Reactions between Methyl-, Acetyl-, and Phenyl-pentacarbonylmanganese and Acetylenes

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Methyl-, acetyl-, and phenyl-pentacarbonylmanganese undergo *cis*-addition reactions with the acetylenes $PhC{\vdots}CH$, $RO_2C{\cdot}C{\vdots}C{\cdot}CO_2R$ (R = Me or H), $MeO_2C{\cdot}C{\vdots}CH$, or $CH{\vdots}C{\cdot}CHO$ to afford stable (vinyl ketone) tetracarbonylmanganese derivatives, in which the keto-group is co-ordinated to a manganese atom. The reactions with phenylacetylene give, in addition, low yields of 2,4,6-trisubstituted-π-pyranyltricarbonylmanganese complexes. The ^1H n.m.r. and i.r. spectra of these new complexes are described.

ALTHOUGH the reactions of alkyl- and acyl-metal carbonyl derivatives with olefins [1,2] and conjugated dienes [3] have been investigated in some detail, little work has been carried out on the corresponding insertion reactions with acetylenes. The reactions reported to date, in the main, have not afforded simple adducts. Thus, alkyl- and acyl-tetracarbonylcobalt complexes give π-(penteno-4-lactonyl)tricarbonylcobalt complexes with disubstituted acetylenes,[4] whereas $MeMn(CO)_5$ [5] and $(\pi\text{-}C_5H_5)Fe(CO)_2Me$ [6] react with acetylenes to yield complex, cyclic

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[1] R. F. Heck, *Adv. Organometallic Chem.*, 1966, **4**, 243.

[2] J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *J. Organometallic Chem.*, 1964, **2**, 119; J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *Proc. Chem. Soc.*, 1963, 218; J. B. Wilford, A. Forster, and F. G. A. Stone, *J. Chem. Soc.*, 1965, 6519; J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 93; B. L. Booth, R. N. Haszeldine, and N. I. Tucker, *J. Organometallic Chem.*, 1968, **11**, P 5.

[3] W. D. Bannister, M. Green, and R. N. Haszeldine, *J. Chem. Soc.* (*A*), 1966, 194; M. Green and R. I. Hancock, *J. Chem. Soc.* (*A*), 1968, 109.

[4] R. F. Heck, *J. Amer. Chem. Soc.*, 1964, **86**, 2819.

[5] A. Nakamura, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, 1962, **19**, 81; *Chem. Abs.*, 1963, **59**, 8786.

[6] T. H. Coffield, K. G. Ihrman, and W. Burns, *J. Amer. Chem. Soc.*, 1960, **82**, 4209.

organometallic compounds. The reaction of $MeMn(CO)_5$ with 3,3-trifluoropropyne has, however, recently been shown [7] to give a stable 1 : 1 adduct although its structure was not unequivocally established. The reactions of $MeMn(CO)_5$ and $PhMn(CO)_5$ with the acetylenes $PhC{\vdots}CH$, $MeO_2C\cdot C{\vdots}C\cdot CO_2Me$, $HO_2C\cdot C{\vdots}C\cdot CO_2H$, $HC{\vdots}C\cdot CO_2Me$, and $HC{\vdots}C\cdot CHO$ to give simple 1 : 1 adducts are now reported.

Methyl- and phenyl-pentacarbonylmanganese reacted with phenylacetylene at room temperature to give the complexes (Ia) and (Ib) respectively in high yields, as stable, crystalline solids. No carbon monoxide evolution was observed during these reactions. The compound (Ia) was also obtained in high yield from the reaction between acetylpentacarbonylmanganese and phenylacetylene at room temperature when *ca.* 1 mol. of carbon monoxide was evolved. The compounds were characterised by chemical analysis (Table 1) and i.r. and n.m.r. spectroscopy. Their i.r. spectra (Table 2) showed the characteristic pattern of one medium and three strong bands ($3A' + A''$) in the metal carbonyl region for a *cis*-$Mn(CO)_4$ group. The presence in these compounds of a ketone group in which the CO is co-ordinated to a manganese atom is established by a medium band at 1570 cm.$^{-1}$ in the spectrum of (Ia) and at 1538 cm.$^{-1}$ in the spectrum of (Ib). A number of complexes have now been described in which the CO of

TABLE 1

Methyl- and phenyl-pentacarbonylmanganese–acetylene adducts

			Found			Required		
Compound	Colour	M.p.	C(%)	H(%)	*M*	C(%)	H(%)	*M*
a) $MeMn(CO)_5$ adducts								
(Ia)	Orange	67—68°	54·0	2·9	322	53·8	2·9	312
(IIa)	Dark red	97—98°	65·4	4·2	374	65·3	3·9	386
(IIIa)	Yellow	53—54°	41·0	2·6	377	40·9	2·6	352
(IIIb)	Orange	*ca.* 100° (decomp.)	37·1	1·4	320	37·0	1·5	324
(IVa)	Yellow	55—56°	41·0	2·5	297	40·8	2·4	294
(IVb)	Red	32—33°	41·2	2·1		40·9	1·9	
(*b*) $PhMn(CO)_5$ adducts								
(Ib)	Red	65—66°	61·6	2·7	382	61·0	2·9	379
(IIb)	Darkred	176—178°	69·9	3·9		69·6	3·8	
(IIIc)	Orange	89—91°	49·6	2·6	419	49·3	2·7	414
(IIId)	Orange	*ca.* 150° (decomp.)	46·7	1·9	381	46·6	1·8	386
(IVc)	Red	85—86°	50·6	2·6	354	50·6	2·5	356
(IVd)	Darkred	117—118°	52·0	2·0	339	51·5	2·2	331

