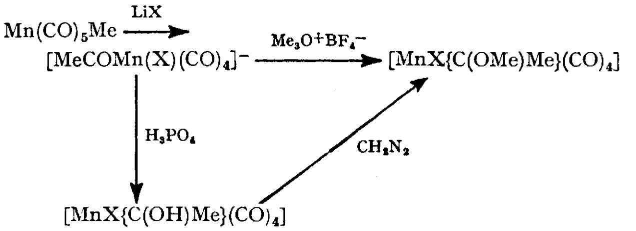
Chemistry of the Metal Carbonyls. Part LXVII.[1] Hydroxycarbene Complexes of Manganese(I)

By **John R. Moss, Michael Green, and F. Gordon A. Stone,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Protonation of solutions containing the anions $[MnX(COMe)(CO)_4]^-$ (X = Br or I) affords the stable crystalline hydroxycarbene complexes *cis*-$[MnX\{C(OH)Me\}(CO)_4]$, characterised by i.r., n.m.r., and mass spectroscopy. Reaction with water yields methyl(pentacarbonyl)manganese, whereas, cyclohexylamine gives acetyl(cyclohexylamine)tetracarbonylmanganese.

FOLLOWING the first synthesis of a transition metal carbene complex,[2] considerable progress has been made towards extending this area of chemistry.[3,4] We became interested in examining the reactions of co-ordinated carbenes within the co-ordination sphere of the metal. A possible approach to this problem involved synthesis of complexes of type *cis*-$[MnX(carbene)(CO)_4]$ (X = halogen, alkyl, or aryl), which it was envisaged would be available by alkylation of the acyl anions formed by reacting halide anion with methyl(pentacarbonyl)manganese (Scheme).

Earlier, the reaction of $Mn(CO)_5Me$ with the anions H^- and OMe^- was investigated [5] with a view to protonating the expected acyl anionic species $[MnX(COMe)(CO)_4]^-$ (X = H or OMe); however, the product isolated after protonation was the trinuclear hydride $[Mn_3H_3(CO)_{12}]$ and not a carbene complex.



SCHEME (X = Cl, Br, or I)

In contrast, we find that protonation of the halogeno-anions $[MeCOMn(X)(CO)_4]^-$ first reported by Calderazzo and Noack,[6] afforded the hydroxycarbene complexes *cis*-$[MnX\{C(OH)Me\}(CO)_4]$ (X = Br or I), which were isolated as low-melting, volatile, orange needles on recrystallisation from light petroleum; they could be stored under a nitrogen atmosphere for several months

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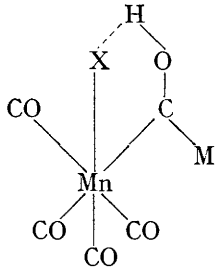
[6] F. Calderazzo and K. Noack, *J. Organometallic Chem.*, 1965, **4**, 250.

without decomposition. The analogous chloro-complex $[MnCl\{C(OH)Me\}(CO)_4]$ was obtained in low yield, and could not be separated efficiently from methyl(pentacarbonyl)manganese into which it readily decomposed. An attempt to prepare a binuclear hydroxycarbene complex of the type $[Mn_2\{C(OH)Me\}(CO)_9]$ by treating $[Mn(CO)_5]^-$ anion with $Mn(CO)_5Me$ followed by protonation, afforded a very unstable orange-red species, which could not be characterised; however, addition of triphenylphosphine to a solution of this complex gave the known[7] compound *ax*-$[Mn_2(CO)_9(PPh_3)]$. The instability of the presumed intermediate $[Mn_2\{C(OH)Me\}(CO)_9]$ contrasts with the stability of the complex $[Mn_2\{C(OMe)Me\}(CO)_9]$.[8,9]



(I; X = Br)
(II; X = I)

