Metal Carbonyl Chemistry. Part XXIV.[1] Reactions of Methyl- and Phenyl-pentacarbonylmanganese with Dicyclopentadiene and Other Dienes

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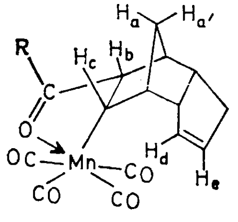
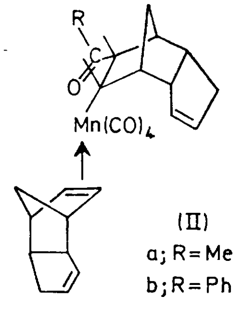
Dicyclopentadiene reacts with $[RMn(CO)_5]$ (R = Me or Ph) in non-donor solvents to afford 1 : 1 adducts, $[(RCO{\cdot}C_{10}H_{12})Mn(CO)_4]$, as the major reaction products, together with small amounts of 2 : 1 adducts, $[(RCO{\cdot}C_{10}H_{12})Mn(CO)_4(C_{10}H_{12})]$. When the reaction of $[MeMn(CO)_5]$ and the diene is carried out in acetonitrile solvent under similar conditions the 2 : 1 adduct is formed as the major product, with the 1 : 1 adduct and an acyl complex, $[(MeCO{\cdot}C_{10}H_{12}{\cdot}CO)Mn(CO)_4(C_{10}H_{12})]$, as minor products. The structures and reactions of some of these compounds with trivalent phosphorus ligands and with sulphur dioxide are described. The attempted reactions of $[MeMn(CO)_5]$ with norbornadiene and cyclo-octa-1,5-diene, and the reactions between dicyclopentadiene and $[MeCo(CO)_4]$ and $[MeRe(CO)_4]$ are also described.

OLEFIN insertion into alkyl- and acyl-transition metal σ-bonds is a well known reaction postulated to occur in many reactions of organometallic compounds. There are, however, very few examples where the simple insertion product is stable enough to be isolated and characterised. In general, such insertion reactions into an alkyl-metal σ-bond are restricted to fluoro-olefins,[2] tetracyanoethylene,[3] and an internal insertion into a norbornenyl palladium complex.[4] Of these, the reactions of the fluoro-olefins are probably not typical of the majority of olefin insertion reactions since they usually require either u.v. irradiation or quite high temperatures, indicating a radical mechanism possibly without prior co-ordination to the metal atom. There are, similarly, very few examples of olefin insertion into acyl-metal bonds which lead to simple intermediates, although reactions with 1,3-[5,6] and 1,2-dienes[7] are known, as are the reactions with alkynes.[8] We now report some reactions between methyl- and phenyl-pentacarbonylmanganese and non-conjugated cyclic dienes which afford stable 1 : 1 and 1 : 2 adducts.

Reactions of Alkyl Metal Carbonyls.—Freshly distilled cyclopentadiene reacts slowly with $[MeMn(CO)_5]$ in hexane at room temperature to give the 1 : 1 adduct (Ia) in 18% yield after 18 h and 61% yield after 3 days. The same compound may be obtained in 84% yield together with a 6% yield of the 2 : 1 adduct (IIa) from the reaction of dicyclopentadiene and $[MeMn(CO)_5]$ under the same conditions, showing that reaction with cyclopentadiene is so slow that dimerisation occurs before reaction with $[MeMn(CO)_5]$. A similar insertion reaction occurs between dicyclopentadiene and pentacarbonylphenylmanganese at room temperature in benzene to afford compound (Ib) as the major product (81% yield) and compound (IIb) in 10% yield. When the reaction of $[MeMn(CO)_5]$ and $C_{10}H_{12}$ is repeated under similar conditions but with acetonitrile as solvent the yield of (IIa) is increased to 34%. Other products from this reaction are (Ia) (20% yield), the acyl complex (III) (8% yield), and compound (IV) which has an analysis consistent with its formation as $[(CH_3COC_{10}H_{12})Mn(CO)_4(OH)]$ (21% yield). These new compounds have all been characterised by elemental analyses (Table), i.r. and n.m.r. spectroscopy and, in some cases, by mass spectrometry and by chemical methods. The evidence for their assigned structures is now discussed.



(I)
a; R = Me
b; R = Ph



(II)
a; R = Me
b; R = Ph

The compounds of type (I) may be handled in air and are thermally stable up to their melting points. The i.r. spectra show four bands in the metal carbonyl region characteristic[9] of *cis*-$[RMn(CO)_4L]$ compounds. The spectrum of (Ia) shows a medium band at 1 639 cm^{-1}, whereas that of (Ib) has a band of similar intensity at 1 611 cm^{-1}. Neither compound shows any band in the region 1 560—1 590 cm^{-1} for the norbornene double-bond. The bands at 1 639 and 1 611 cm^{-1} respectively are assigned to keto-groups which are co-ordinated to the manganese atom. A saturated acyclic ketone

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[1] Part XXIII, B. L. Booth, G. C. Casey, and R. N. Haszeldine, *J.C.S. Dalton*, preceding paper.

[2] J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *J. Organometallic Chem.*, 1964, **2**, 119; J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 93; J. B. Wilford, A. Forster, and F. G. A. Stone, *J. Chem. Soc.*, 1965, 6519.

[3] S. Su, J. A. Hanna, and A. Wojcicki, *J. Organometallic Chem.*, 1970, **21**, P. 21.

[4] D. R. Coulson, *J. Amer. Chem. Soc.*, 1969, **91**, 200; E. Forsellini, G. Bombieri, B. Crociani, and T. Boschi, *Chem. Comm.*, 1970, 1203.

[5] 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.