TABLE 2

I.r. spectral bands (cm.$^{-1}$)

Compd.	Carbonyl stretching frequencies [a]	Other bands [b]
(Ia)	2078m, 1997s, 1991s, 1948s.	3086w, 3040w, 2941vw, 1597vw, 1570m, 1493w, 1466m—s, 1460m—s, 1453msh, 1441w, 1420w, 1374w, 1333m, 1211vw, 1193m, 1159vw, 1075w, 1028w, 1018w, 987w, 964w, 918vw, 837w, 764m, 756m, 698m, 694m, 668w, 652m
(Ib)	2077m, 1999s, 1994s, 1947s.	3067w, 2933w, 2857w, 1600w, 1583w, 1538m, 1497w, 1462m, 1429w, 1358m, 1300w, 1278w, 1223m, 1204w, 1179w, 1158w, 1080w, 1060m, 1026w, 1000w, 934w, 845w, 838w, 788m, 756m—s, 692m—s, 685msh, 661m, 650m
(IIa)	2005s, 1960s, 1927s.	3058w, 3030w, 2967w, 2907w, 1599w, 1581w, 1550w, 1500m, 1469w, 1454w, 1440w, 1430w, 1385w, 1361w, 1313m, 1285m, 1266m, 1227w, 1170m, 1080w, 1036w—m, 1030w—m, 1012w—m, 1000w, 972m, 922w, 915w, 891w, 849w, 840w, 789w, 761m—s, 740m, 725m, 693m—s, 672w—m, 652m—s, 638m—s
(IIb)	2009s, 1952s, 1929s.	3058w, 3021w, 1592w, 1535w, 1500w, 1488m, 1451m, 1441m, 1332w, 1319w, 1278w, 1260w, 1210w, 1180w—m, 1162w, 1158w, 1100w, 1077w, 1038w, 1029w, 1013w—m, 1008w—m, 1001w—m, 960w, 930w, 920w, 915w, 893w, 841w, 785w, 761m, 722w, 690m—s, 681m—s, 665w, 650m—s, 639m—s
(IIIa)	2095m, 2018s, 2015s, 1968s.	3448w, 3012w—msh, 2967m, 2933msh, 2857w—m, 2740w, 2457w, 1721s, 1590s, 1492m, 1437m—s, 1378m—s, 1330s, 1232m—s, 1210m—s, 1085m—s, 1002m, 993m, 949m, 879w—m, 786m—s, 773w—m, 735m, 662s
(IIIb)	2095s, 2010vs, 1957vs [c]	2985m—s, 2882m—s, 2653m—s, 2597m—s, 1698ssh, 1683s, 1672s, 1577m, 1507w, 1431w—m, 1410w—m, 1376w—m, 1330m, 1266m, 1257m, 1207w, 1120m, 1095w, 1083w, 1046w, 1027w, 1015w, 928w—m, 893w, 886w, 873m, 794w, 706w, 678m, 654m
(IIIc)	2095m, 2018s, 2015s, 1967s	3067w, 3003w, 2874m, 1718s, 1706s, 1597m, 1585m, 1540s, 1535ssh, 1470m—s, 1460m—s, 1442s, 1426s, 1342s, 1264s, 1218s, 1157m, 1140m—s, 1035m, 977m, 941m, 926msh, 873m, 837m, 810m, 782m, 770m, 731m, 707m, 691m, 654s
(IIId)	2079m, 2013vs, 1961vs [c]	4310m, 2935m—s, 2873m—s, 2618m—s, 2545m—s, 1678s, 1600m, 1585m, 1548s, 1504msh, 1479m, 1451m—s, 1425s, 1398m—s, 1340s, 1316m, 1282s, 1259s, 1183m, 1167m, 1012m—s, 974w, 918w, 843w, 815m, 780m, 722m, 700m, 675m, 663m, 652m
(IVa)	2091w, 2007s, 1963s.	3030w, 2976m, 1706s, 1592s, 1495m—s, 1431m—s, 1374m—s, 1326s, 1202s, 1024m—s, 990m—s, 853m, 779m, 731m, 656s
(IVb)	2090m, 2008ssh, 2005s, 1971s.	2924w, 2865w, 2786w, 1679m—s, 1583m—s, 1492m, 1419w, 1380m, 1309m—s, 1192m, 1100m, 1049w, 1021w, 988w, 918w, 833w, 704w, 656m
(IVc)	2090m, 2008s, 1961s.	2967w, 1718m, 1698m, 1656w, 1639w, 1600m—w, 1587m—w, 1555m—s, 1488m, 1445m, 1431m, 1353m—s, 1299m, 1230m, 1209s, 1178m, 1053w—m, 1017m, 999w—m, 935w, 857w, 842w, 793w—m, 774w—m, 721w—m, 701w—m, 683m, 658s, 649s
(IVd)	2087m, 2002s, 1967s	2959w, 2924w, 2857w, 1678m, 1597w, 1582w, 1542m, 1494m, 1478w, 1438w, 1380w, 1340m, 1318w, 1298w, 1234m, 1181w, 1160w, 1105w, 1078vw, 1057w, 1021w, 999vw, 988vw, 850w, 785m, 698m, 681m, 662m, 650m

[a] Cyclohexane solution, unless otherwise indicated. [b] Nujol and hexachlorobutadiene mulls. [c] Acetone solution.

