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[η^5-1,2,3,4,5-PENTAKIS(CARBOMETHOXY)CYCLOPENTADIENYL]-TRICARBONYLMANGANESE(I): SYNTHESIS, SPECTROSCOPY AND REACTIVITY

CLÉMENT ARSENAULT, PETER BOUGEARD, BRIAN G. SAYER, SHAHIN YEROUSHALMI and MICHAEL J. McGLINCHEY*

Department of Chemistry, McMaster University, Hamilton, Ontario, L8S 4M1 (Canada)

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Summary

Treatment of the potassium salt of pentakis(carbomethoxy)cyclopentadiene with bromopentacarbonylmanganese(I) gives pentakis(carbomethoxy)cyclopentadienyltricarbonylmanganese(I) in good yield. Photochemical substitution of a metal carbonyl group by tributylphosphine, triphenylphosphine and triethyl phosphite is reported. Attempts to modify the ester function are described; hydrolysis or amination give mixed products but reduction with lithium aluminum hydride yields ultimately the pentamethylcyclopentadienyl complex.

Introduction

Although cyclopentadienyl derivatives of transition metals encompass an enormous range of chemistry, penta-substituted cyclopentadienyls still present something of a synthetic challenge [1]. Pentamethylcyclopentadienyl complexes have been intensely studied [1,2] and new or improved routes continue to appear [3]. In contrast, the pentachloro [4], pentacyano [5], pentakis(trifluoromethyl) [1c], pentakis(methylmercapto) [6] and pentaphenyl [1d] systems have not been widely exploited. A recent series of papers by M.I. Bruce [7–11] discussing the chemistry of the pentakis(carbomethoxy)cyclopentadienyl moiety prompts us to report some data on the synthesis and reactivity of $[C_5(CO_2Me)_5]Mn(CO)_3$.

Discussion

Synthesis and characterisation of $[C_5(CO_2Me)_5]Mn(CO)_3$

The pentakis(carbomethoxy)cyclopentadienide ion, $C_5(CO_2Me)_5^-$, has recently been reported to undergo reactions with a number of transition metals [7,8,11]. In particular, the mixed sandwich compound $[C_5(CO_2Me)_5]Ru(C_5H_5)$ has been characterised by X-ray crystallography [8]. However, the great stability of the

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$C_5(CO_2Me)_5^-$ anion results for the most part in the formation of ionic systems [7] or oxygen-bonded molecules [11,12] rather than covalent analogues of the known C_5H_5 complexes. We now report that a pentahapto $C_5(CO_2Me)_5$ complex is obtainable in 80% yield, in a straightforward manner, by reaction of the potassium salt with bromo(pentacarbonyl)manganese(I) in methanol at 50°C; the reaction occurs under even milder conditions if one uses $[BrMn(CO)_4]_2$ presumably since cleavage of the halogen bridge yields a coordinatively unsaturated reagent. Unlike the pentachlorocyclopentadienyl moiety which can bond in a monohapto fashion (to $Mn(CO)_5$) or in a pentahapto fashion (to $Mn(CO)_3$) [4d], the $C_5(CO_2Me)_5$ ligand apparently yields only the η^5-derivative. The infrared spectrum of $[C_5(CO_2Me)_5]Mn(CO)_3$ exhibits bands at 2020 and 1940 cm^{-1}, somewhat lower than might have been anticipated for a ligand bearing so many electron-withdrawing substituents (see Table 1). However, crystallographic data on the currently known $C_5(CO_2Me)_5$ systems reveal that the ester groups are staggered rather than coplanar [7–10]. This structural feature not only reduces steric interactions but also lowers the degree of conjugation with the ring. One can also invoke this non-planarity of the ester functionalities to rationalise the ^1H NMR spectrum which exhibits a rather broad methoxy resonance. The sample was cooled in an attempt to freeze out the favored conformation on the NMR time scale and so differentiate between methyl groups proximate or distal to the metal as has already been done for several π-complexes of hexaethylbenzene [13]. However, lowering the temperature resulted only in further broadening and a limiting spectrum was not obtainable even at −90°C on a 250 MHz spectrometer. Of course, the presence of the quadrupolar ^{55}Mn nucleus ($I = 5/2$, 100% abundance, $Q = 0.55 \times 10^{-28}$ m^2) does not help the situation. Indeed, when the sample was heated to 60°C (at which temperature some decomposition was apparent) the resonance line narrowed to a half-width of ~ 5 Hz. The ^{55}Mn NMR spectrum showed a very broad line ($W_{1/2}$ ~ 13200 Hz) at a similar shift to that for $(C_5H_5)Mn(CO)_3$ (see Table 1) [14].

