Chemistry of the Metal Carbonyls. Part LXVIII.[1] Complexes of Manganese, Iron, and Ruthenium Containing the Cyclic Carbene 2-Oxacyclopentylidene

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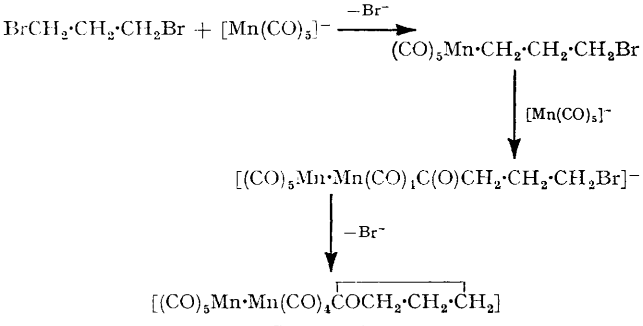
Addition of $[\mathrm{Mn(CO)_5}]^-$ to an excess of 4-chlorobutyryl chloride affords $[\mathrm{Mn(COCH_2{\cdot}CH_2{\cdot}CH_2Cl)(CO)_5}]$ (I), which reacts with $[\mathrm{Mn(CO)_5}]^-$ or I^- to afford respectively the carbene complexes $[\mathrm{Mn(X)}\overline{\mathrm{COCH_2{\cdot}CH_2{\cdot}CH_2}}\mathrm{(CO)_4}]$ [X = $\mathrm{Mn(CO)_5}$ or I]. Thermal decacarbonylation of (I) gives $[\mathrm{Mn(CH_2{\cdot}CH_2{\cdot}CH_2Cl)(CO)_5}]$ (II), which rapidly reacts with lithium iodide to give *cis*-$[\mathrm{Mn(I)(}\overline{\mathrm{COCH_2{\cdot}CH_2{\cdot}CH_2}}\mathrm{)(CO)_4}]$. Treatment of (II) with the ligands L [L = $\mathrm{P(OCH_2)_3CMe}$, $\mathrm{P(OMe)_3}$, $\mathrm{PMe_2Ph}$, $\mathrm{P(OMe)_2Ph}$, or $\mathrm{AsMe_2Ph}$] gives *cis*-$[\mathrm{Mn(COCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}Cl)(CO)_4L}]$, which cyclise on treatment with $\mathrm{AgBF_4}$ to give the cationic carbene complexes *cis*-$[\mathrm{Mn}\overline{\mathrm{COCH_2{\cdot}CH_2{\cdot}CH_2}}\mathrm{(CO)_4L}]^+$. Thermal decarbonylation of *cis*-$[\mathrm{Mn(COCH_2{\cdot}CH_2{\cdot}CH_2Cl)(CO)_4\{P(OCH_2)_3CMe\}}]$ gives *cis*-$[\mathrm{Mn(CH_2{\cdot}CH_2{\cdot}CH_2Cl)(CO)_4\{P(OCH_2)_3CMe\}}]$ which forms the carbene complex *fac*-$[\mathrm{Mn(I)}\overline{\mathrm{COCH_2{\cdot}CH_2{\cdot}CH_2}}\mathrm{(CO)_3\{P(OCH_2)_3CMe\}}]$ with lithium iodide. The corresponding reaction, starting with 5-chlorovaleryl chloride, affords only a low yield of the 2-oxacyclohexylidene complex *cis*-$[\mathrm{Mn(I)}\overline{\mathrm{COCH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2}}\mathrm{(CO)_4}]$. The formation of the cationic carbene complexes $[\mathrm{M}\overline{\mathrm{COCH_2{\cdot}CH_2{\cdot}CH_2}}\mathrm{(CO)_2(\pi\text{-}C_5H_5)}]^+$ (M = Fe or Ru) is also described.

FOLLOWING Fischer's investigations,[2] various alternative synthetic approaches to transition metal carbene complexes have been developed.[3,4] Recently, there has also been interest in the possible intermediacy of carbene complexes in homogeneous catalytic reactions, for example, in olefin dismutation.[5] As an initial step in a study of the reactions of co-ordinated carbenes within the co-ordination sphere, we became interested in the possibility of extending the internal cyclisation route to carbene complexes demonstrated by Casey and Anderson.[6,7] These workers reinterpreted (Scheme 1) an earlier investigation by King[8] of the reaction of 1,3-dibromopropane with the anion $[\mathrm{Mn(CO)_5}]^-$. The same dinuclear manganese carbene complex was also obtained by reacting 4-chlorobutyryl chloride with $[\mathrm{Mn(CO)_5}]^-$. However, in both of these reactions the assumed intermediates were not isolated. In a separate investigation[9] the intramolecular cyclisation reaction has been elegantly used to synthesise the cationic molybdenum complex $[\mathrm{Mo(}\overline{\mathrm{COCH_2{\cdot}CH_2{\cdot}CH_2}}\mathrm{(CO)_2(PPh_3)(\pi\text{-}C_5H_5)}]^+$. Herein we describe several carbene–manganese complexes following a reinvestigation of the reaction of the anion $[\mathrm{Mn(CO)_5}]^-$ with 4-chlorobutyryl chloride; our initial results have been reported[10] in a preliminary communication. The new complexes obtained have been characterised by elemental analysis, ¹H n.m.r. and i.r. spectroscopy.



$$\mathrm{BrCH_2{\cdot}CH_2{\cdot}CH_2Br} + [\mathrm{Mn(CO)_5}]^- \xrightarrow{-\mathrm{Br}^-} \mathrm{(CO)_5Mn{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br}$$
$$\Big\downarrow [\mathrm{Mn(CO)_5}]^-$$
$$[\mathrm{(CO)_5Mn{\cdot}Mn(CO)_4C(O)CH_2{\cdot}CH_2{\cdot}CH_2Br}]^-$$
$$\Big\downarrow -\mathrm{Br}^-$$
$$[\mathrm{(CO)_5Mn{\cdot}Mn(CO)_4}\overline{\mathrm{COCH_2{\cdot}CH_2{\cdot}CH_2}}]$$

SCHEME 1

Although, as mentioned above, addition of $[\mathrm{Mn(CO)_5}]^-$ to 4-chlorobutyryl chloride affords only the dinuclear carbene complex (III), if a reverse addition is carried out to an excess of the acid chloride using a short reaction time, then the ω-chloroacyl complex (I) can be isolated in good yield (54%). Complex (I) forms pale yellow needles, and shows the expected five terminal carbonyl stretching bands in the i.r. spectrum in addition to an acyl band at 1651 cm^{-1}. The ¹H n.m.r. spectrum showed three resonances with relative intensity 1 : 1 : 1, and in agreement with the proposed structure, molecular weight measurements in solution confirmed that the complex is mononuclear.