an aldehyde,[7] ketone [7,8] or methoxycarbonyl [9,10] group is co-ordinated to the metal atom. In these compounds a band in their i.r. spectra in the region of 1490—1500 (CHO or COR group) or 1550—1600 cm.$^{-1}$ (CO_2Me group) has been attributed to the co-ordinated CO group. The i.r. spectra of (Ia) and (Ib) show, in addition to the medium band in the region 1530—1570 cm.$^{-1}$, a medium band in the region 1460—1466 cm.$^{-1}$ [1460 or or 1466 cm.$^{-1}$ (Ia) and 1462 cm.$^{-1}$ (Ib)] which is also in approximately the region expected for a co-ordinated ketone group. It is considered unlikely, however, that the band in this latter region is due to a co-ordinated carbonyl group as no appreciable shift is observed on comparison of the spectrum of (Ia; R = Ac) with that of (Ib; R = Bz) in this region. The increased conjugation of the CO group with the phenyl group in (Ib) might reasonably be expected to shift the ν(CO) band of the co-ordinated ketone by *ca.* 30 cm.$^{-1}$ to longer wavelength, *i.e.* the order of shift observed for the band in the region of 1530—1570 cm.$^{-1}$. The mass spectrum of (Ia) showed a parent ion *m/e* 312, and peaks at *m/e* 284, 256, 228, and 200 corresponding to successive loss of four carbon monoxide molecules in agreement with the assigned structure. Compound (Ib) did not give a parent ion in its mass spectrum and showed only ions formed by the breakdown of the organic fragment.

Although the i.r. and ^1H n.m.r. spectra (Table 3) and analytical data support the assignment of (Ia) and (Ib) as 1 : 1 adducts, they do not allow a distinction to be drawn between the two possible structures, namely, RCO·CH:CPh·Mn$(CO)_4$ and RCO·CPh:CH·Mn$(CO)_4$ (Ia; R = Me; Ib; R = Ph). An attempt to unequivocally establish the structure of (Ia) by cleavage of the –Mn$(CO)_4$ fragment with hydrogen chloride was unsuccessful, and an alternative synthesis of the MeMn$(CO)_5$–PhC:CH adduct was therefore sought.

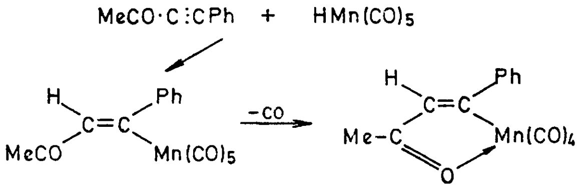
TABLE 3

^1H Chemical shifts (τ) [a]

Compound	Assignments							
	CHO	OH	=CH	C_6H_5	C_6H_5CO	OCH_3	CH_3CO	CH_3C
(Ia) [b]			3·02s(1)	2·62s(5)			7·72a(3)	
(Ib)			2·31s(1)	2·0—2·1 b,s(2) 2·56s(8)				
(IIa)			4·56s(1) 5·28s(1)	2·15m(2) 2·65m(8)				8·01s(3)
(IIb) [c]			4·31s(2)	2·00m 2·52s } (15)				
(IIIa)						6·12s(3) 6·24s(3)	7·32s(3)	
(IIIc)					2·49s(5)	6·10s(3) 6·33s(3)		
(IIId) [b]		−0·42s(2)			2·43s(5)			
(IVa)			2·83s(1)			6·18s(3)	7·58s(3)	
(IVb)	−0·43s(1)		2·63s(1)				7·51s(3)	
(IVc)			[d]		1·90—2·20 b,s 2·40—2·60 b,s } (6)	6·12s(3)		
(IVd)	−0·63s(1)		1·57s(1)		2·06m(5)			

[a] Except where stated spectra were recorded at 60 MHz on solutions in CCl_4 with Me_4Si as internal reference. Numbers in parentheses indicate relative intensities of peaks. [b] Solution in acetone. [c] Solution in $CDCl_3$. [d] Absorption of the vinylic proton masked by absorptions due to the phenyl protons.

Previous work has shown [10] that the unsymmetrical acetylene, HC:C·CO_2Me, reacts with HMn$(CO)_5$ by a stereospecific *trans*-addition to afford *cis*-MeO_2C·CH:CH·-Mn$(CO)_5$. Thus, it was considered that reaction between HMn$(CO)_5$ and the acetylene, MeCOC:CPh, would similarly give the compound MeCO·CH:CPh·Mn$(CO)_5$, in which the acetyl group and the Mn$(CO)_5$ group have a *cis*-arrangement, and which could readily lose carbon monoxide by co-ordination of the acetyl group to the manganese atom to give one of the possible isomers of the product from the reaction of MeMn$(CO)_5$ with PhC:CH.



When this reaction was carried out at room temperature 1 mol. of carbon monoxide was evolved to give an 11% yield of a compound identical to that obtained from the reaction of MeMn$(CO)_5$ or MeCOMn$(CO)_5$ with PhC:CH. This evidence supported the assignment of structure (Ia) to this compound and, by analogy, the similar structure (Ib) assigned to the PhMn$(CO)_5$–PhC:CH adduct. The low yield of adduct from the reaction of MeCO·C:CPh and HMn$(CO)_5$ is attributed to extensive hydrogenation of the acetylene, as evidenced by the high yield of $Mn_2(CO)_{10}$ from this reaction, which also occurred under the reaction conditions employed; attempts to isolate an olefinic product from this reaction were unsuccessful.

[7] D. A. Harbourne and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 1765.

[8] R. B. King and A. Fronzaglia, *Inorg. Chem.*, 1966, **5**, 1837.

[9] M. Dubeck and R. A. Schell, *Inorg. Chem.*, 1964, **3**, 1757.

[10] B. L. Booth and R. G. Hargreaves, *J. Chem. Soc.* (*A*), 1969, 2766.