Reactivity of $[C_5(CO_2Me)_5]Mn(CO)_3$

Since the synthesis of $(C_5H_5)Mn(CO)_3$ in 1954, [15] a variety of $(C_5X_nH_{5-n})Mn(CO)_3$ analogues have been described [16]; the reactions of these compounds fall into two main categories. The first of these consists of reactions at the $Mn(CO)_3$ centre in which one or more of the carbonyl groups is substituted, under the influence of UV irradiation, by other donor molecules such as thiocarbonyl, [17] dinitrogen, [18] and alkyne [19] or a phosphine [20]. It is interesting to

TABLE 1

INFRARED AND ^{55}Mn NMR DATA FOR C_5X_5 DERIVATIVES OF MANGANESE

	IR (cm^{-1})	^{55}Mn NMR	
		δ (ppm)	1/2 width (Hz)
$(C_5H_5)Mn(CO)_3$	2023, 1939	−2225	10039
$(C_5Me_5)Mn(CO)_3$	2020, 1930	–	–
$[C_5(CO_2Me)_5]Mn(CO)_3$	2020, 1940	−2196	13200
$(C_5Cl_5)Mn(CO)_3$	2050, 1982	–	–
$(C_5Cl_5)Mn(CO)_5$	2128, 2077, 2044, 2011	–	–

note, however, that Kochi has recently reported some electrochemically induced substitution reactions of $(CH_3C_5H_4)Mn(CO)_3$ [21]. The second category includes reactions in which the cyclopentadienyl ring undergoes electrophilic substitution, such as Friedel–Crafts acylation [22]; nucleophilic substitutions have also been reported but these occur only in cationic complexes [23]. Surprisingly, there appears to have been little use of the $Mn(CO)_3$ moiety to modify the normal organic chemistry of π-complexed ligands as has been widely documented for the $Cr(CO)_3$ [24] and $Fe(CO)_3$ [25] fragments.

The photochemical substitution of a carbonyl group in $[C_5(CO_2Me)_5]Mn(CO)_3$ by phosphines led to slightly impure products of low stability which could, however, be adequately characterised spectroscopically. Thus, $[C_5(CO_2Me)_5]Mn(CO)_2P(n\text{-}Bu)_3$ was identified by its ^1H and ^{31}P NMR and by infrared and mass spectrometric analyses. The triphenylphosphine analogue is less stable presumably because of unfavorable steric interactions between the bulky phosphine and the pendant ester functionalities. (In $(C_6Et_6)Cr(CO)_2PPh_3$ all six ethyl groups are directed away from the chromium tripod [13c]). The use of triethylphosphite, i.e., a better σ-donating ligand, gave the somewhat more stable complex $[C_5(CO_2Me)_5]Mn(CO)_2P(OEt)_3$. These reactions are summarized in Fig. 1.

Attempts to synthesize other dicarbonylmanganese species not accessible photochemically, e.g. $(C_5E_5)Mn(CO)_2CS$, via the intermediacy of complexes containing readily displaceable ligands (THF, cyclo-octene) resulted in decomposition. This is in marked contrast to the behavior observed for $C_5H_5Mn(CO)_2L$ (L = THF, cyclo-octene) [17,18].

The presence of the five ester groups in the $Mn(CO)_3$ complex suggests that other penta-functionalised molecules may be accessible. It is known that non-complexed $C_5(CO_2Me)_5^-$ reacts with ammonia over a 3 month period to give a penta-amido derivative $C_5(CONH_2)_5H$ [26]. In our hands, the reaction of $[C_5(CO_2Me)_5]Mn(CO)_3$

