

SPECTRA AND SYNTHESSES OF SOME MONOSUBSTITUTED DERIVATIVES OF CYCLOPENTADIENYLMANGANESE TRICARBONYL

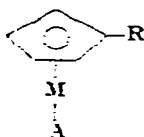
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INTRODUCTION

In recent years numerous compounds containing a monosubstituted cyclopentadienyl ring π -bonded to a metal have been synthesized¹, *i.e.*,



(where R is a covalently bound substituent and M is a transition metal which may be bound to one or more additional groups, A). We have prepared a number of such compounds which are derivatives of cyclopentadienylmanganese tricarbonyl in order to examine their nuclear magnetic resonance and infrared spectra and to compare these with the respective spectra of the parent compound. This particular series was chosen because of the stability of the $-\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$ nucleus and because the spectra of compounds with only a single cyclopentadienyl ring would be as simple as possible. Many of the compounds have been previously reported by other workers. The substances synthesized for the study are listed in Table 1. In addition to these, cyclopentadienylmanganese tricarbonyl and methylcyclopentadienylmanganese tricarbonyl, which were obtained from The Ethyl Corporation, Detroit, Michigan, are also included in the study.

RESULTS AND DISCUSSION

NMR Spectra

The proton nuclear magnetic resonance data of the cyclopentadienylmanganese tricarbonyl derivatives are summarized in Table 2. In compounds (I), (II), (III), (IV) and (XIII) the resonance signals of the α - and β -protons appeared as triplets with a plane of symmetry between them, in accordance with an A_2B_2 system. The observation of the two triplets does not necessarily mean that $J_{AB} = J_{AB'}$, but is probably more consistent with A_2B_2 spectra in which $J_{BB'} \gg J_{AA'}$ ¹⁰. With the exception of compounds (VII) and (XII), the α - and β -protons of the remaining compounds appeared as broad singlets.

In compound (I), both the α - and β -protons are deshielded with respect to the parent cyclopentadienylmanganese tricarbonyl (X). The strong deshielding of the

TABLE I

THE CYCLOPENTADIENYLMANGANESE TRICARBONYL DERIVATIVES, $RC_5H_4Mn(CO)_3$, PREPARED TOGETHER WITH ANALYTICAL RESULTS AND MELTING POINTS

-R	Analyses (%)		Melting point (°C)		Ref.
	Calcd.	Found ^a	Found ^a	Literature	
-COCH ₃		b	39-40	39.5-40.0	2
-C=NOHCH ₃		b	96-98	99 subl.	3
-CONH ₂	C 43.75	43.93	152-154	c	
	H 2.45	2.69			
	N 5.67	5.56			
-COOH		b	190-199	189-197	4
-CH(CH ₃)NH ₂ ·HCl	C 42.35	42.20	249.5-250	c	
	H 3.91	4.08			
	N 4.94	4.88			
-NH ₂ ·HCl	C 37.60	37.86	182-184	242 decomp., subl. ^e	5
	H 2.76	2.60			
	N 5.48	5.38			
-NHCOCH ₃	C 46.00	45.89	136-138	145 ^e	5
	H 3.09	3.03		132-138	6
	N 5.36	5.52			
-SO ₂ H		b	95-105	95-105	7
			211 ^f	213-215 ^f	7
-SS-	C 40.87	40.48	126.5-127.5	c	
	H 1.71	1.88			
	Mn 23.37	23.13			
	S 13.64	13.66			
-HgCl		b	135	135-136	7
				132-133	8
-CHO		b	54-56	oil ^d	9
-CH=C-CO	C 57.62	57.43	176-177	c	
	H 2.68	2.63			
	N 3.73	3.99			
-CON ₃	C 39.58	39.59	37-38	42.5 ^e	5
	H 1.48	1.65		41-42 ^e	6
	Mn 20.12	20.38			
-NHCOOCH ₂ C ₆ H ₅		b	117-118	116 ^e	5
				115-116	6
-PO(H)OH	C 35.85	35.59	>295	c	
	H 2.27	2.20			
	P 11.56	11.23			
	Mn 20.50	20.19			
-P(O)(OH)-	C 40.88	41.75	155-157	c	
	H 1.93	2.21			
	Mn 23.37	23.49			
	P 6.59	6.69			

^a All melting points were determined on Fischer-Johns melting point block corrected with U.S.P. Standards. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

^b Analyses are not given for these compounds since they have been previously characterized in the papers cited for literature melting points. ^c Compounds not previously reported. ^d These authors report the formation of a 2,4-dinitrophenylhydrazone (m.p. 260° with decomposition). Our compound also forms a 2,4-dinitrophenylhydrazone (m.p. 260° with decomposition). ^e The previous report of this compound did not include analytical data. ^f M.p. of the sodium salt.