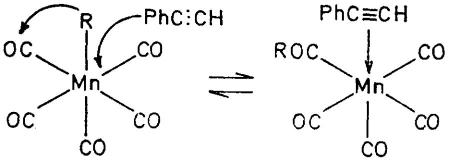
The reactions of methyl- and phenyl-pentacarbonylmanganese with PhC⋮CH gave, in addition to the compounds (Ia) and (Ib) described above, low yields (*ca.* 5%) of deep red, crystalline solids (IIa) and (IIb) which had analyses consistent with their formulation as 2 : 1 adducts of PhC⋮CH and $RMn(CO)_5$. The ^1H n.m.r. spectrum (Table 3) of (IIa) showed two vinylic protons in magnetically different environments, 10 aromatic protons, and a singlet (τ 8·01) for the protons of a CH_3 group, confirming the stoicheiometry of the adduct. The observed chemical shift of the methyl protons was different from that observed for a CH_3CO group, and was more consistent with a CH_3 group attached to an unsaturated system. The ^1H n.m.r. spectrum of (IIb) showed the presence of 15 aromatic protons, and two equivalent vinylic protons, suggesting a symmetrical molecule. In both spectra the bands were sharp indicating that the compounds are diamagnetic. The u.v. spectra (Table 4) of (IIa) and (IIb) showed a very intense absorption at 200—203 nm., indicative of a highly conjugated system; the spectra were different from those of the simple 1 : 1 adducts also prepared in this work. Their i.r. spectra (Table 2) showed only three strong bands of approximately equal intensity in the metal-carbonyl region, and no strong bands in the 1535—1600 cm.$^{-1}$ region for a co-ordinated ketone group. The spectra did, however, show a medium band at 1170 cm.$^{-1}$ (IIa) and 1180 cm.$^{-1}$ (IIb), not present in the spectra of the 1 : 1 adducts, which could be assigned to the CO stretching vibrations associated with a cyclic ether. The analytical and spectroscopic data seem explicable only in terms of the structures (IIa) and (IIb), in which the pyran ring acts as a five-electron donor.

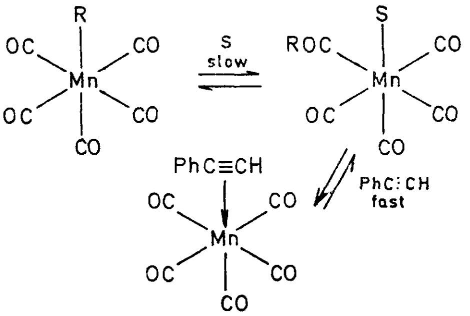
TABLE 4

U.v. spectral bands

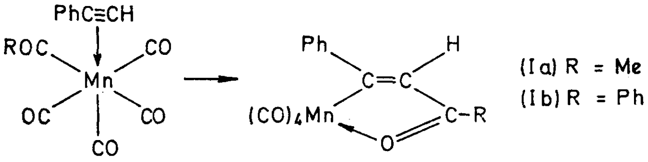
Compound (solvent)		$\lambda_{max.}$(nm.)
(Ia)	EtOH	210·5 (ε 32,600), 324—326 (ε 10,500)
(Ib)	EtOH	208·5 (ε 37,400), 226—228 (ε 32,900), 347—348 (ε 13,000), 401 (ε 10,200)
(IIa)	EtOH	200—203 (ε 62,500)
(IIb)	EtOH	201 (ε 77,600), 236—240 (ε 40,300)
(IIIa)	EtOH	207—208 (ε 25,400), 371—376 (ε 5080)
(IIIb)	EtOH	208—211 (ε 19,400), 367—369 (ε 3800)
(IIIc)	Hexane	205 (ε 32,500), 250—256 (ε 14,400), 396 (ε 7250)
(IIId)	EtOH	206—207 (ε 32,100), 389 (ε 7170)
(IVa)	EtOH	210—211·5 (ε 22,800), 367—370 (ε 3780)
(IVc)	Hexane	208—210 (ε 39,400), 222·5—224 (ε 28,400), 270 (ε 26,400), 408 (ε 9480)
(IVd)	EtOH	209—210 (ε 28,200), 276 (ε 20,200), 401—405 (ε 6000)

These observations can be rationalised if the reaction of phenylacetylene with $MeMn(CO)_5$ or $PhMn(CO)_5$ proceeds as illustrated below. Reaction first involves co-ordination of the acetylene to the manganese atom with displacement of CO into the methyl- or phenyl-manganese bond *via* a methyl- or phenyl-migration. This reaction could occur, either by a direct S_N2 reaction, as suggested[11] for the carbonylation of methylpentacarbonylmanganese at low carbon monoxide concentrations or by a solvent-assisted migration followed by rapid displacement of the solvent molecule by the acetylene, as postulated for the reactions of methylpentacarbonylmanganese with amines and phosphines.[12]

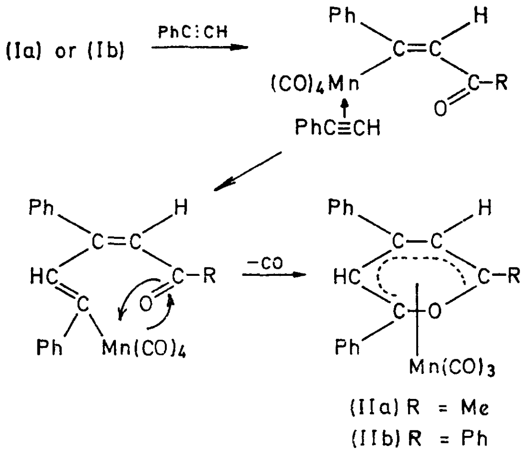




This is then followed by a *cis*-addition to the acetylenic bond to give the isolated complexes (Ia) and (Ib).