As would be expected from King's results,[8] reaction of (I) with the anion $[\mathrm{Mn(CO)_5}]^-$ in tetrahydrofuran gave the known carbene complex (III). A similar slow reaction of (I) with lithium iodide gave in low yield (16%)

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[1] Part LXVII, J. R. Moss, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 975.

[2] E. O. Fischer, *Pure Appl. Chem.*, 1970, **24**, 407; 1972, **30**, 353.

[3] D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545.

[4] F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1972, **16**, 487.

[5] D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, 99; and references cited therein.

[6] C. P. Casey, *Chem. Comm.*, 1970, 1220.

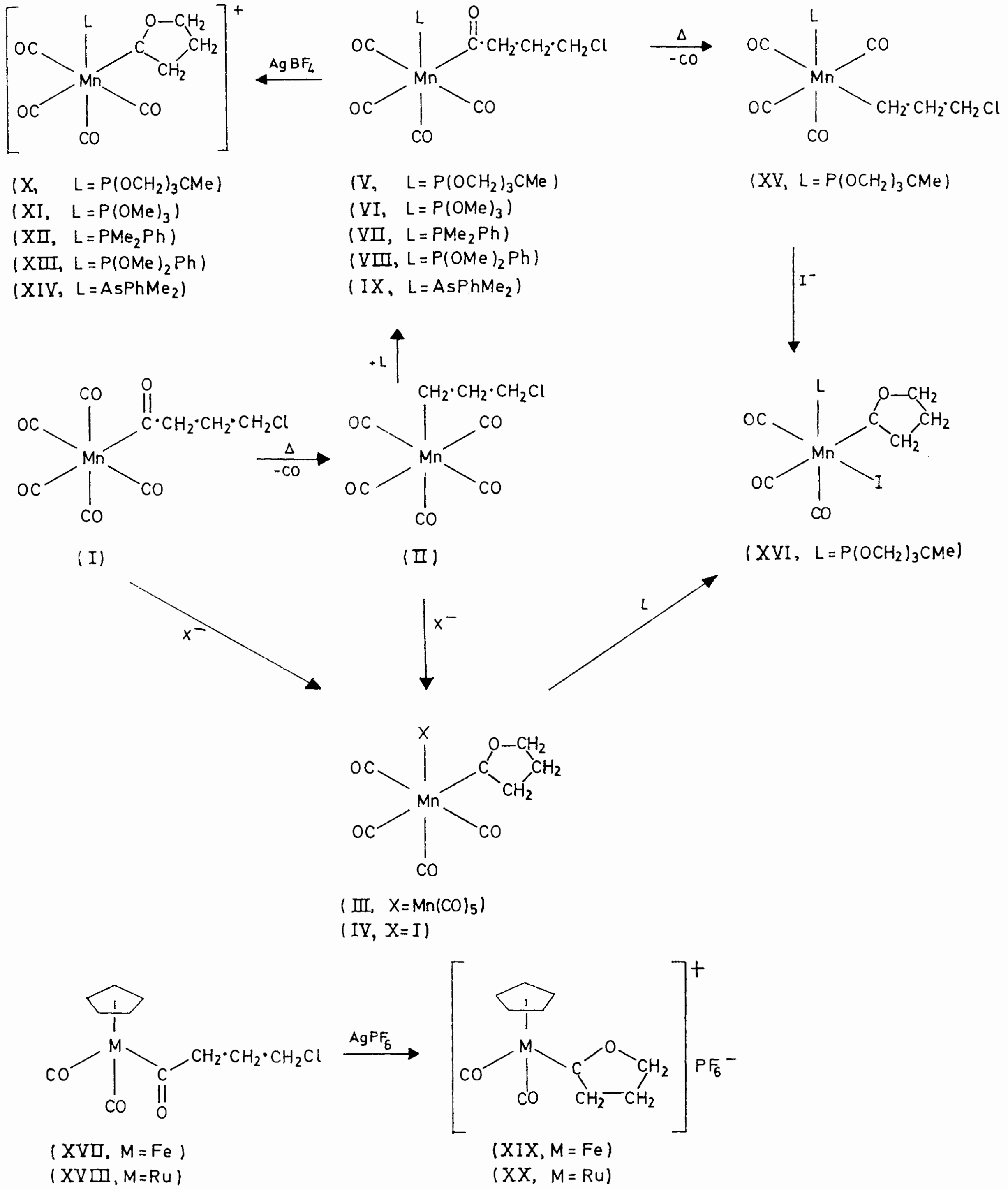
[7] C. P. Casey and R. L. Anderson, *J. Amer. Chem. Soc.*, 1971, **93**, 3554.

[8] R. B. King, *J. Amer. Chem. Soc.*, 1963, **85**, 1922.

[9] F. A. Cotton and C. M. Lukehart, *J. Amer. Chem. Soc.*, 1971, **93**, 2672; *ibid.* 1973, **95**, 3552.

