceding ether. Yield: 11.20 g (64.3%) of a yellow liquid, b.p. 39-40° ($1 \cdot 10^{-2}$ mm Hg), n_D^{20} 1.5461, d_4^{20} 1.2495.

Found, %: C 54.19, 54.14; H 5.23, 5.34; Mn 18.56, 18.11
$C_{13}H_{15}O_4Mn$. Calculated, %: C 53.80; H 5.22; Mn 18.93

IR spectrum (ν, cm^{-1}):
432 (w), 470 (w), 495 (w), 542 (s), 637 (s), 688 (s), 705 (s), 720 (s), 770 (w), 842 (m), 850 (m), 910 (m), 938 (m), 975 (m), 998 (m), 1050 (m), 1067 (m), 1103 (s), 1156 (m), 1218 (w), 1240 (m), 1280 (w), 1305 (w), 1342 (m), 1350 (m), 1384 (m), 1420 (m), 1440 (w), 1470 (m), 1680 (w), 1920 (s), 2019 (s), 2380 (w), 2425 (w), 2520 (w), 2570 (w), 2880 (s), 2940 (s), 2970 (s), 3120 (w).

Allyloxymethylcyclopentadienylmanganese tricarbonyl. From 15.2 g (0.06 mole) of the chloride and 1.5 g of sodium in 45 ml of allyl alcohol, as

described for the preparation of n-propoxymethylcyclopentadienylmanganese tricarbonyl, there was obtained 13.94 g (84.6%) of a yellow liquid, b.p. 39-40° ($1 \cdot 10^{-2}$ mm Hg), n_D^{20} 1.5692, d_4^{20} 1.3185.

Found, %: C 52.73, 52.50; H 4.36, 4.15; Mn 19.26, 20.09
$C_{12}H_{11}O_4Mn$. Calculated, %: C 52.57; H 4.05; Mn 20.03

IR spectrum (ν, cm^{-1}):
428 (w), 433 (w), 494 (w), 541 (s), 640 (s), 688 (s), 705 (s), 725 (s), 775 (w), 850 (m), 937 (s), 998 (m), 1012 (m), 1021 (m), 1037 (m), 1051 (m), 1092 (s), 1105 (s), 1110 (s), 1130 (s), 1210 (w), 1220 (w), 1250 (m), 1272 (m), 1295 (w), 1345 (m), 1355 (m), 1385 (m), 1390 (m), 1400 (m), 1420 (m), 1460 (m), 1478 (m), 1665 (w), 1922 (s), 2020 (s), 2380 (w), 2435 (w), 2520 (w), 2575 (w), 2670 (w), 2700 (w), 2720 (w), 2865 (m), 2900 (m), 2925 (m), 2990 (w), 3020 (w), 3090 (m), 3110 (m), 3125 (m).

Benzyloxymethylcyclopentadienylmanganese tricarbonyl. To a solution of sodium alcoholate (1.5 g of sodium in 40 ml of anhydrous benzyl alcohol) was added a solution of 15.2 g (0.06 mole) of the chloride in 10 ml of alcohol. The mixture was heated with stirring and kept at 60-70° for 1 h; after cooling it was poured into 200 ml of water and extracted with 150 ml of ether. The extracts were dried over $MgSO_4$, the ether was distilled off, and the residue, consisting of benzyl alcohol and the ether obtained, was distilled in vacuo. At $1 \cdot 10^{-2}$ mm Hg, fractions were collected. Fraction 1: b.p. 26-27°, n_D^{20} 1.5395, benzyl alcohol. Fraction 2: b.p. 27-39°, n_D^{20} 1.5458, a light-yellow liquid—benzyl alcohol with a small content of ether. Fraction 3: b.p. 84-85°, 13.45 g (69.2%), n_D^{20} 1.5990, d_4^{20} 1.3254, a yellow viscous liquid.

Found, %: C 59.60, 59.37; H 4.34, 4.16; Mn 16.75, 16.44
$C_{16}H_{13}O_4Mn$. Calculated, %: C 59.27; H 4.05; Mn 16.94

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REFERENCES

1. A. N. Nesmeyanov, K. N. Anisimov, Z. P. Valueva, *Izv. AN SSSR, OKhN*, **1963**, 2233.

2. A. Reyschler, *Bull. Soc. chim.*, (4) **1**, 1195 (1907).

Note: Figure translations are in progress. See original paper for figures.