α -protons in comparison to the β -protons is indicative of conjugation of the cyclopentadienyl ring with the substituent ring system.

The presence of the carbonyl group is the substituent of compounds (II) to (V) is reflected by a deshielding of both the α - and β -protons. The more deshielded protons

therefore would not be expected to show any spin-spin interaction with the phosphorus nucleus. Based on this assignment, it appears that the α -protons are more deshielded than the β -protons in compound (VIII), since the sulfinio group is also known to be an electron-withdrawing substituent.

The methyl substituent in compound (XI) produces an upfield shift of 0.17 ppm for both the α - and β -protons. This effect is similar to that in toluene where the *ortho* and *meta* protons show identical chemical shift values, 0.10 ppm upfield from benzene¹¹.

The NMR spectra of compounds (XII) to (XV) are consistent with the designated structures, but the assignment of the α - and β -protons is tentative and subject to further investigation.

Infrared spectra

The infrared absorption frequencies observed in the 2100–300 cm^{-1} range which are characteristic of $\text{RC}_5\text{H}_4\text{Mn}(\text{CO})_3$ are listed in Table 3. In the spectrum of cyclopentadienylmanganese tricarbonyl, Fritz and Paulus¹⁴ have assigned the two intense bands at 2025 and 1930 cm^{-1} to C–O stretching and the bands at 632 and 538 cm^{-1} as the antisymmetric and symmetric M–C stretching frequencies. As would be expected these frequencies appear throughout the spectra of the entire series of compounds with relatively small shifts in position. The bands associated with the cyclopentadienyl ring may be readily picked out by comparing the spectra of these manganese compounds with the spectrum of ferrocene to which Lippincott and Nelson¹⁵ have made the following assignments: 1411 cm^{-1} , antisymmetric C–C stretch; 1108 cm^{-1} , antisymmetric ring bend; 1002 cm^{-1} , C–H parallel bend; 834 cm^{-1} , C–H perpendicular bend; and 811 cm^{-1} C–H perpendicular bend. At times some of the weaker ring frequencies are undoubtedly masked by bands associated with the R group. A strong band that occurs in the spectrum of each compound between 675 and 649 cm^{-1} must be the ring-metal stretching frequency.

The IR spectrum of the monosubstituted nucleus, $-\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$, does not differ markedly from the spectrum of the parent compound, cyclopentadienylmanganese tricarbonyl. The main differences seem to be in the intensities of frequencies near 1420 and 1100 cm^{-1} which are associated with skeletal structure of the ring. These frequencies are readily observed in the unsubstituted compound, but are much less intense or not observed in the substituted compounds.

In some instances two bands are observed where only one is expected, *e.g.*, near 840 cm^{-1} . This may be due to splitting introduced by the KBr pellet. In other instances one of the bands may be due to the cyclopentadienylmanganese tricarbonyl moiety and the other to the R group. A detailed study would be required to determine which band is associated with a particular group. Both bands are therefore recorded in Table 3 and bracketted together.

EXPERIMENTAL

Nuclear magnetic resonance spectra

The NMR spectra were measured on a Varian Model HA-100 spectrometer in dimethyl sulfoxide- d_6 solution with tetramethylsilane as an internal reference. Spectra are not reported for several compounds due to their low solubility.

