Journal of Organometallic Chemistry, 297 (1985) C1—C4
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE SYNTHESIS AND REACTIVITY OF μ(1,4)-BUTANEDIYLBIS-(MANGANESE PENTACARBONYL)

SELWYN F. MAPOLIE, JOHN R. MOSS* and LOUISE G. SCOTT**
Department of Inorganic Chemistry, University of Cape Town, Rondebosch 7700 (South Africa)

(Received August 29th, 1985)

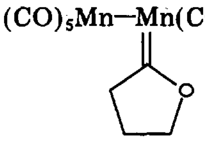
Summary

The synthesis of μ(1,4)-butanediylbis(manganese pentacarbonyl) and its reactions with a number of nucleophilic and electrophilic reagents are described.

$\mu(\alpha,\omega)$-Alkanediyl complexes (also known as polymethylene bridged complexes) are binuclear compounds in which the metal atoms are bridged by an alkyl chain via the latter's two terminal carbons [1]. These complexes can be represented by the general formula $LxM(CH_2)_nM^1Ly$ ($n \geq 2$).

Recently considerable attention has been focused on $\mu(\alpha,\omega)$-alkanediyl complexes because of their possible rôle in catalytic processes. In the Fischer—Tropsch reaction [2] for example it has been suggested that μ-polymethylene bridged complexes could be models for hydrocarbon fragments bound to a catalytic metal surface. These complexes could also act as models for chain extension in polymerization catalysis.

The binuclear iron complexes, $[CpFe(CO)_2]_2\{\mu\text{-}(CH_2)_n\}$ (n = 3—12; Cp = η-C_5H_5) are well known [3], and constitute the most extensive series of μ-alkanediyl complexes. We are at present investigating their reactivity [4]. The iron complexes can be prepared by the reaction of $CpFe(CO)_2Na$ with the appropriate α,ω-dihaloalkanes, $X(CH_2)_nX$, (X = Br or I; n = 3—12). Attempts to prepare related polymethylene bridged complexes of manganese pentacarbonyl using an analogous method have failed; these attempts resulted only in the formation of a cyclic carbene complex such as $(CO)_5Mn{-}Mn(CO)_4$ [5].



$(CO)_5Mn{-}Mn(CO)_4{=}\overline{C(CH_2)_3O}$

---

*To whom correspondence should be addressed.

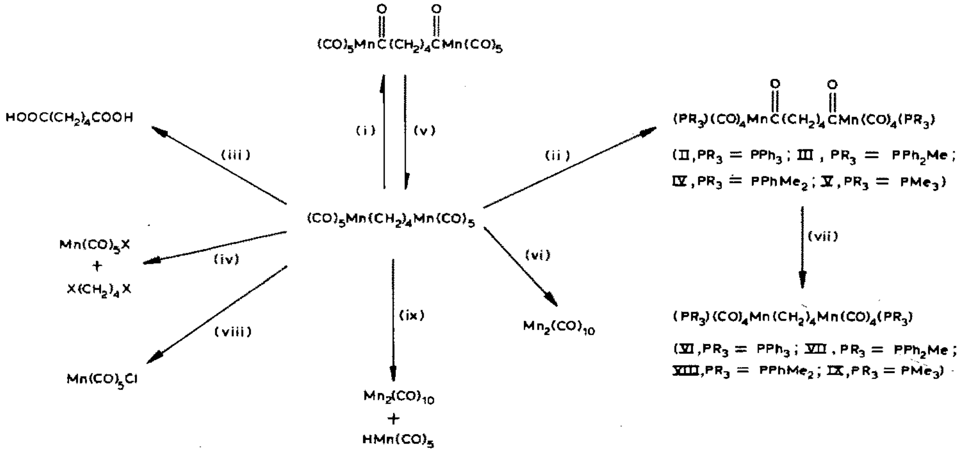
**Present address: University Chemical Laboratory, University of Cambridge, Lensfield Road, Cambridge (Great Britain).

0022-328X/85/$03.30

Until now the only known alkanediyl bridged manganese complex has been the $\mu(1,2)$-ethanediylmanganese species, $[Mn(CO)_5]_2\{\mu\text{-}(CH_2)_2\}$, which was prepared by the reaction of $[(CO)_5Mn(C_2H_4)]^+$ with $[Mn(CO)_5]^-$ [6]. We now report the synthesis and reactions of the new $\mu(\alpha,\omega)$-alkanediyl complex of manganese, $(CO)_5Mn(CH_2)_4Mn(CO)_5$ (I), which was prepared by the following route:

$$2Mn(CO)_5^- + ClCO(CH_2)_4COCl \xrightarrow[\text{r.t.}]{\text{THF}} (CO)_5MnCO(CH_2)_4COMn(CO)_5 + 2Cl^-$$

The diacyl species $(CO)_5MnCO(CH_2)_4COMn(CO)_5$ [7] is decarbonylated by refluxing in hexane for 15 min. This affords I as a white microcrystalline solid, which is stable in the atmosphere at room temperature for at least several months. I has been fully characterised* by IR, ^1H NMR and mass spectroscopy (IR: (ν(CO) ($CHCl_3$), 2104w, 2007s, 1980sh cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.70 (4H, m), 1.09 (4H, m); mass spectrum, $M^+ = 446$, followed by loss of ten CO groups). The stability of the compound is remarkable in comparison with mononuclear alkyl complexes of manganese pentacarbonyl which contain β-hydrogens. Ethylmanganese pentacarbonyl for example is reported to decompose slowly even when kept in the dark, in vacuo and at −10°C [8].