[6] R. F. Heck, *J. Amer. Chem. Soc.*, 1963, **85**, 3381.

[7] S. Otsuka and A. Nakamura, *Inorg. Chem.*, 1972, **11**, 644.

[8] B. L. Booth and R. G. Hargreaves, *J. Chem. Soc.* (*A*), 1970, 308 and references therein.

[9] B. L. Booth and R. N. Haszeldine, *J. Chem. Soc.* (*A*), 1966, 157.

normally absorbs in the region of 1 705—1 725 cm^{-1}, and co-ordination of such a group to a manganese atom would be expected to cause a shift of *ca.* 80 cm^{-1} to lower frequency as observed previously for similar co-ordinated keto-groups.[8,10] When the keto-group is also conjugated to an aromatic ring as in (Ib) an additional shift of *ca.* 30—35 cm^{-1} is to be expected. These bands in the 1 610—1 640 cm^{-1} region must mask the ν(C=C) band of the cyclopentene double-bond which should absorb in the same region (*cf.* 1 616 cm^{-1} for dicyclopentadiene). Evidence for the presence of an unco-ordinated cyclopentene bond is provided by the ^{1}H n.m.r. spectrum which shows the olefinic protons, H_d and H_e, at τ 4.16 and 4.40 respectively * (Ia) and τ 4.22 (Ib). Apart from the co-ordinated acetyl and benzoyl groups at τ 7.92 (Ia) and 2.45 (Ib) respectively, the spectra closely resemble those of similar cyclopentadiene compounds,[11,12] although coupling constants could not be determined. As the keto-group is co-ordinated to the manganese atom both these substituents must be on the same side of the molecule, *i.e.* a *cis*-insertion reaction, and the complexes are probably the *endo*-isomers since the bridging methylene protons, H_a and $H_{a'}$, are equivalent in the n.m.r. spectra and appear as only one band at τ 8.51 (Ia) and 8.46 (Ib). The *endo*-configuration is also suggested by the chemical shift value for H_b of τ 6.83 (Ia) and 6.84 (Ib)which is in the region expected for an *exo*-H atom,[12] whereas an *endo*-proton would have a much lower chemical shift. The mass spectrum of (Ia) shows a parent ion at *m/e* 342, and peaks at *m/e* 314, 286, 258, and 230 corresponding to successive loss of four CO groups before fragmentation of the main skeleton occurs. A similar fragmentation pattern is observed for compound (Ib).

Further evidence for the structure of (Ia) is that on hydrogenation at 70 °C over a palladium-on-charcoal catalyst it affords 9-acetyltricyclo[5.2.1.0^{2,6}]dec-4-ene (73%), and a small amount of the corresponding fully saturated derivative, together with $[Mn_2(CO)_{10}]$ (62%). The tricyclodecene derivative has been fully characterised by elemental analysis, molecular weight, and i.r. and n.m.r. spectroscopy. Its i.r. spectrum shows a ketone ν(CO) band at 1 710 cm^{-1}, and a weak ν(C=C) band at 1 615 cm^{-1}. The ^{1}H n.m.r. spectrum shows the cyclopentene protons at τ 4.30 and 4.44, and the bridging methylene protons at τ 8.34—8.80, together with the methylene protons on C_8 which also appear in this region. The H atoms of the acetyl group are at τ 8.10, and the single H atom attached to the same carbon atom C_9 is at τ 6.93, which is the chemical shift value expected[12] for an *exo*-hydrogen, and is additional evidence that in (Ia) the MeCO and $Mn(CO)_4$ groups are *cis* and *endo*. Attempts to cleave compound (Ia) with anhydrous hydrogen chloride gave no identifiable organic product, and only $[ClMn(CO)_5]$ and $[\{Mn(CO)_4Cl\}_2]$ could be isolated.

The compounds of type (II) are viscous oils, which are unstable in air, but stable for several days under vacuum. Their i.r. spectra in the metal carbonyl region are similar to those of type (I) showing that there is a similar *cis*-stereochemistry around the manganese atom. There are no bands in the region 1 610—1 640 cm^{-1} for a co-ordinated keto-group, but there is a band at 1 710 cm^{-1} (IIa) and 1 697 cm^{-1} (IIb) for an unco-ordinated acetyl- and benzoyl-group respectively. The assigned structures are fully confirmed by the n.m.r. spectra which show four protons in the region τ 3.98—4.48 for the two cyclopentene double-bonds, and two further olefinic protons at τ 6.85 for the co-ordinated norbornene bond which overlaps the *exo*-H atom geminal to the MeCO-group. Further confirmation of the structure of compound (IIa) comes from its reaction with $(PhO)_3P$ in benzene at 70 °C for 4 days to give (V) in 55% yield by displacement of the less strongly co-ordinating dicyclopentadiene ligand.

