Methoxycarbonyl derivatives of the cyclopentadienyl metal carbonyls*

Recently alkoxycarbonyl derivatives of the types ROCOCo(CO)$_3$L [R = (CH$_3$)$_3$C, L = (C$_6$H$_5$)$_3$P][1] and ROCOMn(CO)$_3$L$_2$ [R = CH$_3$, C$_2$H$_5$, C$_5$H$_{11}$, and C$_6$H$_5$CH$_2$, L = (C$_6$H$_5$)$_3$P; R = C$_2$H$_5$, L = CO][2] have been prepared either by treatment of a metal carbonyl cation with an alkoxide anion, treatment of a metal carbonyl anion with ethyl chloroformate, or treatment of a metal carbonyl anion with *tert*-butyl hypochlorite. We have now prepared similar methoxycarbonyl derivatives of the cyclopentadienylmetal carbonyls of iron and manganese. Since both the syntheses and reactions of our new compounds have certain novel and useful features, we are now reporting some preliminary results.

Treatment of (CH$_3$)$_2$NCOFe(CO)$_2$C$_5$H$_5$ (readily accessible from NaFe(CO)$_2$C$_5$H$_5$ and dimethylcarbamoyl chloride[3]) with boiling methanol gives a 49% yield of the yellow-orange volatile (90°/0.1 mm) methoxycarbonyl derivative CH$_3$OCOFe(CO)$_2$-C$_5$H$_5$, (I), m.p. 34–36°. (Found: C, 46.1; H, 3.6; Fe, 23.6; O, 26.5; mol. wt. osmometer in C$_6$H$_6$, 248. C$_9$H$_8$FeO$_4$ calcd.: C, 45.8; H, 3.4; Fe, 23.7 O, 27.1%; mol. wt., 236.) The infrared spectrum** of (I), besides exhibiting the usual strong terminal metal carbonyl bands at 2020 and 1945 cm^{-1}, exhibits an additional strong band at 1615 cm^{-1} which may be assigned to the carbonyl group of the σ-bonded methoxycarbonyl group. The proton NMR spectrum of (I) exhibits sharp singlet resonances at τ 5.14 and τ 6.61 of approximate relative intensities 5:3 which may be assigned to the π-cyclopentadienyl and methyl protons, respectively.

Kruck and Noack[2] found their alkoxycarbonyl derivatives of manganese to react with hydrogen chloride and other acids to give salts of manganese carbonyl cations. We have likewise found CH$_3$OCOFe(CO)$_2$C$_5$H$_5$ (I) to react with hydrogen chloride in ether or benzene solution to form pale-yellow hygroscopic water-soluble [C$_5$H$_5$Fe(CO)$_3$]$^+$[HCl$_2$]$^-$ completely analogous to the manganese salt [Mn(CO)$_6$]$^+$[HCl$_2$]$^-$ prepared by Kruck and Noack. This synthesis of [C$_5$H$_5$Fe(CO)$_3$]$^+$[HCl$_2$]$^-$ is the first synthesis of a derivative of the [C$_5$H$_5$Fe(CO)$_3$]$^+$ cation[4] from [C$_5$H$_5$Fe(CO)$_2$]$_2$ which does not require the use of carbon monoxide under pressure; in this new synthesis of [C$_5$H$_5$Fe(CO)$_3$]$^+$ the "extra" carbonyl group originates from the dimethylcarbamoyl chloride.

We have also investigated the reaction between CH$_3$OCOFe(CO)$_2$C$_5$H$_5$, (I), and Grignard reagents. Thus treatment of (I) with methylmagnesium bromide in diethyl ether solution does *not* give the expected tertiary alcohol (CH$_3$)$_2$C(OH)Fe(CO)$_2$C$_5$H$_5$. Instead a 78% yield of the known[3] acetyl derivative CH$_3$COFe(CO)$_2$C$_5$H$_5$, (II), m.p. 57–59° (lit.[3] m.p. 56–57°) was obtained. The infrared spectrum of (II) obtained from CH$_3$MgBr and CH$_3$OCOFe(CO)$_2$C$_5$H$_5$ was identical to that of (II) obtained from acetyl chloride and NaFe(CO)$_2$C$_5$H$_5$. Similar treatment of CH$_3$OCOFe(CO)$_2$C$_5$H$_5$ with phenylmagnesium bromide in diethyl ether solution gives the corresponding benzoyl derivative C$_6$H$_5$COFe(CO)$_2$C$_5$H$_5$, (III), m.p. 63–64° (lit.[5] m.p. 59–62°) but in only 3% yield. Thus the acyl carbonyl groups of these acyliron compounds appear to be relatively unreactive to addition of the alkylmagnesium halide.

In order to prepare a manganese analogue of the iron complex (I) a synthetic

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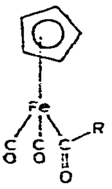
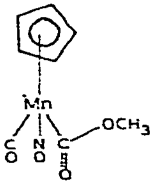
** These infrared spectra were taken in potassium bromide pellets.

method analogous to that of Kruck and Noack[2] was used. Thus treatment of $[C_5H_5Mn(CO)_2NO][PF_6]$[5] with methanolic sodium methoxide gives a 23% yield of orange crystalline $CH_3OCOMn(CO)(NO)C_5H_5$, (IV), m.p. 56–58°. (Found: C, 39.1; H, 3.5; Mn, 23.4; N, 5.6; O, 27.5. $C_8H_8MnNO_4$ calcd.: C, 40.5; H, 3.4; Mn, 23.2; N, 5.9; O, 27.0%.)



(I) R = OCH_3
(II) R = CH_3
(III) R = C_6H_5



(IV)

The spectroscopic properties of $CH_3OCOMn(CO)(NO)C_5H_5$ are in accord with the proposed structure (IV), unambiguously excluding any of the alternative possibilities. Thus the infrared spectrum* exhibits terminal metal carbonyl bands at 2005 (s) and 1985 (s) cm^{-1}; a terminal metal nitrosyl band at 1750 (s) cm^{-1}; and an ester carbonyl band at 1615 (s) cm^{-1}. The proton NMR spectrum exhibits sharp singlet resonances at τ 4.90 and τ 6.54 of approximate relative intensities 5:3 which may be assigned to the π-cyclopentadienyl and methyl protons, respectively.

This new manganese compound (IV) is significant in representing the first known compound of the type $RMn(CO)(NO)C_5H_5$, the existence of which was first predicted by Piper and Wilkinson[7] in 1956. With four different ligands bonded to the manganese atom, the compounds $RMn(CO)(NO)C_5H_5$ should be separable into optically active isomers.

Further studies on these and related compounds are in progress. Details will be reported in future publications.

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