[10] M. Green, J. R. Moss, I. W. Nowell, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1972, 1339.

the orange, air-stable, crystalline carbene complex (IV). In agreement with the illustrated structure, the i.r. spectrum showed four terminal carbonyl bands (3*A'* + *A''*) characteristic of a *cis*-disubstituted octahedral complex with C_s symmetry, there being no evidence in the spectrum of a band assignable to a metal acyl group. In [$^2H_4$]methanol, the ^1H n.m.r. spectrum of (IV) exhibits three resonances at τ 4·89(t), 5·80(t), and 8·0(q); addition of a catalytic amount of CD_3ONa caused disappearance of the resonance at τ 5·80, the triplet at τ 4·89 broadening, and the resonance at τ 8·00 collapsing to a broad triplet. These observations are consistent with exchange of the methylene protons, α to the carbene-carbon atom, for deuterium. Similar observa-



(X, L = $P(OCH_2)_3CMe$)
(XI, L = $P(OMe)_3$)
(XII, L = PMe_2Ph)
(XIII, L = $P(OMe)_2Ph$)
(XIV, L = $AsPhMe_2$)

(V, L = $P(OCH_2)_3CMe$)
(VI, L = $P(OMe)_3$)
(VII, L = PMe_2Ph)
(VIII, L = $P(OMe)_2Ph$)
(IX, L = $AsPhMe_2$)

(XV, L = $P(OCH_2)_3CMe$)

(I)

(II)

(XVI, L = $P(OCH_2)_3CMe$)

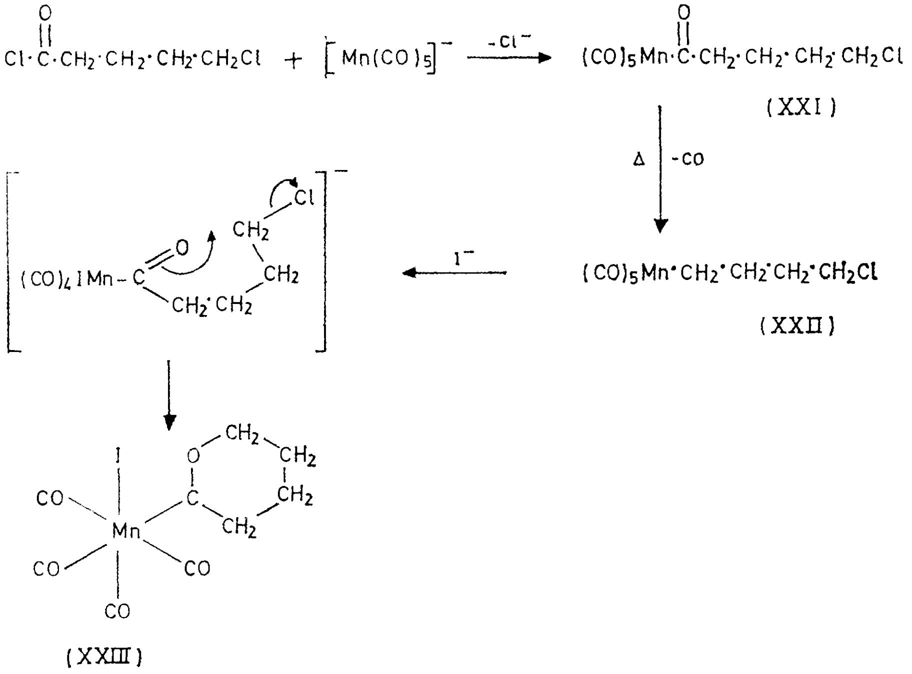
(III, X = $Mn(CO)_5$)
(IV, X = I)

(XVII, M = Fe)
(XVIII, M = Ru)

(XIX, M = Fe)
(XX, M = Ru)

tions have been made for other carbene complexes,[11] including (III).[6]

The formation of (IV) can be envisaged as involving an initial displacement of a carbon monoxide ligand *cis* to the acyl group by iodide anion. There is precedent for a process of this kind in the reaction:[12] $[\mathrm{MnI(CO)_5}] + \mathrm{I^-} \xrightarrow{-\mathrm{CO}}$ *cis*-$[\mathrm{MnI_2(CO)_4}]^-$. The resultant anionic species $[\mathrm{MnI(COCH_2{\cdot}CH_2{\cdot}CH_2Cl)(CO)_4}]^-$ could then undergo a fast intramolecular cyclisation reaction with extrusion of chloride anion. An alternative and potentially more versatile approach to (IV) would be the reaction of $[\mathrm{Mn(CH_2{\cdot}CH_2{\cdot}CH_2Br)(CO)_5}]$ with iodide anion with resultant migration[13] of the γ-bromopropyl group onto a co-ordinated carbon monoxide, *i.e.* carbonyl insertion, to give a similar anionic species, which would collapse to (IV). However, as remarked earlier, reaction of 1,3-dibromopropane with $[\mathrm{Mn(CO)_5}]^-$ gives (III), and even a reverse addition did not give the required complex.



Scheme 2

The decarbonylation of (I) was therefore examined, and complex (II) was formed in good yield (73%) in refluxing light petroleum (b.p. 80—100°). The i.r. spectrum showed no acyl band and four terminal carbonyl bands in agreement with an $[\mathrm{XMn(CO)_5}]$ species in which an organic group X with low symmetry[14] is present. In addition, the ^{1}H n.m.r. spectrum showed three resonances one of which occurred at high field (τ 9·38) characteristic of protons bonded to a carbon atom which in turn is bonded to a metal. Reaction of (II) with lithium iodide in tetrahydrofuran led to the rapid formation of (IV).

Attempts to effect the thermal isomerisation of (I) to a chloro-analogue of (IV) were unsuccessful. Moreover, cyclisation of (I) to a cationic carbene complex $[\mathrm{Mn\overline{COCH_2{\cdot}CH_2{\cdot}CH_2}(CO)_5}]^+$ could not be achieved on addition of silver tetrafluoroborate.