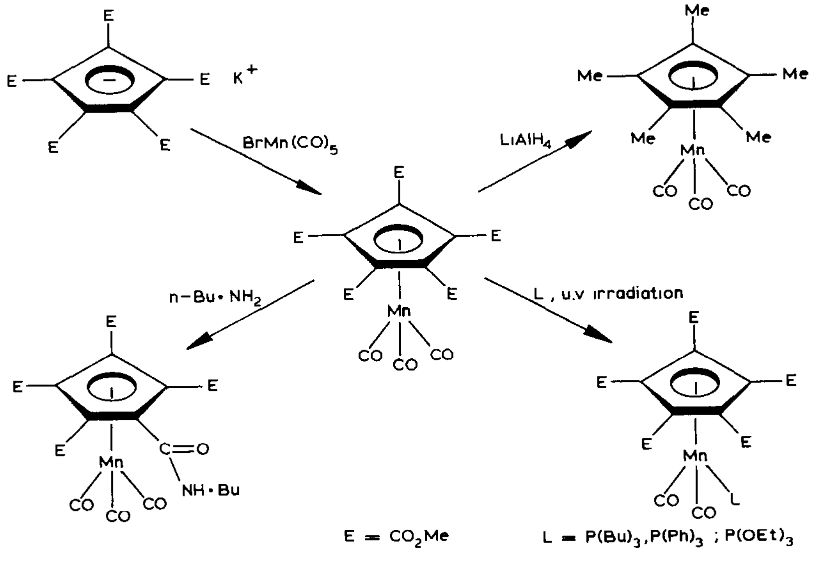

Fig. 1. Some reactions of $(C_5E_5)Mn(CO)_3$.

with NH_3 gave low yields of mixed amide/ester complexes. It is however, possible to characterize spectroscopically the mono-amide, $[C_5(CO_2Me)_4CONHBu]Mn(CO)_3$, obtained via the careful reaction with n-butylamine in the dark for 5 days. Nevertheless, it became apparent that a delicate balance exists between the degree of functional group manipulation and the extent of decomposition of the complex. Thus, basic hydrolysis gave a mixture of free and complexed carboxylic acids and esters. We note that Bruce has previously reported the loss of two ester functionalities from each ring during the attempted synthesis of $[C_5(CO_2Me)_5]_2Rh^+$ [27]. Presumably, this was the result of ester hydrolysis and subsequent decarboxylation of the resulting acid.

In an attempt to reduce the penta-ester complex to the corresponding penta-alcohol, it was treated with lithium aluminum hydride. The only product isolated, however, was pentamethylcyclopentadienyltricarbonylmanganese(I). Interestingly, Le Plouzennec and her co-workers have reported that a cyclopentadienyl-manganese complex containing a single carbomethoxy substituent could be converted to the corresponding methyl-substituted analogue using the strongly reducing system $LiAlH_4/AlCl_3$ [28].

A further attempt to prepare the penta-alcohol using the milder reducing agent diisobutylaluminum hydride (DIBAL) gave the mixed ester as the only identifiable product.

Experimental

All reactions were carried out under an atmosphere of nitrogen and all organic solvents (except methanol) were dried in a manner appropriate to each. ^1H NMR spectra were recorded on a Varian EM 390 spectrometer, ^{31}P NMR spectra were measured on a Bruker WH90 spectrometer operating at 36.43 MHz, and ^{13}C and ^{55}Mn spectra were obtained on a Bruker WM250 spectrometer operating at 62.895 and 62.066 MHz, respectively. ^1H and ^{13}C shifts are relative to TMS, ^{31}P shifts relative to 85% H_3PO_4 and ^{55}Mn shifts relative to saturated $KMnO_4$ in D_2O. Positive shifts are to high frequency. Infrared spectra were measured on a Perkin–Elmer model 283 spectrometer. Mass spectrometry was performed on a VG 7070F micromass spectrometer fitted with a VG 2035 data system.

Preparation of $[C_5(CO_2Me)_5]Mn(CO)_3$

The potassium salt of 1,2,3,4,5-pentakis(carbomethoxy)cyclopentadiene was prepared as described by Cookson [26]; ^1H NMR (D_2O), δ 4.3 (OCH_3); ^{13}C NMR (in D_2O), δ 170.62 (C=O), 117.98 (ring C), 53.38 (OCH_3); IR (Nujol) 1700 cm^{-1} *asym*, 1585 *sym* (ester carbonyls).

Bromopentacarbonylmanganese(I) was prepared by the reaction of decacarbonyldimanganese (Pressure Chemical Co.) with bromine in carbon tetrachloride. [29]