The evidence for the air-stable solid (III) is based mainly on its i.r. spectrum, which shows an acyl ν(CO) band at 1 620 cm^{-1} in addition to the unco-ordinated acetyl ν(CO) band at 1 714 cm^{-1}. Elemental analysis and molecular-weight data are also in agreement with the assigned structure. There is some doubt about the structure of compound (IV) since it could only be purified by chromatography and resisted crystallisation from organic solvents. Elemental analysis agrees with a structure, $[(CH_3CO{\cdot}C_{10}H_{12})Mn(CO)_4OH]$ and its molecular weight indicates that it is dimeric. Evidence for the presence of hydroxo-ligands rests on the i.r. spectrum which shows two weak bands at 3 640 and 3 430 cm^{-1}. These bands do not diminish in intensity when (IV) is heated at 80 °C under full vacuum for several hours and it seems unlikely that they are due to traces of moisture. The i.r. spectrum also shows one medium and two strong bands in the metal carbonyl region, and a band at 1 710 cm^{-1} for an unco-ordinated acetyl group. The ^{1}H n.m.r. spectrum, apart from showing a band at τ 4.4 for an unco-ordinated cyclopentene double-bond, was poorly resolved and not very helpful. It is possible that the compound has hydroxo-bridges and only three CO ligands on each manganese atom, but this is only speculative in the absence of further data. Attempts have been made to carry out bridge-cleavage reactions with CO (100 atm at 50 °C for 3 days) or $P(OPh)_3$ at room temperature for several days. The starting material was recovered almost quantitatively from these reactions, whereas reaction of $P(OPh)_3$ at 70 °C for 6 days gave a complex mixture of organic products and a pale yellow solid believed to be an isomer of $[Mn_2(CO)_8\{(PhO)_3P\}_2]$ which shows bands at 2 080w, 2 006s, and 1 961m–s cm^{-1} in the metal carbonyl region of its i.r. spectrum. This pattern is different from that reported for the well-known diaxial isomer,

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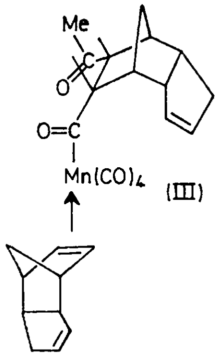
* These assignments for the olefinic protons could be reversed.

[10] W. D. Bannister, B. L. Booth, R. N. Haszeldine, and P. Loader, *J. Chem. Soc. (A)*, 1971, 930.

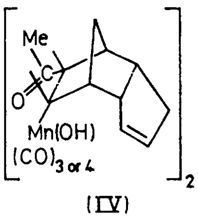
[11] G. Carturan, M. Graziani, R. Ros, and U. Belluco, *J.C.S. Dalton*, 1972, 262; G. Carturan, M. Graziani, and U. Belluco, *J. Chem. Soc. (A)*, 1971, 2509.

[12] L. F. Hines and J. K. Stille, *J. Amer. Chem. Soc.*, 1972, **94**, 485.

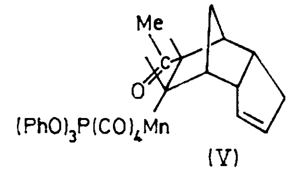
$[\{(PhO)_3P\}(CO)_4Mn{\cdot}Mn(CO)_4\{P(OPh)_3\}]$ [*cf.* ν(CO) 2 003sh and 1 981s cm^{-1}].[13] The possibility that this compound may be the *ortho*-metallated complex $[(OC)_4\overline{Mn\{(PhO)_2P\text{-}\mu\text{-}OC}_6H_4\}]$ cannot be discounted in view of the molecular-weight figure obtained.



(III)

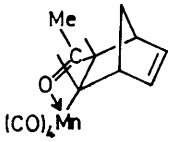


(IV)

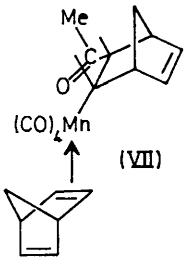


(V)

Pentacarbonylmethylmanganese reacts with norbornadiene in hexane at room temperature over 6 days to give an unstable brown solid. Elemental analysis suggests that this solid is a mixture of the 1 : 1 and 1 : 2 adducts (VI) and (VII) respectively. This is confirmed by its i.r. spectrum which shows the ν(CO) band of a co-ordinated acetyl group at 1 626 cm^{-1}, a band at 1 704 cm^{-1} for an unco-ordinated acetyl group, and a very weak band at 1 560 cm^{-1} assigned to a norbornene double-bond. Several attempts to separate the mixture by chromatography were unsuccessful and resulted in extensive decomposition.



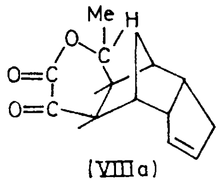
(VI)



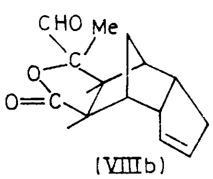
(VII)

Attempts to react $[MeMn(CO)_5]$ with cyclo-octa-1,5-diene, norbornene, cyclohexene, and *cis*-but-2-ene were not very successful. I.r. evidence suggests that some reaction occurs with all these olefins, but the complexes formed are very unstable and could not be isolated. It is noteworthy also that with the exception of norbornene, these reactions required a temperature of 80 °C before any complex formation occurred. This is a reflection of the enhanced reactivity of the strained norbornene olefinic bond.

The less reactive $[MeRe(CO)_5]$ does not react with dicyclopentadiene during 5 weeks at 50 °C, but it is possible that the use of more drastic conditions could provide complexes similar to those obtained with $[MeMn(CO)_5]$. The reaction of $[MeCo(CO)_4]$, on the other hand, occurs quite rapidly at 0 °C to give an unstable adduct, which showed metal carbonyl bands at 2 075 and 2 008 cm^{-1} in its i.r. spectrum, and additional bands at 1 724 (unco-ordinated ketone) and 1 786 cm^{-1} (possibly lactone CO). Attempted chromatographic purification of this adduct gave a 24% yield of an organic compound of empirical formula $C_{14}H_{16}O_3$. Its ^1H n.m.r. spectrum shows that it contains the basic cyclopentadiene skeleton with a cyclopentene double-bond (τ 4.38), and non-equivalent bridging methylene protons (τ 8.58 and 9.08). In addition the spectrum shows a methyl group (τ 8.71) and an additional proton which absorbs in the region 7.05—8.00, and is masked by the complex multiplet for the protons of the dicyclopentadiene skeleton. On the basis of the n.m.r. spectrum the structure (VIIIa) is tentatively proposed. The i.r. spectrum shows two strong ν(CO) bands at 1 780 and 1 700 cm^{-1} for a lactone and a ketone group respectively. It is known that there is little interaction, generally, between α-diketone groups,[14] and the carbonyl groups in a structure such as (VIIIa) should absorb approximately in the regions expected for a six-membered ring ketone (*ca.* 1 710 cm^{-1}) and a δ-lactone (*ca.* 1 750 cm^{-1}). The spectrum also shows a weak ν(C=C) band at 1 611 cm^{-1} for the cyclopentene double-bond. Structure (VIIIb) is another possibility, but no evidence for reducing properties was found, and no absorption for the aldehydic H in the n.m.r. spectrum was evident. Attempts to stabilise the cobalt complex precursor of of this organic product by the addition of trivalent phosphorus ligands proved unsuccessful and led only to various ligand-substituted derivatives of $[Co_2(CO)_8]$.