An important factor in the intramolecular cyclisation reaction must be the nucleophilicity of the acyl oxygen atom. It was thought therefore that replacement of terminal bonded carbon monoxide ligands on the manganese by poorer π-acceptors might increase back-bonding from the metal to the acyl group, *viz* $\overset{+}{\mathrm{Mn}}\mathrm{=C(O^-)}$ in valence bond terms, and thus achieve an increase in the reactivity of the acyl oxygen atom. Treatment of (II) with the ligand $\mathrm{P(OCH_2)_3CMe}$ led to the stereospecific formation of the *cis*-acyl complex (V), which showed the expected four bands in the terminal carbonyl region of the i.r. spectrum. In this reaction there was no evidence for the formation of the corresponding *trans*-isomer, a result which parallels the kinetically controlled formation[15] of *cis*-$[\mathrm{MeCOMn(CO)_4\{P(OCH_2)_3CMe\}}]$ on reaction of $[\mathrm{MeMn(CO)_5}]$ with this sterically compact ligand. Under similar conditions stereospecific reactions occurred between (II) and $\mathrm{P(OMe)_3}$, $\mathrm{PMe_2Ph}$, and $\mathrm{P(OMe)_2Ph}$ to give respectively the acyl complexes (VI)—(VIII). Examination of the i.r. spectrum of the acyl complex

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[11] C. G. Kreiter, *Angew. Chem. Internat. Edn.*, 1968, **7**, 390; see also C. P. Casey, R. A. Boggs, and R. L. Anderson, *J. Amer. Chem. Soc.*, 1972, **94**, 8947.

[12] E. W. Abel and I. S. Butler, *J. Chem. Soc.*, 1964, 434.

[13] F. Calderazzo and K. Noack, *J. Organometallic Chem.*, 1965, **4**, 250; 1967, **10**, 101.

[14] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 389.

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

(IX), obtained from (II) and the arsine $AsMe_2Ph$, suggested the presence of some of the *trans*-acyl isomer formed as a result of a subsequent thermodynamically controlled reaction.[16]

In agreement with the above considerations concerning partial negative charge on the oxygen atom, the substituted acyl complexes (V)—(IX) all smoothly cyclised on treatment with silver tetrafluoroborate to give the cationic carbene complexes (X)—(XIV). These compounds all showed resonances in their ^1H n.m.r. spectra typical of the 2-oxacyclopentylidene ligand.

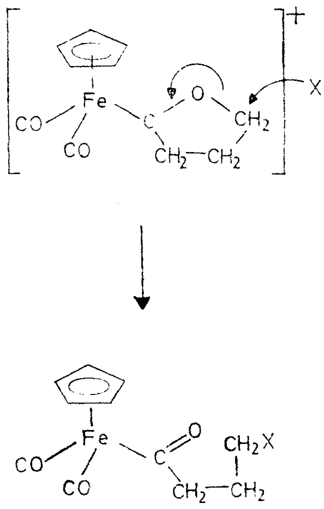
Thermal decarbonylation of the acyl complex (V) gave the *cis*-substituted complex (XV) in good yield. Treatment of (XV) with lithium iodide in tetrahydrofuran afforded the neutral iodo-complex (XVI); the illustrated stereochemistry (C_1 symmetry) follows from the presence in the i.r. spectrum of three strong terminal carbonyl bands of equal intensity. The ^1H n.m.r. spectrum confirmed the presence in (XVI) of the 2-oxacyclopentylidene ligand. Reaction of the complex (IV) with $P(OCH_2)_3CMe$ in refluxing light petroleum also gave the *fac*-substituted complex (XVI), but in low yield. It was shown in separate experiments that at 60°, (IV) formed a mixture of $[MnI(CO)_5]$ and $[Mn_2I_2(CO)_8]$, a reaction which involves displacement of the carbene, and which clearly competes with the replacement of carbon monoxide in (IV) by $P(OCH_2)_3CMe$. The fate of the displaced carbene has so far not been elucidated.

The intramolecular cyclisation reaction, which is an important step in this synthesis of carbene complexes, is an example of a neighbouring group effect in which the rate of the S_N2 attack by an acyl oxygen on the carbon carrying the halogen would be expected to be very dependent on the number of atoms separating the reacting centres. In order to obtain some ideas as to the importance of this effect the reaction of 5-chlorovaleryl chloride with the anion $[Mn(CO)_5]^-$ was examined. Reverse addition and the use of an excess of the acid chloride resulted in selective attack on the acyl group and formation of the crystalline acyl complex (XXI) (Scheme 2).

Decarbonylation of (XXI) by heating in light petroleum gave a good yield (70%) of the alkyl complex (XXII). However, reaction of (XXII) with lithium iodide gave only very low yields (*ca.* 2%) of the expected 2-oxacyclohexylidene complex (XXIII), which was isolated as orange needles. Attempts to improve the yield of (XXIII) were unsuccessful. Thus, ring size would appear to be of considerable importance in determining the ease of cyclisation.

The extension of these reactions to iron and ruthenium π-cyclopentadienyl chemistry has also been briefly examined. Addition of the anion $[Fe(CO)_2(\pi\text{-}C_5H_5)]^-$ to an excess of 4-chlorobutyryl chloride gave a low melting solid characterised as (XVII). The i.r. spectrum showed two terminal carbonyl bands and an acyl band at 1656 cm^{-1}; the ^1H n.m.r. spectrum showed the expected three CH_2 resonances of equal intensity. Treatment of (XVII) with an acetone solution of $AgBF_4$ led to the immediate precipitation of silver chloride and the formation of the cationic complex (XIX), isolated as pale yellow needles. The i.r. spectrum showed only two carbonyl bands at 2073vs and 2029vs, there being no acyl band. The ^1H n.m.r. spectrum showed a π-cyclopentadienyl resonance and bands typical of the carbene ligand. A similar sequence of reactions, but without full characterisation of the intermediate acyl complex (XVIII), afforded, on treatment with $AgPF_6$, the corresponding cationic ruthenium carbene complex (XX). The ready cyclisation of (XVII) and (XVIII) with $AgPF_6$ contrasts with our inability to effect a similar cyclisation of the chloro-complex (I); this possibly reflects the relative nucleophilicities of the different acyl oxygen atoms.

Iodide anion failed to react with (XVII), and treatment of the cationic complex (XIX) with halide anions led to a ring opening reaction:



A result which serves to emphasise the carbonium ion character of these cationic complexes.

EXPERIMENTAL

^1H N.m.r. spectra were recorded on a Varian Associates T60 spectrometer at 60 MHz; chemical shifts are relative to tetramethylsilane (τ 10·00). I.r. spectra were recorded using a Perkin-Elmer 257 spectrometer. Mass spectra were measured on an A.E.I. MS 902 double focussing mass spectrometer. Light petroleum refers to the fraction b.p. 60—80°. All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen in deoxygenated dry solvents. Conductivity measurements were made using a Cambridge Instruments conductance bridge.

