The Synthesis and Mass Spectral Fragmentation of Some 1,2-Disubstituted Tricarbonyl-η-cyclopentadienylmanganese Derivatives: 2-Lithiation of Tricarbonyl(η-*NN*-dimethylsulphamoylcyclopentadienyl)manganese[1]

By **Ronald G. Sutherland** * and **Ayalur K. V. Unni**, Department of Chemistry and Chemical Engineering, the University of Saskatchewan, Saskatoon, Canada S7N OWO.

Tricarbonyl(η-*NN*-dimethylsulphamoylcyclopentadienyl)manganese (Ic) is metallated in the 2-position to give the intermediate (II) which can be trapped by electrophilic reagents to give 1,2-disubstituted tricarbonyl-η-cyclopentadienylmanganese derivatives (III) whose ^{1}H n.m.r. and mass spectral fragmentation are discussed as are those of tricarbonyl(η-azidosulphonylcyclopentadienyl)manganese (Ia).

An extensive chemistry of 1,2-disubstituted ferrocenes developed from Hauser's discovery that *NN*-dimethylaminomethylferrocene underwent specific lithiation at the 2-position [2] and this area has recently been reviewed.[3,4] For tricarbonyl(η-azidosulphonylcyclopentadienyl)manganese (Ia), which we synthesised by treating the corresponding chlorosulphonyl compound (Ib) with sodium azide in ice-cold aqueous acetone, it was necessary to make specific assignments for the ^{1}H n.m.r. resonances of the $H_{2,5}$ and $H_{3,4}$ protons; the signals occurred as an A_2B_2 pattern centred at δ 5.6 and 5.0 respectively. From earlier studies [5,6] it would be expected that the $H_{2,5}$ protons should constitute the downfield signal since they are adjacent to the highly deshielding sulphonyl group but it was decided to prepare a related compound where $H_{2(5)}$ had been replaced by deuterium and confirm the assignments. Accordingly (Ic) was synthesised by refluxing (Ib) with dimethylamine hydrochloride in acetone; (Ic) was obtained in 49% yield and its ^{1}H n.m.r. spectrum showed two triplets at δ 5.25 and 4.80 and a singlet at δ 2.5 with integral ratios 1 : 1 : 3. The latter signal is due to the *N*-methyl protons and the other two signals the A_2B_2 grouping of the cyclopentadienyl protons. Treatment of (Ic) with methyl-lithium at −70 °C gave the 2-lithiated intermediate (II) which on quenching with D_2O gave the deuteriated product (IIIa) whose ^{1}H n.m.r. shows attenuation of the downfield resonance giving integral ratios of 1 : 1.5 : 4.5 which corresponds to *ca.* 50% incorporation of deuterium at the 2(5) position. In addition, the mixture of (Ic) and (IIIa) obtained shows two parent peaks at *m/e* 311 and 312 respectively in the relative abundance ratios of 11.5 : 11.3. Hence the nitrogen atom of the SO_2NMe_2 group serves to direct metallation of the cyclopentadienyl ring into the 2-position, the SO_2NMe_2 group serving to activate the ring towards anion formation. Hauser *et al.*[7] have noted a similar effect with *NN*-dimethylbenzenesulphonamide which is metallated exclusively in the *ortho*-position. Further proof that lithiation had occurred in the 2-position was obtained by trapping (II) with a variety of electrophilic species whereby (IIIb—i) were obtained; analytical data for these compounds is found in Table 1.