(VIIIa)



(VIIIb)

Some Reactions of the Complexes of Type (I).—Triphenyl phosphite reacts with (Ia) at 20 °C in diethyl ether during 5 days to afford complex (IXa) in 82% yield. A benzoyl analogue (IXb) has also been prepared in 88% yield by reaction of (Ib) with the sterically-constrained phosphite, $P(OCH_2)_3CEt$, in benzene at 50 °C for 5 days. The i.r. spectra of these compounds show only three intense bands in the metal-carbonyl region indicating that the three carbonyl ligands are mutually *cis*.[15] The presence of the co-ordinated ketone

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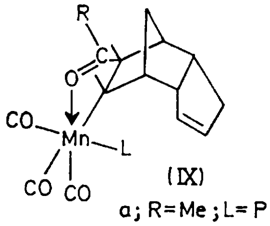
[13] A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 1964, 634.

[14] L. J. Bellamy, ' The Infrared Spectra of Complex Molecules,' Methuen, London, 1964, p. 128.

[15] B. L. Booth, M. Green, R. N. Haszeldine, and N. P. Woffenden, *J. Chem. Soc.* (*A*), 1969, 920.

group is shown by the medium band at 1 638 (IXa) and 1 608 cm^{-1} (IXb) respectively. In these reactions the labile CO ligand *trans* to another CO ligand is replaced to give the kinetically controlled product. A surprising feature of these reactions is that no alkyl migration occurs, whereas under similar conditions the compounds [RMn(CO)$_5$] readily afford acyl complexes upon reaction with phosphine or phosphite ligands.[15-18]



(IX)

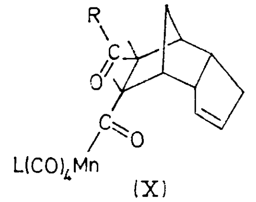
a; R=Me; L=P(OPh)$_3$
b; R=Ph; L=P(OCH$_2$)$_3$CEt

The alkyl migration reactions are known to occur by the reaction sequence

$$[\text{RMn(CO)}_5] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\text{RCOMn(CO)}_4] \xrightarrow{k_2(\text{L})} [\text{RCOMn(CO)}_4\text{L}]$$

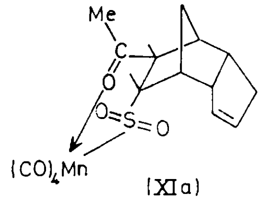
and it seems probable that in these particular reactions the approach of the ligand is so sterically hindered that $k_{-1} \gg k_2$, and that ligand replacement occurs by a competing dissociative (S_N1) mechanism.

Triphenylphosphine does not react with (Ia) in diethyl ether at 20 °C after 5 days, but on warming at 50 °C for 3 days the mixture afforded a 14% yield of compound (Xa), together with a yellow solid (60% yield), m.p. 160 °C (decomp.), which has an analysis consistent with its formulation as [Mn$_2$(CO)$_8$(PPh$_3$)$_2$] but which has an i.r. spectrum [CCl$_4$ solution, ν(CO) 2 042w, 1 959s, and 1 930m cm^{-1}] different from that of the previously reported diaxial substituted derivative,[19a] and more consistent with that reported [hexane, 2 067m, 1 987s, 1 983s, and 1 952s cm^{-1}] for the *ortho*-metallated complex [Ph$_2$P-μ-C$_6$H$_4$-Mn(CO)$_4$] [19b] and in accord with the low molecular-weight figure obtained. Compound (Xa) shows four terminal metal-carbonyl bands in its i.r. spectrum with an intensity pattern expected for a mixture of *cis*- and *trans*-isomers. In addition, medium bands in the spectrum at 1 705 and 1 617 cm^{-1} indicate the presence of an unco-ordinated acetyl group and an acyl-metal group respectively. It appears that in this reaction the initially formed complex, which is presumably of type (IX), where L = PPh$_3$, undergoes appreciable decomposition to the manganese carbonyl derivative, while a small amount reacts with carbon monoxide, arising perhaps from degradation of some of the yellow complex to give compound (Xa). Surprisingly, in view of its reaction with P(OCH$_2$)$_3$CEt, a similar compound (Xb) is obtained from the reaction of (Ib) and P(OPh)$_3$ in dichloromethane at 50 °C for 4 days. The major product from this reaction is a pale yellow solid (64%) thought to be either an isomer of [Mn$_2$(CO)$_8$-{P(OPh)$_3$}$_2$] or [(OC)$_4$Mn{(PhO)$_2$P-μ-OC$_6$H$_4$}] as described above from a previous reaction. The i.r. spectrum of (Xb) shows a similar pattern in the terminal metal-carbonyl region to that of (Xa), a band for the unco-ordinated benzoyl group at 1 680 cm^{-1}, and the metal acyl band at 1 622 cm^{-1}.

