Synthesis of Manganese(I) Carbene Complexes

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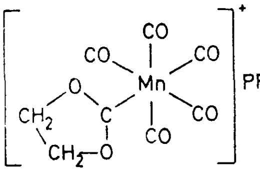
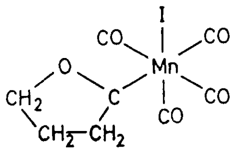
Summary Formation of the carbene complexes $[Mn(\overline{COCH_2CH_2O})(CO)_5]PF_6$, *cis*-$[MnCl(\overline{COCH_2CH_2O})(CO)_4]$, *fac*-$[MnCl(PPh_3)(\overline{COCH_2CH_2O})(CO)_3]$, and *cis*-$[MnI(\overline{COCH_2CH_2CH_2})(CO)_4]$ is described; an *X*-ray crystallographic study confirms the identity of the second complex.

Fischer and co-workers[1] established that certain carbenes can be stabilised by co-ordination to low valent metal species, and there has been a growing interest in this field.[2–6] We report a synthesis of manganese(I) carbene complexes.

Reaction of $ClCH_2CH_2OCOCl$ with $[Mn(CO)_5]^-$ in tetrahydrofuran afforded pale yellow needles of an acyl complex $Mn(COOCH_2CH_2Cl)(CO)_5$ (I), m.p. 71—73° [ν_{max}(CO) 2129m, 2036vs, 2015s and ν_{max}(acyl), 1659m; ^1H n.m.r. triplet resonances at τ 6·02 and 6·92]; also prepared from $[Mn(CO)_6]BF_4$ with 2-chloroethanol in the presence of base.



(II)



(VI)

Treatment of (I) with $AgPF_6$ led to an intramolecular cyclisation reaction giving a cationic carbene complex (II), white needles m.p. 163—166° [ν_{max} 2156w, 2106w, 2069vs; ^1H n.m.r. singlet resonance at τ 4·90]. In order to obtain neutral carbene complexes from (II) the reaction with halide anions was examined, however, the reaction proved to be solvent dependent, and only in methanol did the required attack on manganese become more important than a competitive ring opening reaction of the carbene. In methanol, lithium chloride reacted with (II) to give yellow needles of (III) *cis*-$[MnCl(\overline{COCH_2CH_2O})(CO)_4]$ m.p. 120—125° (dec.) [ν_{max} 2107m, 2025vs, 1967s; ^1H n.m.r. singlet resonance at τ 5·02].

The presence of the co-ordinated carbene in (III) was confirmed by an *X*-ray crystallographic study (Figure). Crystal data: orthorhombic, with a = 17·44, b = 11·24, and c = 10·47 Å; space group *Pbca*, D_m = 1·75, D_c = 1·73 for Z = 8; R = 0·083 for 539 independent reflections. The manganese atom is in a slightly distorted octahedral environment (angles at Mn 87—93°) with the carbene and chlorine ligands *cis* to one another. The angle (49°) between the mean plane for C(5)O(5)O(6) and that encompassing Mn, C(5), C(4), C(2) and C(1) is distinctly different from the planar arrangement found[7] in $[Mn_2\{C(OMe)Ph\}(CO)_9]$, but is similar to the values reported[8,9] for a number of chromium carbene complexes.

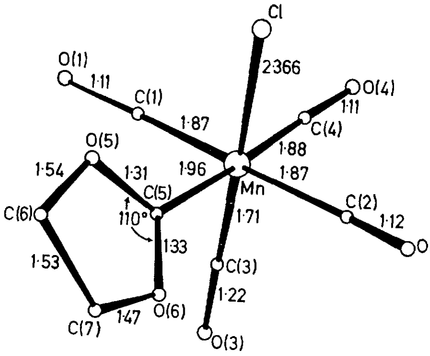


Figure. *Molecular structure of cis*-$[MnCl(\overline{COCH_2CH_2O})(CO)_4]$. *Mean e.s.d's: carbonyl fragments.* σ (Mn–C) = 0·01 Å, σ (C–O) = 0·02 Å; ring, σ (C–O) = 0·03 Å, σ (C–C) = 0·04 Å.

Treatment of (III) with triphenylphosphine afforded (IV) *fac*-$[MnCl(CO)_3(PPh_3)(\overline{COCH_2CH_2O})]$ yellow needles, m.p. 143—145° [ν_{max} 2036s, 1967s, and 1923s, ^1H n.m.r. resonance at τ 5·8].

Reaction of $[Mn(CO)_5]^-$ with 4-chlorobutyryl chloride gave (V) $[Mn(COCH_2CH_2CH_2Cl)(CO)_5]$, m.p. 70—72°; contrasting with the previous report[5,10] that the only product of this reaction is $[Mn_2(\overline{COCH_2CH_2CH_2})(CO)_9]$. Reaction of (V) with lithium iodide in tetrahydrofuran afforded orange needles of the neutral complex (VI), m.p. 57—58°. This reaction undoubtedly involves initial formation of the anionic species $[MnI(COCH_2CH_2CH_2Cl)(CO)_4]^-$, which extrudes chloride anion with concomitant intramolecular cyclisation to form the cyclic carbene complex. In agreement with this idea, reaction of (V) with $[Mn(CO)_5]^-$ led to the slow formation of the known[5,10] binuclear carbene complex $[Mn_2(\overline{COCH_2CH_2CH_2})(CO)_9]$. Attempts to cleave the metal-metal bond in the binuclear complex with halogens did not lead to compounds of the type $[MnX(\overline{COCH_2CH_2CH_2})(CO)_4]$. A similar difficulty was observed[11] in attempted cleavage with sodium amalgam of $[Mn_2\{C(OMe)Me\}(CO)_9]$, which seems to underline the importance of the synthetic approach outlined in this paper.

Preliminary studies suggest that this synthesis can be extended to other systems, for example, *cis*-[ReCl-

$(\overline{\text{COCH}_2\text{CH}_2\text{O}})(\text{CO})_4]$, m.p. 151—156° (dec.) has been prepared.

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