TABLE 3
 INFRARED FREQUENCIES OBSERVED IN CYCLOPENTADIENYL-MANGANESE TRICARBONYL AND ITS DERIVATIVES

Group substituted on the cyclopentadienyl ring	C=O	C=O	C=C	Ring	C-H	C-H	C-H	Ring-Mn	Mn-C	Mn-C
-H	2045 vs	1935 vs	1421 m	1107 m	1064 w	1058 w	834 s	665 s	632 s	541 s
-CH ₃	2025 vs	1937 vs	<i>b</i>		1066 w	1044 w	838 m	670 s	632 s	539 m
-COOH	2039 vs	1945 vs	1410 m	<i>b</i>	1063 w	1047 m	855 m	667 s	649 s	554 m
-CHO	2038 vs	1946 vs	1422 w		1064 w	1048 m	850 m	668 s	630 s	541 m
-COCH ₃	2030 vs	1940 vs	1419 m	<i>b</i>	1063 w	1047 m	843 m	654 s	631 s	539 s
-C≡N(OH)CH ₃	2048 vs	1930 vs	1414 m		1067 w	1047 m	849 m	675 s	630 s	537 m
-CON ₃	2030 vs	1945 vs	1416 sh	1119 w	1063 w	1040 m	848 m 830 s	663 s	629 s	533 s
-NH ₂ ·HCl	2025 vs	1950 vs 1930 vs	1423 w	1109 m	1062 w	1034 m	842 m 833 m	666 s	630 s	532 m
-NHCOOCH ₂ C ₆ H ₅	2020 vs	1933 vs	1409 sh	1101 vw	1060 w	1033 w	845 m 838 m	670 m	630 m	535 m
-NHCOCH ₃	2020 vs	1925 vs	1403 sh		1064 w	1042 w	840 m 830 m	670 s	631 s	532 m
-CONH ₂	2025 vs	vs ^c	1412 s	1103 m	1064 w	1048 w	855 m	662 s	634 s	537 m
-CH(C ₆ H ₅)NH ₂ ·HCl	2030 vs	1932 vs	1418 m	~ 1100 sh	1063 vw	1045 m	848 m 840 m	666 s	632 s	537 m
-SS-	2020 vs	1940 vs	1410 m		1061 s	1041 w	840 m 832 m	667 s	630 s	532 m
-P(O)(H)(OH)	2029 vs	1938 vs	1407 w	<i>b</i>	1060 sh	1032 w	845 w	669 m	631 m	532 m
-P(O)(OH)-	2030 vs	1946 vs	1409 m		1064 w	1032 w	844 w	670 s	630 s	540 m
-CH≡C-CO	2025 vs	1942 vs	1419 w 1410 sh	1109 w	1059 w	1048 w 1040 w	848 w	670 m	630 s	531 m
-CH≡C-NHCOC ₆ H ₅	2027 vs	1934 vs	1412 vw	1100 vw	1070 w	1045 w	840 w	667 m	630 s	532 m
-CONHC ₆ H ₅										

^a vs vs very strong, s = strong, m = medium, w = weak, vw = very weak, vs = very weak, sh = shoulder, ^b Masked, ^c Band actually shows up as four intense peaks: 1966, 1953, 1938, 1930.

Infrared spectra

The infrared spectra were recorded on a Perkin-Elmer Model 521 spectrometer. Solids were pressed into KBr discs (1 mg of sample/400 mg of KBr); liquids were dissolved in carbon tetrachloride and in carbon disulfide to form 5 volume percent solutions.

(Hydroxyphosphinyl)cyclopentadienylmanganese tricarbonyl and bis(cyclopentadienylmanganese tricarbonyl)phosphinic acid

The procedure was similar to that used by Sollott and Howard for the reaction of phosphorus(III) chloride with ferrocene¹⁶. A slurry of 40.8 g (0.2 mole) of cyclopentadienylmanganese tricarbonyl in 41.2 g (0.3 mole) of PCl_3 was rapidly added to a slurry of 20.1 g (0.15 mole) of anhydrous aluminum chloride in 41.2 g (0.3 mole) of PCl_3 . The mixture was stirred a few minutes, then gently heated to reflux and allowed to stir and reflux for 4 h. The reaction was protected from moisture and a slow stream of dry nitrogen was maintained through the reaction flask. During the course of the reaction, the contents of the flask thickened and an additional 25 ml of PCl_3 was added.

The reaction mixture was extracted initially with 100 ml of PCl_3 and then with several 50 ml portions of PCl_3 . The combined extracts were distilled at reduced pressure to remove the solvent. A small amount of yellow residue remaining in the distillation flask was cautiously treated with 25 ml of water. The solid that formed was filtered, washed with two 10-ml portions of water and dissolved in 100 ml of 5% NaOH. A brown insoluble fraction was removed by filtration and discarded. The filtrate was acidified with dilute HCl to yield a yellow precipitate of (hydroxyphosphinyl)cyclopentadienylmanganese tricarbonyl which was filtered, washed and air dried (yield 2.2 g, 4%).

The solid remaining after the above PCl_3 extraction was treated cautiously with 200 ml of ice-water. Heat was evolved and the brown mass softened and turned yellow. The aqueous layer was removed by decantation and the solid extracted several times with 50-ml portions of hot benzene. The benzene extracts were combined and the benzene evaporated to leave a solid residue. This solid was extracted twice with 10-ml portions of 5% NaOH. Upon acidification of the NaOH extracts a small amount of bis(cyclopentadienylmanganese tricarbonyl)phosphinic acid precipitated. It was recrystallized from benzene to yield a cream colored powder (0.7 g, 0.6%).

The solid residue left after the above benzene extraction was treated with 400 ml of 5% NaOH and the insoluble portion was filtered off and discarded. Acidification of the clear yellow solution yielded a cream-colored precipitate (48 g, 60% of the manganese) which was air dried. Analysis of this acidic material gave: C, 39.50; H, 3.46; P, 13.25; Mn, 16.35% which if the remainder is assumed to be oxygen corresponds to the empirical formula $\text{C}_{22}\text{H}_{22}\text{O}_{11}\text{Mn}_2\text{P}_3$. It is interesting to note that Nesmayanov *et al.*¹⁷ report isolation of a substance having the empirical formula $\text{C}_{15}\text{H}_9\text{O}_5\text{Mn}_2\text{PCl}_2$ from a similar reaction.