SCHEME 1. Reagents: (i) CO, 1 atm r.t.; (ii) PR_3 (PPh_3, PPh_2Me, $PPhMe_2$, PMe_3), THF, 1 h, r.t.; (iii) X_2 (Br and I), THF, 1 h, r.t.; (iv) X_2 (Br and I), CH_2Cl_2, 1 h, r.t.; (v) reflux hexane, 15 min; (vi) reflux in toluene, 30 min; (vii) reflux in hexane, 1 h; (viii) dry HCl gas in CH_2Cl_2; (ix) H_2, 63 atm, in CH_2Cl_2, 3 h.

The reactions of compound I with a number of nucleophilic and electrophilic reagents have been investigated. Some of these reactions are outlined in Scheme 1. Compound I was found to react with CO to yield $(CO)_5MnCO(CH_2)_4COMn(CO)_5$. It also reacts with tertiary phosphines (PPh_3, PPh_2Me, $PPhMe_2$, PMe_3) in THF, under mild conditions (25°C, 30—40 min) to yield phosphine-substituted diacyl products; for example reaction with PPh_3 in a 1/2 molar ratio gives $(CO)_4(PPh_3)MnCO(CH_2)_4COMn(PPh_3)(CO)_4$ (II) (IR: ν(CO) ($CHCl_3$) 2067m,

---

*Satisfactory microanalyses were obtained for all new compounds.

1994s, 1962vs, 1604mbr cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.38 (30H, s) C_6H_5, 2.66 (4H, s br) CH_2CO, 1.24 (2H, s br) and 0.88 (2H, s br) CH_2CH_2). Similarly, the reactions of PPh_2Me, $PPhMe_2$ and PMe_3 give rise to analogous diacyl products (III—V). The IR spectra of the diacyl species (II—V) show four bands in the ν(CO) region. This suggests that the molecules have C_s local symmetry and hence we have the *cis* configurations of ligands around both Mn atoms, i.e. a *cis,cis*-configuration. The isolation of *cis*- rather than *trans*-isomers, is analogous to the results obtained in a study of methylmanganese pentacarbonyl with similar ligands [9]. Thermal decarbonylation of the phosphine diacyl species (II—V) gave disubstituted phosphinebutanediyl complexes (VI—IX); again only *cis,cis*-isomers were obtained.

The reaction of I with halogens, X_2 (X = Br and I) was also investigated. In THF as solvent, the reaction yields adipic acid, $HOOC(CH_2)_4COOH$ and an unidentified inorganic product, but in CH_2Cl_2 it gives $Mn(CO)_5X$ and $X(CH_2)_4X$ as expected. The isolation of adipic acid, can be accounted for by the fact that THF is a good coordinating solvent, and this promotes initial CO insertion to form a THF adduct, compound X.

$$\mathrm{(CO)_5Mn(CH_2)_4Mn(CO)_5 \xrightarrow[r.t.]{THF} \underset{(X)}{(THF)(CO)_4MnCO(CH_2)_4COMn(CO)_4(THF)} \xrightarrow{X_2}}$$

$$\mathrm{XOC(CH_2)_4COX + unidentified\ inorganic\ product}$$

$$\mathrm{\xrightarrow{hydrolysis\ during\ work\text{-}up} HOOC(CH_2)_4COOH}$$

It is thought that possibly the THF-adduct, compound X, undergoes Mn—C bond cleavage in the presence of X_2, yielding the corresponding acid dihalide. This is then hydrolyzed during the work-up to give adipic acid.

The reaction of I with HCl yields $Mn(CO)_5Cl$, while reaction with H_2 gives $Mn_2(CO)_{10}$ as the major product. The formation of $HMn(CO)_5$ was also detected in the latter reaction.

From the results obtained, it is clear that compound I is highly reactive under mild conditions, yielding stable products. The reactions of I are analogous to those of mononuclear alkyl complexes of manganese pentacarbonyl with similar reagents.

We are currently investigating the synthesis of other alkanediyl complexes containing other metals and various polymethylene chain lengths. The aim is to compare the chemistry of these novel binuclear complexes with that of mononuclear complexes and to elucidate their importance as models of intermediates in catalytic reactions.

Acknowledgements. The authors thank the University of Cape Town Research Committee and the C.S.I.R. for financial assistance.

References

1 J.R. Moss and L.G. Scott, Coord. Chem. Rev., 60 (1984) 171.
2 W.A. Hermann, Angew. Chem. Int. Ed. Engl., 21 (1982) 117.
3 (a) R.B. King, Inorg. Chem., 2 (1963) 531; (b) J.R. Moss, L.G. Scott, M.E. Brown and K.J. Hindson, J. Organomet. Chem., 282 (1985) 255; (c) L. Pope, P. Sommerville, M. Laing, K.J. Hindson and J.R. Moss, J. Organomet. Chem., 112 (1976) 309.
4 J.R. Moss and L.G. Scott, unpublished results.
5 (a) R.B. King, J. Am. Chem. Soc., 85 (1963) 1922; (b) C.P. Casey, J. Chem. Soc. Chem. Commun., (1970) 1220.
6 K. Raab, U. Nagel and W. Beck, Z. Naturforsch. B, 38 (1983) 1466.
7 (a) C. Kraihanzel and L.G. Herman, J. Organomet. Chem., 15 (1968) 397; (b) A.N. Nesmeyanov, K.N. Anisimov and N.E. Kolobova, Dokl. Akad. Nauk SSSR, Bull. Div. of Chem. Science, (1963) 1225.
8 M.L.H. Green and P.L.I. Nagy, J. Organomet. Chem., 1 (1963) 58.
9 C.S. Kraihanzel and P.K. Maples, Inorg. Chem., 7 (1968) 1806.