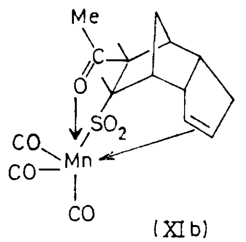


(X)

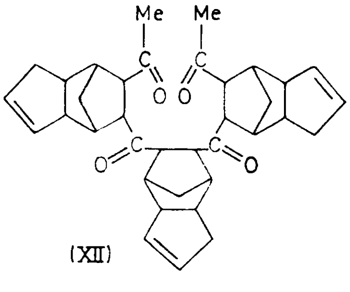
a; R=Me; L=PPh$_3$
b; R=Ph; L=P(OPh)$_3$



(XIa)



(XIb)



(XII)

The reaction between SO$_2$ and (Ia) at 20 °C in tetrahydrofuran affords an *S*-sulphinate derivative in 68% yield. There is some doubt as to whether this is the expected tetracarbonyl derivative (XIa) or a tricarbonyl derivative in which the cyclopentene olefinic bond co-ordinates to the metal atom (XIb). An n.m.r. spectrum could not be obtained as the compound is insoluble in all suitable organic solvents; hence characterisation is based solely on the analysis and i.r. spectrum. The spectrum, as a solution in nitromethane, shows only three strong bands in the metal-carbonyl region at 2 038s, 1 960s, and 1 920s cm^{-1} typical of three mutually *cis*-CO groups (XIb), but four strong bands are apparent in a Nujol mull. The spectrum also shows bands at 1 155 and 1 144 cm^{-1} for ν_{as}(SO$_2$) and a strong band at 1 027 cm^{-1} for the symmetrical ν(SO$_2$) vibration. These bands are characteristic of *S*-sulphinate complexes [20,21] rather than the recently reported unstable

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[16] M. Green and D. C. Wood, *J. Amer. Chem. Soc.*, 1966, **88**, 4106.

[17] W. D. Bannister, B. L. Booth, M. Green, and R. N. Haszeldine, *J. Chem. Soc.* (*A*), 1969, 698.

[18] B. L. Booth, R. N. Haszeldine, and N. P. Woffenden, *J. Chem. Soc.* (*A*), 1970, 1979.

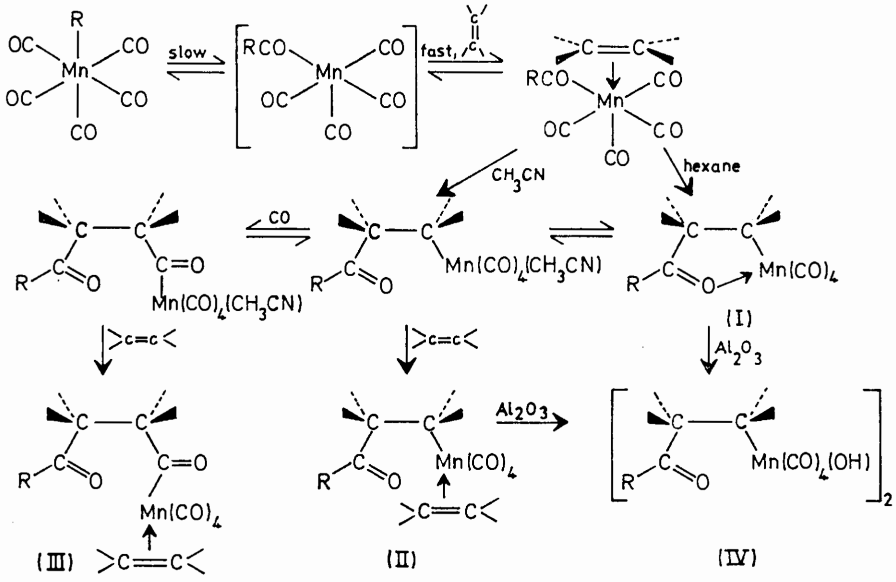
[19] (*a*) D. J. Parker and M. H. B. Stiddard, *J. Chem. Soc.* (*A*), 1966, 695; (*b*) R. Hoxmeier, B. Deubzer, and H. D. Kaesz, *J. Amer. Chem. Soc.*, 1971, **93**, 536.

[20] J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, 1966, **88**, 4862; F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, 1968, **7**, 1504; M. Graziani, J. P. Bibler, M. Montesano, and A. Wojcicki, *J. Organometallic Chem.*, 1969, **16**, 507.

[21] C. A. Reed and W. R. Roper, *Chem. Comm.*, 1971, 1556.

O-sulphinate derivatives,[21,22] or sultine complexes.[10,23] The band for the co-ordinated acetyl carbonyl group appears as a medium band at 1 640 cm^{-1}.

When a 1 : 1 mixture of (Ia) and (IIa) is heated at 200 °C under vacuum for 2 h, $[Mn_2(CO)_{10}]$ is formed together with a pale yellow solid which is tentatively identified as (XII) on the basis of its elemental analysis, molecular weight, and i.r. and ^1H n.m.r. spectra. The i.r. spectrum shows a strong, broad ketonic carbonyl band at 1 700 cm^{-1} and a weak band at 1 605 cm^{-1} for the cyclopentene double-bond. The ^1H n.m.r. spectrum (CCl_4 solution) is complex, but shows a band at τ 4.42 (rel. int. 6) for the olefinic protons; a band at τ 6.95 (rel. int. 6) for the *exo*-hydrogens of the substituted norbornane rings; a broad multiplet over the region τ 7.10—8.00 (rel. int. 18); a singlet at τ 8.00 (rel. int. 6) for the two CH_3CO-groups; and a multiplet in the region of τ 8.40—8.90 (rel. int. 6) for the bridging methylene protons. This product must arise by homolytic breakdown of the carbon–metal σ-bonds of (Ia) and (IIa).