Reaction of 4-Chlorobutyryl Chloride with Sodium Pentacarbonylmanganese.—A solution of sodium pentacarbonylmanganese (30·8 mmol) in tetrahydrofuran (80 ml) was added dropwise with stirring to 4-chlorobutyryl chloride (6·25 g, 44·3 mmol) in tetrahydrofuran (50 ml) over a period of 25 min, and the resultant mixture stirred for a further 1 h. Solvent and unreacted butyryl chloride were removed *in vacuo*. The residue was extracted with methylene chloride

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

(2 × 50 ml), centrifuged, and the solvent removed from the clear solution. The resulting crystalline solid was recrystallised from light petroleum to give yellow *needles* of (I) (5·0 g, 54%), m.p. 70—72° [Found: C, 36·1; H, 2·0; Cl, 11·9%; *M*, 309 (in benzene). $C_9H_6ClMnO_6$ requires C, 36·0; H, 2·0; Cl, 11·8%; *M*, 301], $\nu_{max.}$ (CO) (cyclohexane) at 2118w, 2054m, 2018sh, 2013vs, 2006s, and 1651 cm^{-1}; ^{1}H n.m.r. resonances (C_6D_6) at τ 6·90 [t, 2H, $\mathrm{CO}CH_2$, *J*(HH) 6·0 Hz], 7·26 [t, 2H, $\mathrm{COCH_2{\cdot}CH_2{\cdot}}CH_2$, *J*(HH) 6·0 Hz], and 8·32 [q, 2H, $\mathrm{CO{\cdot}CH_2{\cdot}}CH_2\mathrm{{\cdot}CH_2}$, *J*(HH) 6·0 Hz].

Decarbonylation of Complex (I).—A solution of (I) (1·17 g, 3·88 mmol) in petroleum (80—100°) (25 ml) was heated under reflux for 45 min; the i.r. spectrum of the solution showed the acyl band of (I) to have disappeared. The solution was filtered and the solvent removed *in vacuo* leaving a pale yellow oil, which was purified by sublimation (25°, 0·1 mmHg) onto a cooled (−78°) probe to give (II) as a pale yellow *oil* (0·77 g, 73%) [Found: C, 35·7; H, 2·2. $C_8H_6ClMnO_5$ requires C, 35·3; H, 2·2%], $\nu_{max.}$ (CO) (hexane) at 2111w, 2047w, 2015vs, and 1996s cm^{-1}; ^{1}H n.m.r. resonances (C_6D_6) at τ 6·93 [t, 2H, CH_2, *J*(HH) 6·0 Hz], 8·20 [m, 2H, CH_2], and 9·38 [m, 2H, $\mathrm{Mn}CH_2$].

Reactions of Complex (I).—(a) *With sodium pentacarbonylmanganese.* A solution of sodium pentacarbonylmanganese (2·06 mmol) in tetrahydrofuran (15 ml) was added to (I) (0·50 g, 1·66 mmol), and the solution allowed to stand at room temperature for 3 days. Solvent was removed *in vacuo*, and the resultant orange oil extracted with light petroleum (3 × 30 ml). The volume of the solvent was reduced *in vacuo* and the solution chromatographed on a Florisil packed column. Elution with light petroleum gave $Mn_2(CO)_{10}$, followed by a bright yellow fraction, which was recrystallised from light petroleum to give yellow needles of (III) (0·28 g, 39%), m.p. 63—65° (lit.,[8] m.p. 67—68°). The i.r. and ^{1}H n.m.r. spectra were identical with an authentic sample of *eq*-[$Mn_2(\overline{COCH_2{\cdot}CH_2{\cdot}CH_2})(CO)_9$].

(b) *With lithium iodide.* A solution of (I) (0·3 g, 1·0 mmol) in tetrahydrofuran (10 ml) was treated with anhydrous lithium iodide (0·85 g, 6·35 mmol) and the solution allowed to stand at room temperature for 4 days. Solvent was removed *in vacuo*, the residue extracted (3 × 30 ml) with light petroleum, and the volume of the solvent reduced. The solution was allowed to stand at 0° to give orange *needles* of (IV) (0·06 g, 16%), m.p. 57—58° [Found: C, 26·8; H, 1·8; I, 34·3%; *M*, 359 (in $CHCl_3$). $C_8H_6IMnO_5$ requires C, 26·4; N, 1·7; I, 34·9%; *M*, 364], $\nu_{max.}$ (CO) (cyclohexane) at 2088m, 2025s, 2005vs, and 1969s cm^{-1}, $\nu_{max.}$ (Nujol) at 1409m, 1401m, 1281w, 1245m, 1232m, 1060m, 1036sh, 980m, 864w, 722w, and 650s cm^{-1}; ^{1}H n.m.r. resonances (CD_3OD) τ 4·89 [t, 2H, $\mathrm{CO}CH_2$, *J*(HH) 8·0 Hz], 5·80 [t, 2H, CH_2, *J*(HH) 8·0 Hz], and 8·00 [q, 2H, CH_2, *J*(HH) 8·0 Hz]. The mass spectrum showed peaks at *m/e* 364 (*P*, 73%), 336 ($P - \mathrm{CO}$, 4%), 308 ($P - 2\mathrm{CO}$, 30%), 280 ($P - 3\mathrm{CO}$, 39%), 252 ($P - 4\mathrm{CO}$, 73%), 238 ($P - 4\mathrm{CO} - \mathrm{CH_2}$, 2%), 224 ($P - 4\mathrm{CO} - 2\mathrm{CH_2}$, 6%), 210 ($P - 4\mathrm{CO} - 3\mathrm{CH_2}$, 12%), 182 ($P - 4\mathrm{CO} - \mathrm{C_4H_6O}$, 100%), 69 (37%), and 55 (37%).

Reactions of Complex (II).—(a) *With lithium iodide.* A solution of (II) (0·40 g, 1·45 mmol) in tetrahydrofuran (10 ml) was treated with anhydrous lithium iodide (1·08 g, 8·0 mmol) and the solution allowed to stand at room temperature for 2 h. Solvent was removed *in vacuo*, and the residue extracted with benzene (3 × 20 ml). The benzene solution was washed with water (2 × 10 ml), dried (Na_2SO_4), and the solvent removed *in vacuo*. Recrystallisation of the orange residue from light petroleum gave (IV) (0·23 g, 44%).