TABLE 1

Analytical data

Compound	M.p. (θ_c/°C)	Yield (%)	*m/e*	Found (%) C	Found (%) H	Found (%) N	Formula	Calculated (%) C	Calculated (%) H	Calculated (%) N
(IIIa)	166—167	44	312				$C_{10}H_9DMnNO_5S$			
(IIIb)	74 (decomp.)	53	355				$C_{11}H_{10}MnNO_7S$			
(IIIc)	121—123	83	369	39.15	3.5	4.1	$C_{12}H_{12}MnNO_7S$	39.04	3.27	3.93
(IIId)	85—86	38	369	42.6	4.35	3.7	$C_{13}H_{16}MnNO_6S$	42.29	4.36	3.71
(IIIe)	148—150	30	431	50.1	4.0	3.15	$C_{18}H_{18}MnNO_6S$	50.10	4.20	3.24
(IIIf)	184—185	39	493	56.35	4.05	2.6	$C_{23}H_{20}MnNO_6S$	56.19	4.10	2.84
(IIIg)	98—99	50	417	48.65	3.8	3.3	$C_{17}H_{16}MnNO_6S$	48.91	3.86	3.35
(IIIh)	201—202	14	525	48.25	3.6	2.7	$C_{21}H_{20}FeMnNO_6S$	48.00	3.83	2.66
(IIIi)	158—159	14	539	48.8	4.15	2.5	$C_{22}H_{22}FeMnNO_6S$	48.99	4.11	2.59

The ^{1}H n.m.r. data in Table 2 confirms that all of these compounds, (IIIb—i), are 1,2-substituted; the 3-, 4-, and 5-protons show up as either ABC or ABX patterns as expected from previous work on 1,2-disubstituted ferrocenes.[8,9] Hence this metallation reaction leads to the specific formation of 1,2-disubstituted tricarbonyl-η-cyclopentadienylmanganese whereas acylation of substituted tricarbonyl-η-cyclopentadienylmanganese leads to mixtures of 1,2- and 1,3-isomers with the latter predominating [10,11] except in the case of methoxy- or methylthio-groups.[12]

The mass spectral fragmentation of some monosubstituted tricarbonyl-η-cyclopentadienylmanganese

---

[1] Preliminary communication, R. G. Sutherland and A. K. V. Unni, *Chem. Comm.*, 1970, 555.

[2] D. W. Slocum, B. W. Rockett, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1965, **87**, 1241.

[3] J. H. Peet and B. W. Rockett, *Rev. Pure and Appl. Chem.*, 1972, **22**, 145.

[4] D. W. Slocum and D. I. Sugarman, *Adv. Chem. Ser.*, 1974, **130**, 222.

[5] L. M. C. Chen, G. G. Long, and C. G. Moreland, *J. Organometallic Chem.*, 1966, **5**, 362.

[6] H. Egger and A. Nikiforov, *Monatsh.*, 1969, **100**, 483.

[7] H. Watanabe, R. A. Schwarz, C. R. Hauser, J. Lewis, and D. W. Slocum, *Canad. J. Chem.*, 1969, **47**, 1543.

[8] M. Hadlington, B. W. Rockett, and A. Nelhans, *J. Chem. Soc.* (*C*), 1967, 1436.

[9] D. J. Booth and B. W. Rockett, *J. Chem. Soc.* (*C*), 1968, 656.

[10] H. Egger and A. Nikiforov, *Monatsh.*, 1968, **99**, 2296.

[11] H. Egger and A. Nikiforov, *Monatsh.*, 1968, **99**, 2311.

[12] H. Egger and A. Nikiforov, *Monatsh.*, 1969, **100**, 1069.