Further reaction of another acetylene molecule with (Ia) or (Ib), could, with insertion into the carbon–manganese bond, followed by addition across the ketonic CO group result in cyclisation to give (IIa) or (IIb).



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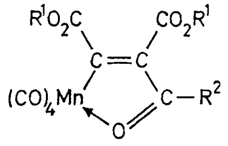
[11] F. Calderazzo and K. Noack, *Co-ordination Chem. Rev.*, 1966, **1**, 118; F. Calderazzo and K. Noack, *J. Organometallic Chem.*, 1967, **10**, 101.

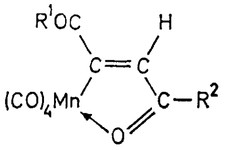
[12] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1964, **86**, 3994.

The formation of (Ia) from the reaction between phenylacetylene and acetylpentacarbonylmanganese probably occurs *via* the same π-acetylene intermediate formed by a dissociative mechanism. A similar mechanism has been shown to occur in the reaction of MeCOMn-(CO)$_5$ with triphenylphosphine,[13] and in some support of a mechanism of this type it is shown here that the similar reaction of MeCOMn(CO)$_5$ with methylpropiolate is almost completely inhibited when carried out under a pressure of carbon monoxide.

$$\mathrm{MeCOMn(CO)_5} \overset{\text{slow}}{\rightleftharpoons} \mathrm{MeCOMn(CO)_4 + CO} \overset{\substack{\text{PhC:CH}\\ \text{fast}}}{\rightleftharpoons} \mathrm{MeCOMn(CO)_4(PhC{:}Ch)}$$



(IIIa) R¹ = Me, R² = Me
(IIIb) R¹ = H, R² = Me
(IIIc) R¹ = Me, R² = Ph
(IIId) R¹ = H, R² = Ph

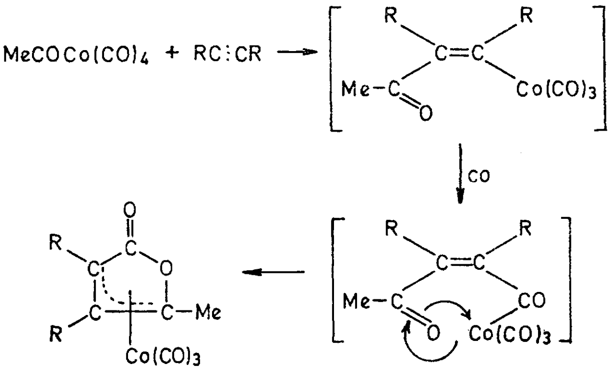


(IVa) R¹ = OMe, R² = Me
(IVb) R¹ = H, R² = Me
(IVc) R¹ = OMe, R² = Ph
(IVd) R¹ = H, R² = Ph

The acetylenes RO$_2$C•C:C•CO$_2$R (R = H or Me), HC:C•CO$_2$Me or HC:C•CHO reacted with phenyl- and methyl-pentacarbonylmanganese at room temperature to give high yields of the 1 : 1 adducts (IIIa—d) and (IVa—d) as air-stable, crystalline solids. The compounds (IIIa, b) and (IVa, b) were also prepared by reaction between acetylpentacarbonylmanganese and the corresponding acetylenes. The compounds have been fully characterised by chemical analysis (Table 1), i.r., n.m.r., and u.v. spectroscopy. The i.r. spectra of the compounds (IIIa, b) and (IVa, b) prepared from methyl- and acetyl-pentacarbonylmanganese all showed a medium-strong band in the region of 1577—1592 cm.$^{-1}$ for a co-ordinated aceto-group. In the spectra of the compounds (IIIc, d) and (IVc, d) prepared from phenyl-pentacarbonylmanganese the band for the co-ordinated CO group is in the region of 1543—1555 cm.$^{-1}$. The mass spectrum of (IIIa) showed a parent ion at *m/e* 352, and a peak at *m/e* 321 [P — OMe]$^+$, with peaks corresponding to successive loss of four CO molecules from the parent and [P — OMe]$^+$ ions. The mass spectra of the compounds (IVa) and (IVc) similarly showed parent ions at *m/e* 294 and 356 for $[P - n\mathrm{CO}]^+$ and $[P - \mathrm{OMe} - n\mathrm{CO}]^+$ respectively, where n = 1—4.

The structures of the adducts from the symmetrical acetylenes, RO$_2$C•C:C•CO$_2$R (R = H or Me) are assigned as (IIIa—d), on the assumption that a *cis*-addition takes place in these reactions as in the reactions of PhC:CH. The structures of the adducts from the unsymmetrical acetylenes cannot be assigned either from the spectroscopic data or by analogy with the phenylacetylene reactions. The assigned structure (IVa) for the adduct from MeMn(CO)$_5$ and methyl propiolate was derived on the basis of the reaction between the adduct and anhydrous hydrogen chloride at room temperature. This gave a 75% yield of [Mn(CO)$_4$Cl]$_2$ and a pale yellow oil, which was shown by ^{1}H n.m.r. spectroscopy to be a mixture consisting mainly of *trans*-MeO$_2$C•CH:CH•COMe, and a small amount of another compound, believed to be either MeO$_2$C•CH$_2$CHCl•COMe or MeO$_2$C•CHCl•CH$_2$•COMe, formed by addition of HCl to the initial cleavage product. No evidence was obtained for the formation of the compound MeO$_2$C•C(COMe):CH$_2$ or its adducts with hydrogen chloride. By analogy the other adducts obtained from HC:C•CO$_2$Me and HC:C•CHO are similarly assigned the structures (IVb—d).