The i.r. spectra of (I) and (II) both showed four bands with relative intensities corresponding to an octahedral complex with *cis*-substituents, *i.e.* C_s symmetry. There were no bands in the 1650 cm^{-1} region typical of acyl–metal stretching frequencies. Weak, broad bands were also observed in the 3000 cm^{-1} region, which were shifted to lower frequencies in the corresponding deuterio-compounds, prepared by protonation of the anions with D_3PO_4. These bands are assigned to $\nu(OH)$, and in the iodo-complex, $\nu(OD)$ occurred at 2200 cm^{-1}, although from the bromo-complex $\nu(OD)$ was partially obscured by the terminal carbonyl stretching frequencies. However, the general trend of $\nu(OH)$ and $\nu(OD)$ $I > Br$ was discernible. In agreement $\nu(OH)$ of the unstable chloro-complex *cis*-$[MnCl\{C(OH)Me\}(CO)_4]$ occurred at lower frequency than for the bromo-compound. The observed position of the hydroxyl stretching frequency is very low for a normal hydroxy-group, and occurs more in the region associated with carboxylic acids. It is suggested that in (I), (II), and the corresponding chloro-complex there is hydrogen bonding, it not being possible to distinguish between intra- or inter-molecular interaction of this kind.

The ^1H n.m.r. spectra of (I) and (II) in C_6D_6 showed sharp singlets for the methyl group at τ 7·74 and 7·72 respectively; no other resonances were detected between τ −10·0 and 30·0. The absence of a signal assignable to the hydroxyl hydrogen, is possibly due to exchange broadening; similarly, no n.m.r. resonance was detected for the hydroxyl hydrogen in the cationic-carbene complex $[Fe\{C(OH)Me\}(CO)(PPh_3)\pi\text{-}C_5H_5]^+$;[10] although a singlet was observed in the spectrum of $Re\{C(OH)Me\}(CO)_2(\pi\text{-}C_5H_5)$ at τ 5·51.[11]

The mass spectra of both (I) and (II) showed a parent ion, and peaks corresponding to the stepwise loss of carbon monoxide. In the case of the iodo-complex, loss of CH_4 formally occurs leading to ions attributable to the species $Mn(CO)_nI$ ($n = 0$—5). Strong peaks assignable to $Mn(CO)_5Me$ were observed indicating the ready elimination of HX (X = Cl, Br, or I).

Solution molecular weight measurements in benzene for both (I) and (II) were high, implying the presence of intermolecular association in solution.

Reaction of water with (I) and (II) gave methyl(pentacarbonyl)manganese, together with the corresponding acid HX (X = Br or I). It is suggested that the hydroxycarbene complexes behave as fairly strong acids, which in water dissociate to give an acyl species; this in turn loses halide anion with migration of the methyl group back onto the manganese, *i.e.* the reverse of the Calderazzo–Noack[6] reaction. It is possible that the migration step, in which the methyl to manganese σ-bond is formed, does not occur simultaneously with the extrusion of halide anion, since treatment of (I) and (II) with cyclohexylamine leads to the immediate formation of cyclohexylammonium chloride or bromide and the known[12] *cis*-acetyltetracarbonyl(cyclohexylamine)-manganese. It is suggested that this results from the capture of the co-ordinately unsaturated species $[Mn(COMe)(CO)_4]$ by cyclohexylamine. Methyl(pentacarbonyl)manganese reacts relatively slowly with cyclohexylamine.[12]

$$[MnX\{C(OH)Me\}(CO)_4] \xrightleftharpoons{-H^+} [MnX(COMe)(CO)_4]^- \xrightleftharpoons{-X^-} [MnMe(CO)_5]$$

Attempts to react both (I) and (II) with diazomethane to form the desired compounds $[MnX\{C(OMe)Me\}(CO)_4]$ were unsuccessful, as was the reaction of the anions $[MnX(COMe)(CO)_4]^-$ with $Me_3O^+BF_4^-$. Alternative routes to neutral manganese(I) carbene complexes are therefore being sought.

EXPERIMENTAL

^1H N.m.r. spectra were recorded on a Varian Associates T 60 spectrometer at 60 MHz; chemical shifts are relative to Me_4Si (τ 10·00). All operations were carried out under dry, oxygen-free nitrogen. Light petroleum refers to the 40—60° fraction.