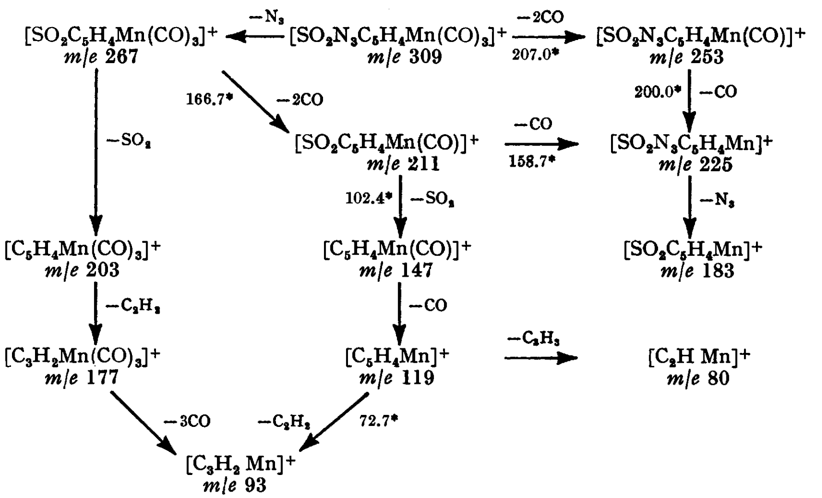
compounds has been examined by Cais [13] and the current study makes available the sulphonyl azide (Ia) and a number of 1,2-disubstituted derivatives (III) derived from (Ic) for comparison. The Scheme shows a possible fragmentation pathway for (Ia). Table 3 shows that the molecular ion M^+ is observed in all cases but that $[M - 3CO]^+$ is usually of much higher intensity. In the case of most monosubstituted tricarbonyl-η-cyclopentadienylmanganese the loss of CO takes place in two steps: the loss of two CO ligands followed by the third, but the loss of one CO ligand was never observed. All of the 1,2-disubstituted tricarbonyl-η-cyclopentadienylmanganese complexes except the methoxycarbonyl derivative lose 3CO ligands directly. The ion $[C_5H_4Mn]^+$, *m/e* 119 was only observed for (Ia), (Ic), (IIa), and (IIIc) and so the loss of 3CO and the side-chains is only a minor fragmentation route. Again the simple manganese-containing ions such as $[C_3H_2Mn]^+$ (*m/e* 93) and $[C_2HMn]^+$ (*m/e* 80) are also only observed with monosubstituted derivatives, the behaviour of (IIIc) being exceptional. It is tempting to suggest that these ions 119, 93, and 80 are good evidence for the presence of monosubstituted tricarbonyl-η-cyclopentadienylmanganese * and this data is compiled in Table 4. Another general feature of these spectra is the presence of ions of the type [Mn—X]$^+$ which appears to be due to the migration of that group to manganese and occurs when X is a stable anion; this data is found in Table 5. The alcohols prepared in this study either lose H_2O from the

TABLE 2

^1H N.m.r. data (τ) for complexes

						X						
Compound	H_3	H_4	H_5	NMe_2	X	H_2	OMe	Me	OH [a]	Ph	H	Ferrocene
(Ic)	← 5.2 →		4.75	7.25	H_2	4.75						
(IIIc)	4.8	5.23	4.53	7.05	CO_2Me		6.13					
(IIId)	5.45	5.71	4.73	7.04	CMe_2OH			8.47	5.45			
(IIIe)	4.9	5.23	4.7	7.48	CPh(Me)OH			8.37	4.36	2.64		
(IIIf)	5.55	5.80	4.55	7.7	CPh_2OH				3.55	2.65		
(IIIg)	5.03	5.45	4.70	7.1, 7.6 [b]	CH(Ph)OH				5.23	2.6	4.06	5.71(7) 5.5(2)
(IIIh)	← 5.3 →		4.66	7.05	CH(Fc)OH				5.5		4.38	5.77(7) 5.5(2)
(IIIi)	← 5.23 →		4.8	7.27	CMe(Fc)OH			8.03	5.23			

[a] Exchanges with D_2O. [b] Restricted rotation.



SCHEME

TABLE 3

Relative abundance of $LMn(CO)_x$ ions where $x = 0, 1$, or 3 [$LMn(CO_2)^+$ not observed]

Compound	M^+	$LMn(CO)_3^+$	$LMn(CO)^+$	LMn^+
(Ia)	309	22.0	3.8	32.5
(Ic)	311	13.0	4.9	64.6
(IIIa)	312	13.0	5.0	61.5
(IIIc)	369	26.3	3.1	100
(IIId)	369	6.8		20.4
(IIIe)	431	5.6		66.6
(IIIf)	493	6.3		100
(IIIg)	417	12.6		100
(IIIh)	525	88		6
(IIIi)	532	33.8		16.1

TABLE 4

Relative abundance of some Mn-containing ions

Compound	$[C_5H_9Mn]^+$ *m/e* 119 [b]	$[C_3H_2Mn]^+$ *m/e* 93	$[C_2HMn]^+$ *m/e* 80
(Ia)	38	26.5	17.0
(Ic)	30.2	30.2	9.0
(IIIa) [a]	19.2	26.0	9.5
(IIIc)	34.1	13.9	10.8

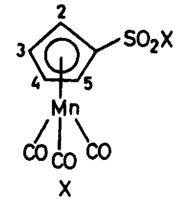
[a] The relative abundance of *m/e* 120 is 88. [b] The relative high abundance of *m/e* 119 could be due to a contribution from $[Mn - SO_2]^+$.