It has been reported[4] that π-(penteno-4-lactonyl)tricarbonylcobalt complexes (V) are obtained from the reactions between acetyltetracarbonylcobalt and disubstituted acetylenes. These reactions are believed to involve the initial formation of 1 : 1 adducts, similar to the ones described in this work, which then undergo further reaction with CO according to the following scheme.



(V)

Attempts to carbonylate the compounds (IIIa), (IIIc), and (IVa) in diethyl ether at room temperature for 7 days under a high pressure of carbon monoxide (180 atm.) did not give lactonyl complexes, and the starting materials were recovered quantitatively.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer model 257 (grating) or model 21 (NaCl or CaF$_2$ optics) spectrometers. The metal carbonyl region was recorded on full-scale expansion. ^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R 10 or Varian HA 100 instrument, and mass spectra were recorded on an AEI model MS 2H spectrometer. U.v. spectra were recorded on a Hilger and Watts Ultrascan or Unicam SP 700 instrument. Chromatographic separations were carried out on alumina (Grade H) deactivated by storage under ethyl acetate for several days. Methyl-, acetyl-, and phenyl-pentacarbonylmanganese were prepared by previously reported methods.[14] Phenylacetylene

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[13] K. Noack, M. Ruch, and F. Calderazzo, *Inorg. Chem.*, 1968, **7**, 345.

[14] T. H. Coffield, J. Kozikowski, and R. D. Closson, *J. Org. Chem.*, 1957, **22**, 598.

(B.D.H. Ltd.), dimethyl acetylenedicarboxylate, and acetylene dicarboxylic acid (Koch-Light Laboratories Ltd.) were commercial samples used without further purification. Methyl propiolate was prepared in 68% yield from propiolic acid and anhydrous methanol,[15] and propiolaldehyde was obtained in 15% yield by dehydration of prop-2-ynyl alcohol with chromic acid.[16] Light petroleum had a boiling range of 30—40°. M.p.s are uncorrected.

Reactions with Methylpentacarbonylmanganese.—(a) *Phenylacetylene*. Methylpentacarbonylmanganese (0·75 g., 3·57 mmoles) and phenylacetylene (0·36 g., 3·56 mmoles) in diethyl ether (10 ml.) were sealed *in vacuo* in a tube, and kept at room temperature for 10 days. Evaporation of the ether solvent and chromatography of the residual orange-brown oil with light petroleum as eluant gave an orange oil, which crystallised from light petroleum at −20° to give (Ia) (0·70 g., 2·24 mmoles, 63%). Further elution with a 9 : 1 mixture of light petroleum–diethyl ether gave a red-brown oil, which crystallised from light petroleum to give (IIa) (0·05 g., 0·13 mmole, 5%).

(b) *Dimethyl acetylenedicarboxylate*. Methylpentacarbonylmanganese (3·00 g., 14·3 mmoles) and dimethyl acetylenedicarboxylate (2·14 g., 15·1 mmoles) in diethyl ether (10 ml.) at room temperature for 7 days gave a yellow-brown solid. Chromatography with light petroleum as eluant gave (IIIa) (4·1 g., 11·6 mmoles, 81%) which was recrystallised from light petroleum.

(c) *Acetylenedicarboxylic acid*. Methylpentacarbonylmanganese (0·52 g., 2·50 mmoles) and acetylenedicarboxylic acid (0·28 g., 2·50 mmoles) in diethyl ether (5 ml.) at room temperature for 4 days gave an orange solid, which was recrystallised from diethyl ether–light petroleum to give (IIIb) (0·65 g., 2·01 mmoles, 81%).

(d) *Methyl propiolate*. Methylpentacarbonylmanganese (0·50 g., 2·38 mmoles) and methyl propiolate (0·20 g., 2·38 mmoles) in diethyl ether (5 ml.) at room temperature for 6 days gave a yellow oil, which after chromatography using a 4 : 1 light petroleum–diethyl ether mixture as eluant, and recrystallisation from light petroleum gave (IVa) (0·51 g., 1·74 mmoles, 73%).

(e) *Propiolaldehyde*. A solution of methylpentacarbonylmanganese (0·85 g., 4·05 mmoles) and propiolaldehyde (0·24 g., 4·48 mmoles) in diethyl ether kept at room temperature for 7 days gave a red oil, which after chromatography (light petroleum eluant) and recrystallisation from light petroleum gave (IVb) (0·75 g., 2·84 mmoles 70%).

Reactions with Acetylpentacarbonylmanganese.—(a) *Phenylacetylene*. Acetylpentacarbonylmanganese (0·90 g., 3·78 mmoles) and phenylacetylene (0·38 g., 3·72 mmoles) in diethyl ether (10 ml.) at room temperature for 7 days gave carbon monoxide (75 ml.; loss of 1 mol. requires 85 ml.) and (Ia) (0·80 g., 2·56 mmoles, 62%).

(b) *Dimethyl acetylenedicarboxylate*. A solution of acetylpentacarbonylmanganese (0·75 g., 3·15 mmoles) and dimethyl acetylenedicarboxylate (0·47 g., 3·31 mmoles) in diethyl ether (5 ml.) kept at room temperature for 7 days gave carbon monoxide (70 ml.; loss of 1 mol. requires 70·5 ml.) and (IIIa) (1·03 g., 2·93 mmoles, 93%).

(c) *Acetylenedicarboxylic acid*. Acetylpentacarbonylmanganese (0·75 g., 3·15 mmoles) and acetylenedicarboxylic acid (0·36 g., 3·16 mmoles) in diethyl ether (5 ml.) at room temperature for 7 days gave carbon monoxide (65 ml.; loss of 1 mol. requires 70·5 ml.) and (IIIb) (1·0 g., 3·09 mmoles, 97%).