Potassium 1,2,3,4,5-pentakis(carbomethoxy)cyclopentadienide (0.5 g, 1.27 mmol) and bromopentacarbonylmanganese(I) (0.35 g, 1.27 mmol) were heated at 40–50°C in methanol (40 cm^3) for 24 h. On completion of the reaction, the solvent was removed under reduced pressure and the resulting solid extracted with methylene chloride to give a yellow solution which, upon removal of solvent, gave the crude product. Complete purification of the crude product proved somewhat difficult and some $Mn_2(CO)_{10}$ was always present, as shown by ^{55}Mn NMR spectroscopy. The best samples were obtained after chromatography on a silica gel column using CH_2Cl_2/CH_3OH (9/1) as eluent to give (η^5-1,2,3,4,5-pentakis(carbomethoxy)cyclopentadienyl)tricarbonylmanganese(I) (0.50 g, 1.0 mmol, 80%) as a yellow/brown solid, m.p. > 170°C decomp; ^1H NMR ($CDCl_3$) δ 3.6, $W_{1/2}$ ~ 15 Hz; ^{13}C NMR (DMSO-d_6) δ 224.6 (C≡O), 170.1 (C=O), 119.7 (ring C), 54.0 (OCH_3); ^{55}Mn NMR (in C_6D_6) δ −2196, $W_{1/2}$ 13200 Hz; IR (CH_2Cl_2) 2020, 1940, 1690, 1600 cm^{-1}; major mass spectral peaks at m/z 493.994, M^+, calcd. 493.9893; 462.965 $[M - CH_3O]^+$, calcd. 462.9709; 410.007 $[M - 3CO]^+$, calcd. 410.0046. High resolution mass spectrometric characterisation was used since the analytical results were unreliable and variable.

Reactions of $[C_5(CO_2Me)_5]Mn(CO)_3$

(a) With tri(n-butyl)phosphine

In a typical reaction, $[C_5(CO_2Me)_5]Mn(CO)_3$ (0.5 g, 1.0 mmol) tri(n-butyl)phosphine (0.22 g, 1.1 mmol) in acetone (10 cm^3) were irradiated, using a 250 watt General Electric tungsten lamp, for 1 h at 25°C. After removal of the solvent under reduced pressure, attempts to purify the compound by recrystallisation or column chromatography (silica gel) resulted in decomposition. However, characterisation by spectroscopic means was possible: ^1H NMR (C_6D_6), δ 4.0 (OCH_3, 15 H) singlet; 1.5 (CH_2, 18H) multiplet; 1.1 (CH_3, 9H) triplet; ^{31}P NMR (C_6D_6) δ −13.7; IR (C_6H_6) ν(CO) at 1935, 1895, 1720 *asym*, 1650 *sym* (ester) cm^{-1}; mass spectrum m/z (%), 612(1), $[M - 2CO]^+$; 576(5), $[M - R_3P]^+$; 410(10), $[M - 2CO - R_3P]^+$; 257(12) $[R_3PMn]^+$, 202(100) $[R_3P]^+$.

(b) With triphenylphosphine

The analogous photochemical reaction with triphenylphosphine yielded a compound which decomposed rapidly in solution, but the following data were obtained: ^1H NMR (C_6D_6) broad signals at δ 7.3 (phenyl, 15H), 3.9 (OCH_3, 15H); IR (C_6H_6) ν(CO) at 1940, 1870, 1730 *asym*, 1655 *sym* (ester) cm^{-1}.

(c) With triethyl phosphite

$[C_5(CO_2Me)_5]Mn(CO)_3$ (1 g, 2 mmol) and triethyl phosphite (0.36 g, 2.2 mmol) in acetone (15 cm^3) were irradiated, using a 250 watt General Electric tungsten lamp, for 1.5 h at 25°C. Removal of solvent and unreacted triethyl phosphite under vacuum left an already quite pure product (0.76 g, 1.2 mmol; 60%) which decomposed during attempts at column chromatography. Spectroscopic data: ^1H NMR (C_6D_6), multiplet centred at δ 4.1 (OCH_3, OCH_2, 21 H), 1.3 (CH_3, 9H) triplet; ^{31}P (C_6D_6), 159.4; ν(CO) 1970, 1880, 1720 *asym*, 1645 *sym* (ester) cm^{-1}; mass spectrum, m/z (%), 632 (1), M^+; 604(2), $[M - CO]^+$; 576(8) $[M - 2CO]^+$; 410(65) $[M - 2CO - (RO)_3P]^+$.

(d) Hydrolysis of ester function in $C_5E_5Mn(CO)_3$

To sodium hydroxide (1.3 g, 0.0325 mol) in water (250 cm^3) was added $C_5E_5Mn(CO)_3$ (1 g, 2×10^{-3} mol) in methanol (20 cm^3). The resulting mixture was refluxed gently for 12 h, allowed to cool, and the solution made acidic (~ pH 1). After saturating with sodium chloride the aqueous layer was then extracted using diethyl ether (2 × 100 cm^3). After drying ($MgSO_4$) the diethyl ether was removed yielding an orange oil. Infra-red spectroscopy indicated that the product was a mixture of the starting material and the acid (IR (CH_2Cl_2) cm^{-1}, 2010, 1975, 1725 (acid)).