---

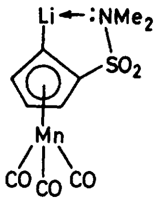
* These ions are observed in the mass spectra of almost all the monosubstituted tricarbonyl-η-cyclopentadienylmanganese prepared in related unpublished work.

[13] M. Cais, M. S. Lupin, N. Maoz, and J. Sharuit, *J. Chem. Soc.* (*A*), 1968, 3086.

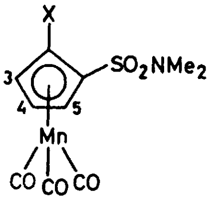
parent ion (IIId, e, h, and i) or an OH radical (IIIf and g) and these processes are all characterised by the presence of a metastable ion.



(I) a; N_3
b; Cl
c; NMe_2



(II)



X
(III) a; D
b; CO_2H
c; CO_2Me
d; CMe_2OH
e; CMe(Ph)OH
f; CPh_2OH
g; CH(Ph)OH
h; CH(Fc)OH
i; CH(Fc)OH

Fc — ferrocenyl

TABLE 5

Relative abundance of $[Mn - X]^+$ ions

Compound	X	m/e	Rel. abundance
(Ia)	N_3	97	10.0
	H	56	13 4
(IIc)	NMe_2	99	4.5
	H	56	7.0
(IIIa)	NMe_2	99	3.8
	H	56	7.3
(IIIc)	OMe	86	6.2
(IIId)	CO	83	27.2
	OH	72	13.6
(IIIe)	OH	72	29.8
(IIIf)	OH	72	9.0
(IIIg)	OH	72	12.6
(IIIh)	OH	72	10

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on Varian T60 and HA100 spectrometers; i.r. spectra were recorded on a Beckman IR8 instrument and the mass spectral studies were carried out using an AEI MS12 spectrometer at 140 °C and 70 eV.

Tricarbonyl(η-azidosulphonylcyclopentadienyl)manganese (Ia).—To tricarbonyl(η-chlorosulphonylcyclopentadienyl)-manganese [14] (10 g) in ice-cold acetone (15 cm^3) was added sodium azide (4 g) in water (12 cm^3) and the mixture was stirred for 10 min. Water (50 cm^3) was added after 24 h and the dark brown precipitate filtered off, dried, and recrystallised from n-hexane to give pale yellow needles (10 g, 70%), m.p. 54—55 °C (Found: C, 30.75; H, 1.6; N, 13.4. $C_8H_4MnN_3O_5S$ requires C, 31.1; H, 1.3; N, 13.6%), *m/e* 309, $\nu(N_3)$ 2 122 cm^{-1} (KBr).

*Tricarbonyl(η-*NN*-dimethylsulphamoylcyclopentadienyl)-manganese* (Ic).—Compound (Ib) (1 g), dimethylamine hydrochloride (1 g), and sodium acetate (1.5 g) were dissolved in acetone (15 cm^3); the mixture was then refluxed for 2 h, cooled in an ice-bath, and then water (20 cm^3) was added when light brown crystals separated. Recrystallisation from 95% ethanol gave light yellow crystals (0.5 g, 49%), m.p. 166—168 °C (Found: C, 38.95; H, 3.5; N, 4.55. $C_{10}H_{10}MnNO_5S$ requires C, 38.6; H, 3.25; N, 4.5%), *m/e* 311.

2-*Lithiation of Compound* (Ic).—Compound (Ic) (1.0 g) was dissolved in dry THF (30 cm^3) and cooled to −70 °C in an acetone–solid CO_2 bath under a stream of dry nitrogen. A solution of methyl-lithium in ether (1M; 7 cm^3) was added and the mixture stirred for a further 30 min to give a solution of compound (II).