(d) *Methyl propiolate*. A solution of acetylpentacarbonylmanganese (1·00 g., 4·20 mmoles) and methyl propiolate (0·35 g., 4·17 mmoles) in diethyl ether (5 ml.) kept at room temperature for 7 days gave carbon monoxide (94 ml.; loss of 1 mol. requires 95 ml.), and (IVa) (0·95 g., 3·23 mmoles, 77%). A small amount of acetylpentacarbonylmanganese (0·01 g., 0·04 mmole, 1%) was recovered.

(e) *Methyl propiolate under a pressure of carbon monoxide*. When a solution of acetylpentacarbonylmanganese (0·75 g., 3·15 mmoles) and methyl propiolate (0·26 g., 3·13 mmoles) in diethyl ether (5 ml.) was kept in a stainless-steel autoclave at room temperature for 7 days under carbon monoxide (180 atm.), methyl propiolate (0·20 g., 2·38 mmoles, 76%) and acetylpentacarbonylmanganese (0·64 g., 2·68 mmoles, 85%) were recovered, together with (IVa) (0·10 g., 0·34 mmole, 11%).

(f) *Propiolaldehyde*. Acetylpentacarbonylmanganese (1·0 g., 4·20 mmoles) and propiolaldehyde (0·23 g., 4·26 mmoles) in diethyl ether (10 ml.) at room temperature for 3 days gave carbon monoxide (84 ml.; loss of 1 mol. requires 95 ml.) and (IVb) (0·80 g., 3·03 mmoles, 72%).

Reactions with Phenylpentacarbonylmanganese.—(a) *Phenylacetylene*. Phenylpentacarbonylmanganese (1·50 g., 5·51 mmoles) and phenylacetylene (0·56 g., 5·49 mmoles) in diethyl ether (10 ml.) at room temperature for 7 days gave a red oil. Chromatography (light petroleum eluant) of the oil gave phenylpentacarbonylmanganese (0·10 g., 0·38 mmole, 7%) and a red oil, which upon recrystallisation from light petroleum at −78° gave (Ib) (1·60 g., 4·22 mmoles, 74%). Further elution with a 4 : 1 light petroleum–ether gave (IIb) (0·15 g., 0·33 mmoles, 6%), which was recrystallised from light petroleum–diethyl ether.

(b) *Dimethyl acetylenedicarboxylate*. Phenylpentacarbonylmanganese (2·61 g., 9·60 mmoles) and dimethyl acetylenedicarboxylate (1·48 g., 10·4 mmoles) in diethyl ether (10 ml.) at room temperature for 14 days gave a red oil. Chromatography of the oil with light petroleum as eluant gave phenylpentacarbonylmanganese (0·05 g., 0·18 mmole, 2%). Further elution with light petroleum–diethyl ether (9 : 1) gave an orange solid, which on recrystallisation from light petroleum–diethyl ether gave (IIIc) (3·2 g., 7·73 mmoles, 78%).

(c) *Acetylenedicarboxylic acid*. Phenylpentacarbonylmanganese (1·36 g., 5·0 mmoles), and acetylene dicarboxylic acid (0·57 g., 5·0 mmoles) in diethyl ether (5 ml.) at room temperature for 7 days gave an orange-yellow solid. Chromatographic separation on a silica gel column gave phenylpentacarbonylmanganese (0·05 g., 0·18 mmole, 4%) upon elution with light petroleum. Further elution with diethyl ether gave (IIId) (1·40 g., 3·62 mmoles, 73%), which was recrystallised from light petroleum–diethyl ether.

(d) *Methyl Propiolate*. Phenylpentacarbonylmanganese (0·81 g., 2·98 mmoles) and methyl propiolate (0·25 g., 2·98 mmoles) in diethyl ether (5 ml.) at room temperature for 7 days gave a red oil. Chromatography (light petroleum eluant) of the oil gave phenylpentacarbonylmanganese (0·29 g., 0·7 mmole, 2%), and a red solid [elution with light petroleum–diethyl ether (4 : 1)], which on recrystallisation from light petroleum gave (IVc) (0·96 g., 2·70 mmoles, 91%).

(e) *Propiolaldehyde*. A solution of phenylpentacarbonylmanganese (1·50 g., 5·51 mmoles) and propiolaldehyde (0·30 g., 5·56 mmoles) in diethyl ether (10 ml.) kept at room temperature for 1 day gave a dark red solid. Chromatography of the solid gave phenylpentacarbonylmanganese

[15] E. H. Ingold, *J. Chem. Soc.*, 1925, **77**, 1199.

[16] F. Wille and L. Saffe, *Annalen*, 1950, **568**, 40.

(0·15 g., 0·55 mmole, 10%) with light petroleum as eluant, and, upon elution with diethyl ether, a dark red solid, which on recrystallisation from diethyl ether gave (IVd) (1·40 g., 4·30 mmoles, 78%).

Reaction of Hydridopentacarbonylmanganese with 3-*Oxo*-1-*phenylbut*-1-*yne*.—3-Oxo-1-phenylbut-1-yne, prepared in 45% yield by the reaction of phenylacetylene with sodium and acetic anhydride,[17] was purified by distillation (b.p. 110—112°/8 mm. Hg); its i.r. spectrum showed bands at 3247vw, 3012w, 2941w, 2198s, 2165w, 2119w, 1727w, 1667s, 1486m, 1435m, 1410m, 1351m, 1287m, 1277m, 1264m,sh, 1178m, 1161m—s, 1153m—s, 1054w, 1021m, 1015m, 977m, 921w, 855w, 762m—s, 757m—s, 690m—s cm.$^{-1}$.