SCHEME

DISCUSSION

These reactions between alkyl manganese carbonyl derivatives and non-conjugated cyclic dienes are probably similar mechanistically to those reported previously for alkynes.[8] Reaction may occur initially by alkyl migration to afford a co-ordinatively unsaturated intermediate (see Scheme); in acetonitrile this reaction may be solvent assisted although there is some doubt about this.[24] This intermediate could then react rapidly with the dicyclopentadiene ligand *via* the strained norbornene bond to form a π-complex. The stability of this olefin complex is obviously an important factor, since with the less-strained cyclic olefin, cycloocta-1,5-diene, and the acyclic olefins the equilibrium must lie well over towards $[RMn(CO)_5]$. The π-complex may then undergo a four-centre insertion [*cis* ' addition '] to afford the isolated compound (I) in a non-polar solvent. In a donor solvent such as acetonitrile the vacant co-ordination site resulting from the insertion reaction is occupied by a solvent molecule, which can be readily displaced by the excess of cyclopentadiene to afford the 1 : 2 complexes of type (II). The minor product (III) formed in the reaction using acetonitrile

Methyl- and phenyl-pentacarbonylmanganese-diene adducts

		Found				Required			
Compd.	M.p. (t/°C) *	C(%)	H(%)	P(%)	*M*	C(%)	H(%)	P(%)	*M*
(Ia)	125—126	56.4	4.4		343 [a]	56.2	4.4		342
(Ib)		62.6	4.5		405 [a]	62.4	4.2		404
(IIa)		65.5	5.9		472 [b]	65.8	5.7		474
(IIb)		69.9	5.8		540 [b]	69.4	5.4		536
(III)	134—135	64.4	5.5		476 [b]	64.5	5.4		502
(IV)	75 (d)	53.6	5.0		738	53.5	4.5		718
(V)		62.6	4.5			62.5	4.6		
(IXa)	101—102	63.6	5.0			63.5	4.8		
(IXb)	112 (d)	57.8	5.3			58.0	5.2		
(Xa)	120 (d)	65.9	5.0	4.9		66.5	4.8	4.9	
(Xb)	120 (d)	64.2	4.3	3.8	683 [b]	64.6	4.3	4.2	742
(XI)[c,d]	175 (d)	47.8	3.8			47.6	4.0		

* d = decomp.

[a] In benzene. [b] In 1,2-dichloroethane. [c] Analytical figures quoted are for structure (XIb). The figures for structure (XIa) are C, 47.2; H, 3.7%. [d] Found: S, 7.2. (XIb) requires S, 8.1%.

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[22] S. E. Jacobson, P. Reich-Rohrwig, and A. Wojcicki, *Chem. Comm.*, 1971, 1526.

[23] J. E. Thomasson, P. W. Robinson, D. A. Ross, and A. Wojcicki, *Inorg. Chem.*, 1972, **10**, 2130.

[24] M. Green, R. I. Hancock, and D. C. Wood, *J. Chem. Soc.* (*A*), 1968, 2718.

solvent may either arise by carbonylation as shown in the Scheme, or *via* initial displacement of the acetonitrile ligand to give an $Mn(CO)_5$ species which then undergoes alkyl migration under the influence of the incoming dicyclopentadiene ligand.* The other minor product (IV) is probably formed during the chromatographic separation of the products.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 grating instrument as Nujol and hexachlorobutadiene mulls except for the metal-carbonyl region which was examined using solutions in hexane or cyclohexane (except where stated) and full scale expansion. ^1H N.m.r. spectra were recorded on a Varian HA 100 spectrometer on solutions in carbon tetrachloride. Molecular weights were determined on a Mechrolab vapour-pressure osmometer, and u.v. spectra were recorded on a Unicam SP 700 spectrophotometer. Except where stated chromatographic separations were carried out on deactivated alumina, and light petroleum had a boiling range of 40—60 °C. All reactions were in sealed tubes or under an atmosphere of dry nitrogen. Methyl- and phenyl-pentacarbonylmanganese were prepared by the standard methods.[25]

Reactions with Pentacarbonylmethylmanganese.—(a) *With cyclopentadiene.* Pentacarbonylmethylmanganese (1.0 g, 4.8 mmol), freshly distilled cyclopentadiene (10.0 g, 150 mmol), and hexane (30 ml) were kept at 20 °C for 18 h in a tube (100 ml) sealed under vacuum. Chromatography using activated alumina with light petroleum eluant gave (Ia) (0.3 g, 0.88 mmol, 18%), which recrystallised from a mixture of diethyl ether–hexane as yellow crystals. Its u.v. spectrum showed $\lambda_{max.}$ 214—216 (ε 22 650) and 357—359 nm (ε 1 285).

(b) *With dicyclopentadiene.* (i) In hexane. A solution of pentacarbonylmethylmanganese (5.0 g, 23.8 mmol) and dicyclopentadiene (8.0 g, 60.7 mmol) in hexane (50 ml) kept at 20 °C for 7 days gave (Ia) (6.8 g, 19.9 mmol, 84%) after chromatography (activated alumina and light petroleum eluant) and sublimation at 100 °C. Further elution with acetone gave (IIa) (0.70 g, 1.48 mmol, 6%) as a viscous oil.