(e) Reduction of $C_5E_5Mn(CO)_3$ with $LiAlH_4$

To a suspension of lithium aluminum hydride (3 g, 8×10^{-2} mol) in anhydrous diethyl ether (100 cm^3) was added, slowly, a solution of the $C_5E_5Mn(CO)_3$ (1 g, 2×10^{-3} mol) in anhydrous diethyl ether (100 cm^3). The resulting mixture was left stirring overnight. The reaction mixture was worked up by dropwise addition of water, until effervescence ceased, and was followed by the addition of ice cold dilute sulphuric acid as described in Vogel [30]. After the aluminum salts had been dissolved the ether layer was removed and the aqueous layer saturated with sodium chloride followed by extraction, using diethyl ether (2 × 50 cm^3). The diethyl ether fractions were dried ($MgSO_4$) and the solvent removed under reduced pressure. Spectroscopic investigation of the compound revealed that the product was mainly pentamethylcyclopentadienylmanganese tricarbonyl; ^1H NMR ($CDCl_3$), δ 1.9 (CH_3); IR (C_6H_6) 2020, 1930 cm^{-1}; Mass spectrum m/z (%) 274(10) M^+; 218(10) $[M-2CO]^+$; 190(15), $[M-3CO]^+$; 135(100) $C_5Me_5{}^+$. These data agree with those in the literature [31].

(f) Reaction of $C_5E_5Mn(CO)_3$ with n-butylamine

To a solution of $C_5E_5Mn(CO)_3$ (0.6 g, 1.2×10^{-3} mol) in methanol (10 cm^3) was added a methanolic solution (10 cm^3) of sodium methoxide (0.2 g, 3.7×10^{-3} mol) and n-butylamine (2.2 g, 3×10^{-2} mol). The reaction mixture was then left stirring for 5 days at ambient temperature in the absence of light. After neutralisation with dilute hydrochloric acid the reaction mixture was extracted using methylene chloride (2 × 25 cm^3) which, after drying ($MgSO_4$) and removal of solvent, yielded a yellow/brown compound 0.3 g (46% yield). Spectroscopic investigation indicated that the compound was 1,2,3,4-tetracarbomethoxy-5-(n-butylamido)cyclopentadienyltricarbonylmanganese(I), ^1H NMR ($CDCl_3$), broad signals, δ 4.0 (OMe, 12H), 3.8 (NCH_2, 2H), 1.6 (CH_2, 4H), 1.1 (CH_3, 3H); IR (CH_2Cl_2) cm^{-1} 1955, 1905, 1735 *asym*, 1700 *sym* (ester), 1675, 1620 (amide); Mass spectrum m/z(%) M^+ 535(3), 507(2), 451(34), 391(40), 324(35), 293(100).

(g) Reduction of $C_5E_5Mn(CO)_3$ with DIBAL

To a hexane solution of DIBAL (24 cm^3, 2.6×10^{-2} mol) was added a methylene chloride solution (20 cm^3) of $C_5E_5Mn(CO)_3$ (0.8 g, 1.6×10^{-3} mol), the reaction temperature being maintained at 0°C during addition (2 h). The reaction mixture was then left stirring overnight at room temperature. After hydrolysis of the reaction mixture using dilute hydrochloric acid the organic layer was separated and the aqueous layer further extracted using methylene chloride (2 × 25 cm^3). The combined organic fractions were dried ($MgSO_4$) and the solvent removed under reduced pressure. Examination of the yellow/brown oil using ^1H NMR spectroscopy indicated that no reduction had occurred. However, the ^1H NMR spectrum did indicate that some trans-esterification had occurred. ^1H NMR ($CDCl_3$) δ 4.0 (OMe, 3H), 3.9 (OCH_2, 2H), 3.5 (CH, 1H), 0.9 (CH_3, 6H).

(h) With ammonia

Gaseous ammonia was slowly bubbled into a methanol solution (40 cm^3), at

$-78°C$, containing $C_5E_5Mn(CO_3)$ (1 g, 2×10^{-3} mol) for approximately 10 min. The reaction mixture was then allowed to slowly warm up overnight, to room temperature, whilst being stirred. After removal of solvent under reduced pressure examination of the residue by ^1H NMR indicated that some of the ester function was still present. Mass spectroscopic investigation indicated that the major component of the residue was starting material, however, peaks identifiable with varying degrees of substitution were evident.

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