When hydridopentacarbonylmanganese (1·44 g., 7·35 mmoles) and 3-oxo-1-phenylbut-1-yne (1·0 g., 6·94 mmoles) were shaken at 10° for 4 hr. in a sealed tube, carbon monoxide (22 ml.) was evolved, to give a red-brown solid. The solid was chromatographed (light petroleum eluant) to give decacarbonyldimanganese (0·50 g., 1·28 mmoles, 35%) and (Ia) (0·20 g., 0·64 mmole, 9%). Further elution with diethyl ether gave an orange oil (0·50 g.) which was shown by i.r. spectroscopy to be mainly 3-oxo-1-phenylbut-1-yne mixed with a small amount of an unidentified metal-carbonyl derivative.

When this reaction was repeated at room temperature with hydridopentacarbonylmanganese (1·10 g., 5·61 mmoles) and 3-oxo-1-phenylbut-1-yne (0·81 g., 5·62 mmoles) in diethyl ether (10 ml.), a higher yield of (Ia) (0·20 g., 0·64 mmole, 11%) was obtained.

Reaction of the Methylpentacarbonylmanganese–methyl propiolate Adduct with Anhydrous Hydrogen Chloride.—Reaction of (IVa) (2·0 g., 8·57 mmoles) and anhydrous hydrogen chloride (1·5 g., 41·0 mmoles) in diethyl ether (15 ml.) in a sealed tube at room temperature for 4 days gave orange crystals. The unchanged hydrogen chloride and the solvent were removed under reduced pressure, and the residual solid was extracted with diethyl ether and filtered to give orange crystals of bis(chlorotetracarbonylmanganese) (1·30 g., 3·21 mmoles, 75%) which was identified by i.r. spectroscopy. Evaporation of the solvent from the filtrate gave an oil (0·80 g.) which on sublimation *in vacuo* at room temperature onto a probe cooled to −78° gave a mixture of white crystals and a yellow oil (0·65 g.). The ^{1}H n.m.r. spectrum of the sublimate recorded as a solution in CCl$_4$ at 60 MHz with Me$_4$Si as an internal reference showed signals at τ 3·02 (d, 1H), 3·34 (d, 1H, AB pattern, *J* 17 Hz), 5·42 (t, 1·3H, the X′ band of an A′B′X′ pattern, *J* 3·5 Hz), 6·22 (s, 6·6H), 6·86 (m, 2·7H, A′B′ band of an A′B′X′ pattern), 7·67 (s, 3H), and 7·83 (s, 4H). Spin decoupling at 100 MHz of the multiplet at τ 6·86 by locking the signal on the triplet at τ 5·42 showed the multiplet to be an AB pattern (*J* 19 Hz). Comparison of the spectrum with that of an authentic sample of methyl *trans*-4-oxopent-2-enoate showed that the reaction product was a mixture containing mainly the latter compound together with either methyl 2-chlorolevulinate or methyl 3-chlorolevulinate [signals at τ 5·42 (C*H*Cl·CH$_2$), 6·22 (OC*H*$_3$), 6·86 (CHCl·C*H*$_2$), and 7·83 (C*H*$_3$CO)].

Methyl *trans*-4-oxopent-2-enoate, m.p. 60° (*lit.*,[18] 60·5°) (Found: C, 56·0; H, 6·2. Calc. for C$_6$H$_8$O$_3$: C, 56·2; H, 6·3%) was prepared from methyl bromoacetate by reaction with triphenylphosphine to give triphenylmethoxycarbonylmethylphosphonium bromide,[19] m.p. 162° (lit.,[19] 163°), which was then treated with aqueous sodium hydroxide to give triphenylmethoxycarbonylmethylphosphonium bromide [19] (76%), m.p. 161° (lit.,[19] 162—163°). Reaction of this latter compound with bromoacetone and methyl bromoacetate gave methyl *trans*-4-oxopent-2-enoate (83%).[17]

The i.r. spectrum of methyl *trans*-4-oxopent-2-enoate showed bands at 2985w, 2933w, 1724s, 1698s, 1686s, 1639w, 1621w, 1431m, 1414w, 1353m, 1302s, 1294s, 1258s, 1247m, 1222m, 1200m, 1175m, 1156m, 1039m, 1019m, 980m, 911w, 868w cm.$^{-1}$. Its ^{1}H n.m.r. spectrum at 60 MHz in CCl$_4$ with Me$_4$Si internal reference showed signals at τ 3·03 (d, 1H), 3·35 (d, 1H, AB pattern, *J* 17 Hz, olefinic H) 6·23 (s, 3H OC*H*$_3$), and τ 7·68 (s, 3H, C*H*$_3$·CO).

Reaction of the Methylpentacarbonylmanganese–phenylacetylene Adduct with Anhydrous Hydrogen Chloride.—Anhydrous hydrogen chloride (1·50 g., 41·1 mmoles), (Ia) (1·8 g., 5·64 mmoles), and diethyl ether (10 ml.) in a sealed tube were put aside at room temperature for 3 days. Removal of the solvent and unchanged hydrogen chloride gave bis(chlorotetracarbonylmanganese) (0·5 g., 1·23 mmoles, 44%) and a black oil (1·5 g.), which was shown by i.r. spectroscopy to be a mixture of unchanged (Ia) and an organic compound which showed strong bands in the ν(C=O) and ν(C=C) regions. Attempts to separate the mixture by chromatography, sublimation, and recrystallisation were unsuccessful.

[9/1153 *Received*, *July 7th*, 1969]

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[19] O. Isler, H. Gutmann, M. Montavon, R. Ruegg, G. Ruper, and P. Zeller, *Helv. Chim. Acta*, 1957, **40**, 1242.