Quenching of Compound (II) *by Electrophilic Reagents*.—Acetone (15 cm^3) freshly distilled from calcium oxide was added to a solution of compound (II) prepared above and the mixture held at −70 °C for 30 min; after this it was poured onto aqueous HCl (5%; 50 cm^3). The separated organic layer was washed (saturated NaCl) and the dried ($MgSO_4$) before removal of solvent under reduced pressure. The products were chromatographed on alumina when elution with benzene gave unchanged (Ic) (0.1 g, 10%); further elution with benzene–ethyl acetate (4 : 1) gave the condensation product (IIId) as a light yellow solid (0.422 g, 38%), m.p. 85—86 °C, after recrystallisation from acetone–ether (1 : 3).

Mass Spectra.—The *m/e* ratio is followed by the relative abundance in parentheses. Metastables (*) and the corresponding transitions are also given.

(Ia): 39 (4.5), 48 (2.4), 55 (100.0), 56 (13.4), 63 (4.0), 64 (3.5), 71 (2.5), 72 (2.5), 72.7 * (119→93), 80 (17.0), 81 (8.0), 87 (2.5), 92 (2.5), 93 (26.5), 97 (10.0), 102.4 * (211→147), 106 (2.5), 107 (5.4), 117 (13.0), 119 (38.0), 120 (2.2), 123.5 * (252→177), 133 (16.0), 145 (1.8), 147 (10.0), 150.9 * (211→178), 158.7 * (211→183), 166.7 * (267→211), 177 (60.5), 178 (4.2), 183 (8.5), 197 (1.9), 200 * (253→225), 203 (2.0), 207 * (309→253), 211 (4.0), 225 (32.5), 253 (3.8), 267 (7.5), 309 (22.0), and (M^+) 310 (0.9).

(Ic): 39 (5.0), 41 (1.2), 42 (13.7), 43 (3.2), 44 (7.8), 55 (98.0), 56 (7.0), 65 (6.5), 66 (1.6), 67 (1.5), 71.8 * (120→93), 72.6 * (119→93), 72 (5.5), 80 (9.0), 88.3 * (163→120), 86 (1.5), 87 (1.0), 89 (7.2), 91 (2.0), 92 (2.1), 93 (30.2), 98 (2.5), 99 (4.5), 108 (74.0), 109 (6.7), 115 (1.9), 119 (30.2), 120 (100.0), 121 (6.2), 136 (1.3), 147 (2.4), 163 (8.5), 166 (2.4), 170 (0.9), 183 (1.5), 184 (4.2), 202.0 * (255→227), 209.0 * (311→255), 227 (64.6), 228 (6.7), 229 (3.9), 255 (4.9), 311 (13.0), and (M^+), 312 (1.7).

(IIIc): 55 (96.1), 80 (10.8), 86 (6.2), 93 (13.9), 99 (17.0), 105 (6.4), 108 (6.2), 118 (9.3), 119 (34.1), 125 (10.8), 129 (6.6), 146 (9.3), 147 (10.8), 148 (21.7), 152 (18.6), 165 * (221→191), 176 (66.2), 177 (18.6), 189 (37.2), 190 (6.2), 191 (83.7), 192 (6.4), 207 (9.3), 221 (30.1), 254 (9.3), 259.5 * (313→285), 265.5 * (369→313), 285 (100), 313 (3.1), 338 (4.6), 369 (26.3), and (M^+) 370 (3.1).

(IIId): 39 (20.4), 41 (18.7), 43 (100), 55 (51.1), 58 (23.8), 59 (32.4), 72 (13.6), 77 (23.8), 78 (66.2), 79 (15.6), 83 (27.2), 91 (13.6), 97 (10.2), 101 (13.6), 106 (13.6), 120 (8.5), 134 (13.6), 148 (25.5), 160 (13.6), 203 (15.6), 250 * (285→267), 267 (23.8), 285 (20.4), 354 (1.0), and 369 (6.8) (M^+).