(b) *With 1-methyl-4-phospha-*3,5,8-*trioxabicyclo*[2.2.2]-*octane.* To a solution of (II) (0·61 g, 2·2 mmol) in light petroleum (40 ml) was added $P(OCH_2)_3CMe$ (0·35 g, 2·37 mmol). The solution was stirred at room temperature for 24 h to give a cream coloured precipitate, which was collected and washed with light petroleum. Recrystallisation (0°) from methylene chloride–light petroleum gave *crystals* of (V) (0·45 g, 48%), m.p. 95—99° (Found: C, 37·0; H, 3·8. $C_{13}H_{15}ClMnPO_8$ requires C, 36·9; H, 3·6%), $\nu_{max.}$ (CO) (CH_2Cl_2) at 2088m, 2011s, 1989s, 1976s, and 1618m (acyl) cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 5·74 [d, 6H, $\mathrm{PO}CH_2$, *J*(PH) 4·0 Hz], 6·50 [t, 2H, *J*(HH) 6·0 Hz], 6·93 [t, 2H, *J*(HH) 6·0 Hz], 8·13 [q, 2H, *J*(HH) 6·0 Hz], and 9·17 [s, 3H, $\mathrm{C}CH_3$].

A similar method was used to prepare the following complexes, which were four times recrystallised (−78°) from light petroleum.

(c) *With trimethyl phosphite.* An *oil* (VI) (62%) or low melting solid was obtained (Found: C, 33·6; H, 4·1. $C_{11}H_{15}ClMnPO_8$ requires C, 33·3; H, 3·8%), $\nu_{max.}$ (CO) (cyclohexane) at 2080m, 2003s, 1988sh, 1977s, and 1621m (acyl) cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 6·27 [d, 9H, $\mathrm{PO}CH_3$, *J*(PH) 12·0 Hz], 6·50 [t, 2H, *J*(HH) 6·0 Hz], 6·90 [t, 2H, *J*(HH) 6·0 Hz], and 8·10 [q, 2H, *J*(HH) 6·0 Hz].

(d) *With dimethylphenylphosphine.* An *oil* (VII) (44%) was obtained (Found: C, 47·1; H, 4·5. $C_{16}H_{17}ClMnPO_5$ requires C, 46·8; H, 4·2%), $\nu_{max.}$ (CO) (cyclohexane) at 2061m, 1993s, 1964vs, 1955sh, and 1615m (acyl) cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) resonances at τ 2·58 (m, 5H, $C_6H_5\mathrm{P}$), 6·55 [t, 2H, *J*(HH) 6·0 Hz], 7·07 [t, 2H, *J*(HH) 6·0 Hz], and 8·18 [d overlapping with q, 8H, *J*(HH) 6·0 Hz, *J*(PH) 9·0 Hz].

(e) *With dimethyl phenyl phosphonite.* An *oil* (VIII) (67%) was obtained (Found: C, 44·3; H, 4·3. $C_{16}H_{17}ClMnPO_7$ requires C, 43·4; H, 3·9%), $\nu_{max.}$ (CO) (cyclohexane) at 2076m, 2005s, 1977vs, 1962sh, and 1618m (acyl) cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 2·50 (m, 5H, $C_6H_5\mathrm{P}$), 6·32 [d, 6H, $\mathrm{PO}CH_3$, *J*(PH) 12·0 Hz], 6·60 [t, 2H, *J*(HH) 7·0 Hz], 7·05 [t, 2H, *J*(HH) 7·0 Hz], and 8·27 [q, 2H, *J*(HH) 7·0 Hz].

(f) *With dimethylphenylarsine.* An *oil* (IX) (49%) was obtained (Found: C, 41·8; H, 3·8. $C_{16}H_{17}AsClMnO_5$ requires C, 42·3; H, 3·8%), $\nu_{max.}$ (CO) (cyclohexane) at 2060m, 2014m, 2005m—w, 1985s, 1967vs, 1955m, and 1617m (acyl) cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 2·50 (m, 5H, $C_6H_5\mathrm{As}$), 6·53 [t, 2H, *J*(HH) 7·0 Hz], 6·93 [t, 2H, *J*(HH) 7·0 Hz], and 8·27 [q overlapping with s, 8H, *J*(HH) 7·0 Hz].

Decarbonylation of Complex (V).—A suspension of (V) (0·42 g, 1·0 mmol) in light petroleum (95—100°) (30 ml) was heated under reflux for 1/2 h; the resultant clear solution was filtered while hot. On cooling to room temperature, pale yellow crystals separated, which were collected and recrystallised from light petroleum to give *crystals* of (XV) (0·21 g, 54%), m.p. 113—117° (Found: C, 37·0; H, 3·9. $C_{12}H_{15}ClMnPO_7$ requires C, 36·7; H, 3·9%), $\nu_{max.}$ (CO) (cyclohexane) at 2076m, 2003m, 1992vs, and 1968s cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 5·80 [d overlapping with t, 8H, *J*(PH) 5·0 Hz, *J*(HH) 7·0 Hz], 6·53 [t, 2H, *J*(HH) 7·0 Hz], 7·93 [q, 2H, *J*(HH) 7·0 Hz], and 9·20 (s, 3H, $\mathrm{C}CH_3$).

Reaction of Complex (XV) *with Lithium Iodide.*—To a solution of (XV) (0·20 g, 0·51 mmol) in tetrahydrofuran (10 ml) was added anhydrous lithium iodide (0·45 g, 3·4 mmol). After stirring at room temperature for 16 h, solvent was removed *in vacuo* and the residue extracted with benzene, filtered, and chromatographed on a Florisil packed column.