Synthesis of Bromotetracarbonyl(methylhydroxycarbene)-manganese.—A solution of methyl(pentacarbonyl)mangan-

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[12] C. S. Kraihanzel and P. K. Maples, *Inorg. Chem.*, 1968, **7**, 1806.

ese (0·94 g, 4·50 mmol) and lithium bromide (0·88 g, 10·10 mmol) in tetrahydrofuran was stirred at room temperature for 1 h. Orthophosphoric acid (1·20 ml) was added to the orange-red solution, and stirring continued for a further 30 min. Solvent was removed *in vacuo*, and the residue extracted with light petroleum (3 × 10 ml). Removal of solvent from the extract gave an orange solid, which on recrystallisation (−78°) from light petroleum gave orange-yellow needles of (I) *bromotetracarbonyl*(*methylhydroxycarbene*)*manganese* (0·87 g, 66%), m.p. 33—34° [Found: C, 24·7; H, 0·9; Br, 27·9; Mn, 18·9; O, 27·6%; *M*, 424 (in benzene). $C_8H_4BrMnO_5$ requires C, 24·8; H, 1·4; Br, 27·5; Mn, 18·9; O, 27·5%, *M*, 291], $\nu_{\text{max.}}$(CO) (cyclohexane) 2104m, 2046s, 2927vs, 1965s cm^{-1}, $\nu_{\text{max.}}$ (OH) (film) 2880w,br cm^{-1}. The mass spectrum showed peaks at *m/e* 291 (*P*, 10%); 235 (*P* − 2CO, 3%); 210 (*P* − HBr, 26%); 207 (*P* − 3CO, 20%); 195 (*P* − HBr − Me, 8%); 182 (*P* − HBr − CO; 32%); 179 (*P* − 4CO, 16%); 167 *P* − HBr − Me − CO, 12%); 163 (*P* − HBr − 3CO, 2%); 154 (*P* − HBr − 2CO, 14%); 139 (*P* − HBr − Me − 2CO, 14%); and 135 (*P* − 5CO − Me − H, 100%).

Synthesis of Iodotetracarbonyl(*methylhydroxycarbene*)*manganese*.—A similar reaction (1 h) of methyl(pentacarbonyl)-manganese (0·60 g, 2·86 mmol) with lithium iodide (0·78 g, 5·81 mmol) in tetrahydrofuran (10 ml) gave, after acidification with orthophosphoric acid (1·0 ml) and crystallisation (−78°) from light petroleum, orange-needles of (II) *iodotetracarbonyl*(*methylhydroxycarbene*)*manganese* (0·71 g, 74%), m.p. 24—26° [Found: C, 21·4; H, 1·1; I, 37·7%; *M*, 1276 (in benzene). $C_6H_4IMnO_5$ requires C, 21·3; H, 1·2; I, 37·6%; *M*, 338], $\nu_{\text{max.}}$(CO) (cyclohexane) 2098m, 2041s, 2023vs, 1970s cm^{-1}, $\nu_{\text{max.}}$(OH) (film) 2920m,br cm^{-1}. The mass spectrum showed peaks at *m/e* 338 (*P*, 11·2%); 282 (*P* − 2CO, 9%); 254 (*P* − 3CO, 16%); 226 (*P* − 4CO, 9·6%); 210 (*P* − HI − CO, 21%), and 182 (*P* − HI − 2CO, 100%).

Reaction of Bromotetracarbonyl(*methylhydroxycarbene*)-*manganese with Cyclohexylamine*.—A solution of (I) (0·18 g, 0·62 mmol) in n-hexane (10 ml) was treated with cyclohexylamine (0·15 ml, 1·31 mmol); the orange-yellow colour of the solution was immediately discharged and a white precipitate formed.

Solvent was removed *in vacuo* and the residue recrystallised from n-hexane to give needles of acetyl(cyclohexylamine)tetracarbonylmanganese (0·14 g, 73%), m.p. 93—94° (dec.) (Found: C, 47·3; H, 5·6; N, 4·4. Calc. for $C_{12}H_{16}MnNO_5$: C, 46·6; H, 5·2; N, 4·5%). The sample was also characterised by its i.r. and ^{1}H n.m.r. spectra which were identical to those values previously reported.[12]

The iodo-complex (II) reacted to give the same product on treatment with cyclohexylamine.

Reaction of Bromotetracarbonyl(*methylhydroxycarbene*)-*manganese with Water*.—A solution of (I) (0·06 g, 0·21 mmol) in diethyl ether (5 ml) was treated with water (0·5 ml). After 5 min at room temperature anhydrous sodium sulphate was added, the solution filtered, and the solvent removed *in vacuo* to give white crystals of methylpentacarbonylmanganese (0·03 g, 69%) identified by i.r. and ^{1}H n.m.r. spectroscopy. A similar reaction occurred with the iodo-complex.

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