(ii) In acetonitrile. When the above reaction was repeated using acetonitrile (50 ml) as solvent, a brown oil was obtained, which on chromatography, using light petroleum eluant, gave (Ia) (1.6 g, 4.68 mmol, 20%). Further elution with a 1 : 1 light petroleum–dichloromethane mixture gave a yellow-brown oil, which on rechromatography (Florisil) gave (IIa) (3.8 g, 8.03 mmol, 34%), and, on elution with a 2 : 3 light petroleum–dichloromethane mixture, (III) (1.0 g, 1.99 mmol, 8%), which recrystallised from a dichloromethane–hexane mixture as yellow crystals. Final elution with acetone gave a yellow solid (IV) (1.8 g, 5.02 mmol, 21%).

(c) *With norbornadiene.* Pentacarbonylmethylmanganese (1.0 g, 4.76 mmol), norbornadiene (2.0 g, 21.8 mmol), and hexane (30 ml) were kept at 20 °C for 6 days in a tube sealed under vacuum. Removal of the solvent gave a brown oily residue which on chromatography (light petroleum eluant) gave norbornadiene, and on further elution with a 5 : 1 mixture of light petroleum–dichloromethane gave a brown oil shown by i.r. spectroscopy to be a mixture of (VI) and (VII) [Found: C, 56.6; H, 4.5%; *M* ($CH_2Cl{\cdot}CH_2Cl$), 385. $C_{13}H_{11}MnO_5$ (VI) requires C, 51.6; H, 3.6%; *M*, 302. $C_{20}H_{19}MnO_5$ (VII) requires C, 60.9; H, 4.8%; *M*, 394]. Attempts to separate the mixture by repeated chromatography and recrystallisation were unsuccessful.

(d) *With cyclo-octa-*1,5-*diene.* A solution of pentacarbonylmethylmanganese (1.0 g, 4.76 mmol) and cyclo-octa-1,5-diene (6.0 g, 55.6 mmol) in hexane (20 ml) heated at 60 °C for 6 days gave a yellow oil, which on chromatography with light petroleum yielded cyclo-octa-1,5-diene, decacarbonyldimanganese (0.3 g, 0.77 mmol), and pentacarbonylmethylmanganese (0.3 g, 1.43 mmol). Further elution with acetone gave an unidentified yellow solid (0.2 g), whose i.r. spectrum (Nujol mull) showed bands at 3 440w—m [ν(O–H)], 2 033s and 1 927s [ν(Mn–CO)], and 1 701w—m [ν(C=O)].

Reaction of Pentacarbonylphenylmanganese with Dicyclopentadiene.—Pentacarbonylphenylmanganese (1.0 g, 3.68 mmol), dicyclopentadiene (2.0 g, 15.2 mmol), and benzene (20 ml) were kept at 20 °C for 6 days in a tube sealed under vacuum. The products were chromatographed to afford dicyclopentadiene using light petroleum as eluant, and on changing to a 10 : 1 light petroleum–dichloromethane mixture (Ib) (1.2 g, 2.97 mmol, 81%) was obtained as a yellow oil. Final elution with a 1 : 1 mixture of light petroleum–dichloromethane gave (IIb) (0.20 g, 0.37 mmol, 10%) as a yellow-brown oil.

Reaction of Pentacarbonylmethylrhenium with Dicyclopentadiene.—When a solution of pentacarbonylmethylrhenium (3.0 g, 8.80 mmol) and dicyclopentadiene (3.0 g, 22.8 mmol) in hexane (60 ml) was sealed in a tube and kept at 50 °C for 5 weeks the starting materials were recovered unchanged.

Reaction of Tetracarbonylmethylcobalt with Dicyclopentadiene.—Methyl iodide (3.0 g, 21.1 mmol) and dicyclopentadiene (3.0 g, 22.7 mmol) were injected *via* a serum cap into a 100-ml flask containing a solution of sodium tetracarbonylcobaltate (2.27 g, 11.7 mmol) in tetrahydrofuran (30 ml) at 0 °C, and the mixture was kept at this temperature for 24 h. Removal of the solvent under vacuum and extraction of the residue with dichloromethane left a blue-green insoluble product. Chromatography of the extract on Florisil gave dicyclopentadiene on elution with light petroleum, and further elution with a 2 : 1 light petroleum–dichloromethane mixture gave an unstable yellow oil (0.2 g). Final elution with dichloromethane gave (VIII) (0.65 g, 2.80 mmol, 24%) as a colourless solid, m.p. 98 °C, which was recrystallised from a mixture of dichloromethane–diethyl ether–hexane [Found: C, 72.2; H, 6.9%; *M* ($ClCH_2{\cdot}CH_2Cl$), 247. $C_{13}H_{16}O_3$ requires C, 72.4; H, 6.9%; *M*, 232].

This reaction was repeated as described above, but triphenyl phosphite (4.0 g, 12.9 mmol) was injected into the mixture after 24 h at 0 °C, and the mixture was put aside for a further 24 h at this temperature. Chromatography gave recovered dicyclopentadiene, triphenyl phosphite, and octacarbonyltetrakis(triphenyl phosphite)tetracobalt (1.1 g, 0.65 mmol, 22%) [Found: C, 56.2; H, 3.8. $C_{80}H_{60}Co_4O_{20}P_4$ requires C, 56.5; H, 3.5%].

Reaction of (IIa) *with Triphenyl Phosphite.*—A solution of (IIa) (0.20 g, 0.42 mmol) and triphenyl phosphite (0.20 g,

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* We thank a Referee for this suggestion.

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

0.65 mmol) in benzene (20 ml) heated at 70 °C for 4 days gave carbon monoxide (0.1 mmol) and a yellow oil. Chromatography of this oil gave a trace of dicyclopentadiene on elution with light petroleum, and an impure yellow oil on elution with a 2 : 1 light petroleum–dichloromethane mixture. A repeated chromatography of this oil on Florisil using the same eluant gave (V) (0.15 g, 0.23 mmol, 55%) as a viscous, yellow oil, which solidified on being put aside *in vacuo* for several days.