(IIIe): 39 (26.2), 41 (42.6), 55 (91.0), 72 (29.8), 77 (22.6), 123 (42.6), 137 (42.6), 152 (29.8), 165 (68.5), 166 (100.0), 167 (42.6), 193 (22.6), 210 (83.0), 222 (22.6), 265 (22.6), 279.3 * (431→347), 311.9 * (347→329), 329 (5.6), 347 (66.6), and 431 (5.6) (M^+).

(IIIf): 55 (33.3), 58 (7.6), 72 (9.0), 77 (9.0), 78 (7.2), 105 (5.4), 152 (6.3), 171 (6.3), 202 (7.6), 226 (13.5), 227 (9.9), 228 (46.1), 229 (43.2), 230 (9.0), 272 (9.4), 284 (7.2), 301 (3.0), 318 (2.9), 331 (2.2), 339.3 * (493→409), 375.6 * (409→392), 392 (0.5), 409 (100.0), 410 (24.7), 493 (6.3), and (M^+) 494 (1.6).

(IIIg): 39 (2.0), 42 (4.2), 44 (5.2), 51 (2.6), 55 (34.0), 56 (2.2), 58 (1.6), 63 (1.8), 72 (12.6), 77 (5.6), 80 (2.6), 91 (1.6), 98 (4.4), 105 (2.2), 115 (4.0), 116 (2.6), 126 (2.0), 127 (2.6), 128 (1.7), 132 (1.8), 136 (1.5), 139 (2.2), 141 (4.2), 151 (5.8), 152 (34.0), 153 (26.0), 154 (6.6), 165 (1.4), 168 (2.0), 169 (2.8), 181 (1.8), 196 (11.6), 197 (5.2), 207 (4.0), 208 (10.8), 209 (1.9), 217 (1.4), 224 (11.2), 229.5 * (333→316), 225 (3.2), 226 (3.1), 245 (7.0), 246 (3.6), 254 (2.1), 261 (2.6), 265.8 * (417→333), 316 (1.0), 333 (100.0), 334 (16.5), 335 (7.6), and 417 (12.6) (M^+).

(IIIh): 55 (50.0), 56 (18.0), 63 (6.0), 72 (10.0), 77 (5.0), 78 (10.0), 98 (10.0), 105 (12.0), 121 (20.0), 139 (70.0), 140 (36.0), 141 (30.0), 171 (16.0), 172 (10.0), 186 (6.0), 195 (12.0), 196 (24.0), 197 (18.0), 212 (6.0), 224 (8.0), 260 (28.0), 266 (10.0), 303 (30.0), 315 (14.0), 380 (8.0), 405.7 * (441→423), 423 (100.0), 441 (6.0), 525 (88.0), and (M^+) 526 (24.0).

(IIIi): 39 (22.4), 41 (13.8), 42 (13.8), 43 (19.3), 50 (16.1), 51 (19.3), 52 (19.3), 55 (23.0), 56 (11.5), 57 (17.1), 58 (23.0), 63 (4.6), 87 (25.7), 88 (100), 89 (9.2), 91 (6.9), 104 (5.7), 105 (5.7), 120 (5.7), 121 (11.5), 139 (6.9), 152 (13.8), 153 (27.6), 154 (11.5), 155 (19.3), 185 (4.6), 208 (4.6), 209 (6.9), 210 (12.3), 211 (9.2), 276 (9.2), 317 (19.3), 328 (14.8), 329 (12.3), 330 (11.2), 419.7 * (455→437), 437 (17.2), 455 (16.1), 521 (3.4), 539 (33.8), and (M^+) 540 (9.2).

We thank the Ethyl Corporation for supplies of tricarbonyl(η-cyclopentadienyl)manganese, the National Research Council of Canada for financial support and the University of Saskatchewan for the award of a Graduate Scholarship (A. K. V. U.).

[6/830 *Received*, 30*th April*, 1976]

---

[14] M. Cais and J. Kozikowski, *J. Amer. Chem. Soc.*, 1960, **82**, 5667.