1-(1-Aminoethyl)cyclopentadienylmanganese tricarbonyl hydrochloride

Zinc dust (7 g, 0.107 g-atom) was added in portions to 5.26 g (0.02 mole) of 1-(1-oximinoethyl)cyclopentadienylmanganese tricarbonyl dissolved in 26.7 ml of glacial acetic acid and 1.3 ml of water. After all of the zinc had been added, the mixture

was stirred and refluxed for an hour. The liquid was filtered, and the filtrate evaporated to dryness in the hood, and the resulting crystals were dissolved in 60 ml of water. This solution was neutralized by carefully adding 6 *N* NaOH (about 40 ml required). The resulting solution was extracted three times with ether and the combined ether extracts were washed with water and dried over sodium sulfate. Evaporation of the ether yielded a liquid which reacted with 6 ml of concentrated HCl to yield a solid. This material was triturated with absolute alcohol, washed with alcohol and then with ether to yield a cream-white crystalline solid, 1-(1-aminoethyl)cyclopentadienylmanganese tricarbonyl hydrochloride (4.5 g, 79%). The analytical sample was prepared by washing several additional times with alcohol and with ether.

α-Benzamido-β-(cyclopentadienylmanganese tricarbonyl)acrylic azlactone

A mixture of 1.232 g (0.0052 mole) formylcyclopentadienylmanganese tricarbonyl, 1.146 g (0.0064 mole) of hippuric acid, 0.5 g freshly fused and powdered sodium acetate and 2 ml of acetic anhydride was heated gently with shaking until the mixture liquified. It was then heated an additional 10 minutes on a steam bath, cooled, and stirred with 10 ml of water. The solid which separated was removed by filtration and washed well with water. Recrystallization was effected by dissolving the crude material in warm benzene and diluting with ethanol. The orange-yellow crystals of azlactone were removed by filtration (m.p. 176–177°). A second crop was obtained when the mother liquor was concentrated at reduced pressure and diluted with additional chilled alcohol. The total yield was 69%.

The anilide derivative may be prepared by warming the above azlactone (0.25 g) in 5 ml of acetone with a few drops of aniline. The solvent was evaporated and the residue was triturated with 10 drops of 3 *N* HCl and washed with water to remove excess aniline. Recrystallization twice from aqueous alcohol yielded a yellow powder, m.p. 194–196°. (Found: C, 61.37; H, 3.79; N, 5.99. C₂₄H₁₇O₅MnN₂ calcd.: C, 61.55; H, 3.65; N, 5.98%.)

Carbamoylcyclopentadienylmanganese tricarbonyl

Carboxycyclopentadienylmanganese tricarbonyl (2 g, 0.008 mole) was stirred with an equal weight of PCl₅ in 30 ml of dry benzene at room temperature for 2 h. The solid was removed by filtration and the filtrate was concentrated at 60° *in vacuo* to remove solvent and phosphorus oxychloride. After cooling, 10 ml of concentrated aqueous ammonia was added to the yellow residue. The resulting mixture was stirred thoroughly and the yellow solid collected by filtration (yield 1.4 g, 70%). Yellow prisms, obtained by two recrystallizations from hot alcohol/water, melted at 152–154°.

Bis(cyclopentadienylmanganese tricarbonyl) disulfide

Sulfinocyclopentadienylmanganese tricarbonyl[†] (9.1 g, 0.034 mole) was stirred at –5° into a slurry of 72 g of ice in 24 g of concentrated sulfuric acid (13 ml, 0.234 mole). Zinc dust (12 g, 0.165 g-atom) was added at a rate such that the temperature of the slurry did not exceed 0°. Stirring was continued for 30 min while the mixture was allowed to warm to room temperature. The mixture was slowly heated until after about 2 h the temperature was 80°. At this temperature a vigorous reaction took place and all of the solids liquified. Heating was continued for an additional half hour until only a single liquid phase remained. The contents of the flask were steam-distilled, the

distillate was saturated with NaCl and extracted with ether. The ether phase was dried and the ether removed at reduced pressure leaving 5.4 g of gray solid. This solid was extracted with alcohol which, upon cooling, yielded 5 g (63%) of shining yellow needles of bis(cyclopentadienylmanganese tricarbonyl) disulfide, m.p. 126.5–127.5°.

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SUMMARY

A number of monosubstituted derivatives of cyclopentadienylmanganese tricarbonyl have been synthesized and their NMR and IR spectra recorded. The NMR spectrum of each of the compounds studied is consistent with an A_2B_2 system. The chemical shift difference between the α - and β -protons is of the same order of magnitude as the difference between *ortho* and *meta* protons in the analogous benzene series. The IR spectra of the monosubstituted derivatives are very similar to the spectrum of the parent compound.

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