Reactions with Compound (Ia).—(a) *With hydrogen*. When a stream of dry hydrogen was bubbled for 10 h through a solution of (Ia) (2.0 g, 5.85 mmol) in benzene (70 ml) at 70 °C containing palladium-on-charcoal (0.1 g), chromatography of the reaction products gave decacarbonyldimanganese (0.70 g, 1.80 mmol, 62%) on elution with light petroleum. Elution with a 3 : 2 light petroleum–dichloromethane mixture gave a trace of *9-acetyltricyclo*[5.2.1.$0^{2,6}$]-*decane* as a colourless liquid, whose i.r. spectrum was identical to that of its derivative (*vide infra*) except for the absence of a ν(C=C) band. Final elution with a 2 : 3 mixture of the same solvents gave *9-acetyltricyclo*[5.2.1.$0^{2,6}$]*dec-4-ene* (0.75 g, 4.26 mmol, 73%) as a colourless, viscous liquid [Found: C, 81.6; H, 9.0%; *M* ($ClCH_2{\cdot}CH_2Cl$), 176. $C_{12}H_{16}O$ requires C, 81.9; H, 9.1%; *M*, 176].

(b) *With triphenyl phosphite*. When a solution of (Ia) (0.50 g, 1.46 mmol) and triphenyl phosphite (0.50 g, 1.61 mmol) in diethyl ether (20 ml) was kept at 20 °C for 2 days, carbon monoxide (1.2 mmol) was evolved to give (IXa) (0.75 g, 1.20 mmol, 82%) as a yellow solid, isolated by chromatography with light petroleum and recrystallisation from a mixture of diethyl ether–hexane.

(c) *With triphenylphosphine*. The similar reaction of (Ia) (0.40 g, 1.17 mmol) and triphenyl phosphine (0.35 g, 1.34 mmol) in ether (50 ml) did not occur at 20 °C during 5 days, but on heating at 50 °C for 3 days carbon monoxide (0.05 mmol) was evolved to give a yellow solid (0.30 g, 0.35 mmol, 60%), m.p. 160 °C (decomp.) [Found: C, 61.5; H, 4.1%; *M* ($CH_2Cl{\cdot}CH_2Cl$), 567. $C_{44}H_{30}Mn_2O_8P_2$ requires C, 61.5; H, 3.5%; *M*, 858. $C_{22}H_{14}MnO_4P$ requires C, 61.7; H, 3.3%; *M*, 428], and (Xa) (0.10 g, 0.16 mmol, 14%) isolated as a yellow solid by chromatography on Florisil (dichloromethane eluant) and recrystallisation from a mixture of dichloromethane–ether.

(d) *With sulphur dioxide*. When dry sulphur dioxide was bubbled through a solution of (Ia) (1.0 g, 2.92 mmol) in tetrahydrofuran (80 ml) for 10 h at room temperature, yellow crystals of (XI) (0.75 g, 1.99 mmol, 68%) were precipitated.

Reactions with Compound (Ib).—(a) *With trimethylolpropane phosphite* (*1-ethyl-4-phospha-3,5,8-trioxabicyclo-*[2.2.2]*octane*). When a solution of (Ib) (0.30 g, 0.74 mmol) and the ligand (0.15 g, 0.93 mmol) in benzene (20 ml) was kept at 50 °C for 5 days carbon monoxide (0.68 mmol) was evolved. Removal of the solvent *in vacuo*, and recrystallisation of the yellow solid residue from a dichloromethane–hexane mixture gave (IXb) (0.35 g, 0.65 mmol, 88%) as a yellow-orange solid.

(b) *With triphenyl phosphite*. A solution of (Ib) (1.0 g, 2.48 mmol) and triphenyl phosphite (0.8 g, 2.58 mmol) in dichloromethane (20 ml) heated at 50 °C for 4 days in a tube sealed under vacuum gave carbon monoxide (0.5 mmol). Removal of the solvent and chromatography of the yellow oily residue on Florisil gave a pale yellow solid (0.75 g, 0.79 mmol, 64%), m.p. 155 °C (with decomp.), which was purified by recrystallisation from a mixture of dichloromethane–diethyl ether [Found: C, 56.0; H, 3.7; P, 6.9%; *M* ($CH_2Cl{\cdot}CH_2Cl$), 606. $C_{44}H_{30}Mn_2O_{14}P_2$ requires C, 55.4; H, 3.2; P, 6.5%; *M*, 954. $C_{22}H_{14}MnO_7P$ requires C, 55.4; H, 3.0; P, 6.5%; *M*, 476]. Further elution with dichloromethane gave (Xb) (0.30 g, 0.40 mmol, 16%) as a pale yellow solid, purified by recrystallisation from dichloromethane–diethyl ether.

Pyrolysis of a Mixture of (Ia) *and* (IIa).—A mixture of (Ia) (0.70 g, 2.05 mmol) and (IIa) (1.0 g, 2.11 mmol) was heated under vacuum at 200 °C for 2 h to give decacarbonyldimanganese which sublimed on to the walls of the vessel. Extraction of the residue with benzene and removal of the solvent under vacuum gave a yellow solid which was recrystallised from diethyl ether to afford (XII) as a pale yellow solid, m.p. 145 °C (decomp.) [Found: C, 80.0; H, 7.6%; *M* (C_6H_6), 536. $C_{36}H_{42}O_4$ requires C, 80.3; H, 7.8%; *M*, 538].

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