Elution with diethyl ether gave a yellow band, which was collected and rechromatographed to give on cooling (0°) orange *crystals* of (XVI) (0·09 g, 36%), m.p. 154—156° (Found: C, 29·8; H, 3·2; I, 26·5; Mn, 11·7. $C_{12}H_{15}IMnPO_7$ requires, C, 29·8; H, 3·1; I, 26·2; Mn, 11·4%), $\nu_{max.}$ (CO) (CH_2Cl_2) at 2043s, 1985s, and 1939s cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 4·90 [t, 2H, COCH_2, J(HH) 7·0 Hz], 5·73 [d overlapping with t, 8H, POCH_2 and CH_2, J(PH) 5·0 Hz, J(HH) 7·0 Hz], 8·05 [q, 2H, J(HH) 7·0 Hz], and 9·20 (s, 3H, CCH_3).

Silver Cation Promoted Cyclisation of Complex (V).—Addition of an acetone (10 ml) solution of silver tetrafluoroborate (0·097 g, 0·5 mmol) to an acetone (10 ml) solution of (V) (0·21 g, 0·5 mmol) afforded an immediate precipitate of silver chloride. After 1/2 h the precipitate was filtered off and solvent removed *in vacuo* from the filtrate. The resultant oil was dissolved in the minimum quantity of methanol and filtered through a layer (2 cm) of Celite. Addition of diethyl ether gave white *crystals* of (X) (0·09 g, 38%), m.p. 199—201° dec. (Found: C, 33·4; H, 3·3; F, 16·0; Mn, 11·6. $C_{13}H_{15}BF_4MnPO_8$ requires C, 33·1; H, 3·2; F, 16·1; Mn, 11·6%), $\nu_{max.}$ (CO) (CH_2Cl_2) at 2117m, 2050sh, and 2032vs cm^{-1}; ^{1}H n.m.r. resonances ($C_6H_5NO_2$) at τ 4·53 [t, 2H, OCH_2, J(HH) 8·0 Hz], 5·43 [d, 6H, POCH_2, J(PH) 5·0 Hz], 5·90 [t, 2H, CH_2, J(HH) 7·0 Hz], 7·60 [m, 2H, $CH_2{\cdot}CH_2{\cdot}CH_2$, J(HH) 7·0 Hz], and 9·10 (s, 3H, CCH_3).

Similar reactions afforded white *crystals* of (XI) (34%), m.p. 60·5—62·0° (Found: C, 29·2; H, 3·3; F, 16·7; Mn, 13·3. $C_{11}H_{15}BF_4MnPO_8$ requires C, 29·5; H, 3·4; F, 17·0; Mn, 12·3%), $\nu_{max.}$ (CO) (CH_2Cl_2) at 2110m, 2042sh, and 2020vs cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 4·63 [t, 2H, OCH_2, J(HH) 8·0 Hz], 6·10 [d overlapping with t, 11H, CH_2, POCH_3, J(PH) 12·0 Hz, J(HH) 8·0 Hz], and 7·80 (q, 2H, $CH_2{\cdot}CH_2{\cdot}CH_2$); *crystals* of (XII) (33%), m.p. 68·5—70·5° (Found: C, 41·8; H, 3·9. $C_{16}H_{17}BF_4MnPO_5$ requires C, 41·6; H, 3·7%), $\nu_{max.}$ (CO) (CH_2Cl_2) at 2101m, 2032sh, and 2013vs cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 3·40 (m, 5H, C_6H_5P), 4·80 [t, 2H, OCH_2, J(HH) 8·0 Hz], 6·30 [t, 2H, CH_2, J(HH) 8·0 Hz], and 8·0 [d overlapping with q, 8H, CH_2, PCH_3, J(PH) 9·0 Hz, J(HH) 8·0 Hz]; *crystals* of (XIII) (60%), m.p. 123—126° (Found: C, 39·3; H, 3·5. $C_{16}H_{17}BF_4MnPO_7$ requires C, 38·9; H, 3·5%), $\nu_{max.}$ (CO) (CH_2Cl_2) at 2105m, 2043sh, and 2020vs cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 2·33 (m, 5H, C_6H_5P), 4·87 [t, 2H, OCH_2, J(HH) 7·0 Hz], 6·13 [d, overlapping t, 8H, CH_2, POCH_3, J(PH) 12·0 Hz, J(HH) 7·0 Hz], and 8·07 [q, 2H, CH_2, J(HH) 7·0 Hz]; and *crystals* of (XIV) (37%), m.p. 82—85° (Found: C, 38·3; H, 3·6. $C_{16}H_{17}AsBF_4MnO_5$ requires C, 38·0; H, 3·4%), $\nu_{max.}$ (CO) (CH_2Cl_2) at 2101m, 2030sh, and 2013vs cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) at τ 2·53 (m, 5H, C_6H_5As), 4·77 [t, 2H, OCH_2, J(HH) 8·0 Hz], 6·17 [t, 2H, CH_2, J(HH) 8·0 Hz], and 8·07 [q, overlapping s, 8H, AsCH_3, CH_2, J(HH) 8·0 Hz].

Reaction of Sodium Dicarbonyl(π-cyclopentadienyl)iron with 4-*Chlorobutyryl Chloride*.—A solution of Na[Fe(CO)$_2$(π-C_5H_5)] (7·34 mmol) in tetrahydrofuran (60 ml) was added dropwise with stirring to 4-chlorobutyryl chloride (2·50 g, 17·7 mmol) at 0 °C over 40 min. The solution was allowed to warm to room temperature with stirring over 45 min. Solvent and unreacted 4-chlorobutyryl chloride were removed *in vacuo* leaving a yellow-brown oil, which was extracted with hexane (2 × 20 ml); the extract was filtered and cooled to −78 °C. The supernatant liquid was removed and the residue recrystallised (−78°) twice from hexane to give a red *oil* (XVII) (1·46 g, 71%) (Found: C, 46·2; H, 4·3. $C_{11}H_{11}ClFeO_3$ requires C, 46·8; H, 3·9%), $\nu_{max.}$ (CO) (hexane) at 2026vs, 1967vs, and 1656m (acyl) cm^{-1}; ^{1}H n.m.r. resonances (C_6D_6) at τ 5·75 (s, 5H, C_5H_5), 6·75 [t, 2H, OCH_2, J(HH) 7·0 Hz], 7·15 [t, 2H, CH_2, J(HH) 7·0 Hz], and 8·26 [q, 2H, CH_2, J(HH) 7·0 Hz].

Cyclisation of Complex (XVII) *with Silver Hexafluorophosphate*.—A solution of (XVII) (1·66 g, 5·88 mmol) in acetone (30 ml) was treated with $AgPF_6$ (1·49 g, 5·89 mmol) and the mixture stirred for 1 h. The precipitated silver chloride was filtered off and solvent removed *in vacuo* from the filtrate. The residue was dissolved in methanol (60 ml), treated with activated charcoal (0·20 g), and then filtered. Addition of diethyl ether gave pale yellow *needles* of (XIX) (1·35 g, 59%), m.p. 115—117° (Found: C, 33·5; H, 2·7; F, 29·3; Fe, 14·2. $C_{11}H_{11}F_6FePO_3$ requires C, 33·7; H, 2·8; F, 29·1; Fe, 14·2%), $\nu_{max.}$ (CO) (CH_2Cl_2) at 2073vs, 2029vs, $\nu_{max.}$ (PF) (Nujol) at 839vs cm^{-1}; ^{1}H n.m.r. resonances ([$^2H_6$]acetone) at τ 4·34 (s, 5H, C_5H_5), 4·39 [t, 2H, OCH_2, J(HH) 8·0 Hz], 6·01 [t, 2H, CH_2, J(HH) 8·0 Hz], and 7·84 [q, 2H, CH_2, J(HH) 8·0 Hz]; the equivalent conductance for a *ca.* 10^{-3}M solution ($C_6H_5NO_2$) was $\Lambda_e = 30{\cdot}7\ \Omega^{-1}$ mol^{-1} cm^2.

Preparation of Complex (XX).—A solution of Na[Ru(CO)$_2$(π-C_5H_5)] in tetrahydrofuran (15 ml) was prepared by stirring a solution of [Ru(CO)$_2$(π-C_5H_5)]$_2$ (0·22 g, 0·50 mmol) in tetrahydrofuran (15 ml) with sodium amalgam (0·20 g Na in 10 ml of Hg) for 5·5 h. The solution of the anion was added dropwise with stirring to 4-chlorobutyryl chloride (0·25 g, 1·77 mmol) and the resultant mixture stirred for 16 h. Solvent was removed *in vacuo* and the residue extracted (3 × 10 ml) with hexane. Reduction of the volume of the solvent *in vacuo* followed by cooling (−78 °C) gave a yellow *solid* (XVIII) (0·24 g), $\nu_{max.}$ (CO) (hexane) at 2035s, 1976vs, and 1656m (acyl) cm^{-1}. The solid was dissolved in acetone (8 ml) and treated with $AgPF_6$ (0·16 g, 0·63 mmol) and the mixture stirred for 1 h. The reaction mixture was filtered, solvent removed from the filtrate, and the residue recrystallised (twice) from methanol–diethyl ether to give pale yellow *needles* of (XX) (0·08 g, 18%), m.p. 119—120° dec. (Found: C, 30·3; H, 2·5. $C_{11}H_{11}F_6O_3PRu$ requires C, 30·2; H, 2·5%), $\nu_{max.}$ (CO) (CH_2Cl_2) at 2083vs and 2033vs cm^{-1}.

Reaction of Sodium Pentacarbonylmanganese with 5-*Chlorovaleryl Chloride*.—A solution of Na[Mn(CO)$_5$] (30·8 mmol) in tetrahydrofuran (80 ml) was added dropwise with stirring to 5-chlorovaleryl chloride (5·50 g, 35·4 mmol) in tetrahydrofuran (50 ml) over a period of 25 min. After 1 h at room temperature solvent was removed *in vacuo*, the residue extracted with methylene chloride (2 × 50 ml), the resultant solution centrifuged, and the solvent evaporated. The residue was recrystallised from light petroleum to give yellow *crystals* of (XXI) (4·5 g. 47%), m.p. 45—47° dec. (Found: C, 37·9; H, 2·5. $C_{10}H_8ClMnO_6$ requires C, 38·2; H, 2·6%), $\nu_{max.}$ (CO) (hexane) at 2116w, 2052m, 2016sh, 2011vs, 2005m, and 1656m (acyl) cm^{-1}; ^{1}H n.m.r. resonances ($CDCl_3$) τ 6·50 (m, 2H, CH_2), 7·00 (m, 2H, CH_2), and 8·24 (m, 4H, CH_2).

Decarbonylation of Complex (XXI).—A solution of (XXI) (0·31 g, 1·0 mmol) in light petroleum (30 ml) was heated under reflux for 45 min. The reaction mixture was filtered and the solvent removed *in vacuo*. Sublimation (25°, 0·1 mmHg) of the residue onto a cold (−78°) probe gave yellow *crystals* of (XXII) low melting (0·20 g, 70%), an oil at 25°. (Found: C, 37·3; H, 2·75. $C_9H_8ClMnO_5$ requires C, 37·7;

H, 2·8%), $\nu_{max.}$ (CO) (hexane) at 2112m, 2011vs, 1995s, and 1977w cm^{-1}; ^{1}H n.m.r. resonances (CDCl$_3$) at τ 6·47 (m, 2H, OCH_2), 8·13 (m, 4H, CH_2), and 9·00 (m, 2H, CH_2).

Reaction of Complex (XXII) *with Lithium Iodide.*—A solution of (XXII) (0·48 g, 1·7 mmol) in tetrahydrofuran (10 ml) was treated with anhydrous lithium iodide (1·20 g, 8·9 mmol) and the solution stirred at room temperature for 2 h. Solvent was removed *in vacuo*, the residue extracted with light petroleum and the resultant orange solution chromatographed on a Silica-gel packed column. Elution with diethyl ether–light petroleum gave a yellow material which on recrystallisation (0°) from light petroleum gave orange *needles* of (XXIII) (0·011 g, 1·7%), m.p. 51—52° (Found: C, 28·7; H, 2·2. $C_9H_8IMnO_5P$ requires C, 28·6; H, 2·1%), $\nu_{max.}$ (CO) (hexane) at 2088w, 2025m, 2003s, and 1969 cm^{-1}.

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