Journal of Organometallic Chemistry, 236 (1982) 221—227
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

HALOALKYL COMPLEXES OF THE TRANSITION METALS

II*. SOME NEW CHLOROMETHYL AND METHOXYMETHYL COMPLEXES OF MANGANESE, RHENIUM AND RUTHENIUM

JOHN R. MOSS * and SIMON PELLING **

Department of Inorganic Chemistry, University of Cape Town, Rondebosch 7700 (South Africa)

(Received April 28th, 1982)

Summary

The reactions of Na[$Mn(CO)_5$] or Na[$Mn(CO)_4(PPh_3)$] with CH_2ClI yield the new chloromethyl complexes $Mn(CO)_5CH_2Cl$ and $Mn(CO)_4(PPh_3)CH_2Cl$. Reaction of Na[$Re(CO)_5$] or Na[$CpRu(CO)_2$] with $ClCH_2OMe$ yields $Re(CO)_5$-CH_2Cl and $CpRu(CO)_2CH_2Cl$ respectively, in addition to the corresponding methoxymethyl complexes ($Cp = \eta^5$-C_5H_5). Reaction of $CpRu(CO)_2CH_2OMe$ with HCl yields the corresponding chloromethyl complex.

Introduction

Whereas many halomethyl complexes of the main group metals are known and have been found to be important reagents in synthetic chemistry [2—4], relatively few such complexes of the transition metals have been synthesized and little is known of their chemistry. Monohalomethyl complexes have been reported for the following transition metals: Mo and W [5,6], Fe [5—7], Os [8], Rh [9,10], Ir [11] and Pt [12—15]. Such complexes may be precursors for some important classes of compounds, for example: complexes with bridging or terminal methylene ligands and complexes containing the group M—CH_2Nu (where Nu is a nucleophile). Included in the latter class of compound would be hydroxymethyl complexes. Thus complexes derived from halomethyl complexes may serve as useful models for intermediates in catalytic reactions [16,17]. We now report in detail on the synthesis and characterization

---

[*] For Part I: see reference 1.

[**] Present address: Research School of Chemistry, Australian National University, P.O. Box 4, Canberra (Australia).

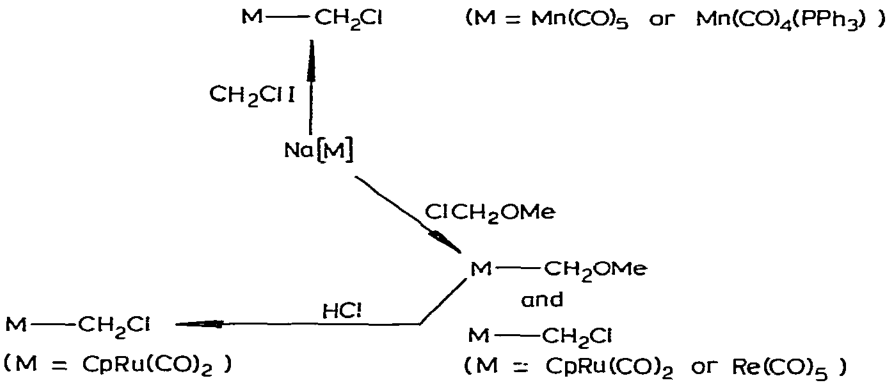
0022-328X/82/0000—0000/$02.75

of some new chloromethyl and methoxymethyl complexes. In a later paper we will describe the reactions of some chloromethyl complexes with nucleophiles. We have already reported briefly on some of these complexes [18].

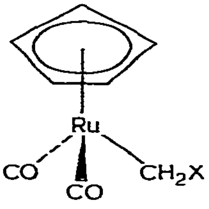
Results and discussion

A number of methoxymethyl complexes of the transition metals have been synthesized by the reaction of the appropriate metal carbonyl anion with chloromethyl methyl ether; subsequent reaction of the methoxymethyl complexes with halogen acids have led to haloalkyl complexes [5]. We have now investigated the reaction of Na[CpRu(CO)$_2$] with ClCH$_2$OMe and find that the main product of this reaction is the methoxymethyl complex CpRu(CO)$_2$CH$_2$-OMe (II), which was isolated as a brown oil. The slightly impure product was contaminated by an unidentified colourless oil which could not be completely separated from II. Traces of CpRu(CO)$_2$CH$_2$Cl (I) were also formed in this reaction as identified by IR spectroscopy. Complex I was also obtained by the reaction of II with HCl gas (see Scheme 1)..

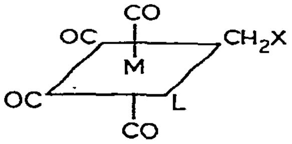
SCHEME 1



The IR spectrum of II in cyclohexane solution showed 4 ν(CO) bands (see Table 1). This, we suggest is due to the presence of rotational isomers in solution as a result of restricted rotation about the Ru—CH$_2$OMe bond. We also observe similar behaviour for the complex CpFe(CO)$_2$CH$_2$OMe. Only 2 ν(CO) bands have been previously reported in the IR spectrum of the iron complex,



(I : X = Cl ;
II : X = OCH$_3$)



(III : M = Re , X = Cl , L = CO ;
IV : M = Re , X = OCH$_3$, L = CO ;
V : M = Mn , X = Cl , L = CO ;
VI : M = Mn , X = Cl , L = PPh$_3$)

TABLE 1

IR AND NMR DATA FOR CHLOROMETHYL AND METHOXYMETHYL COMPLEXES

Compound	No.	ν(CO) (cm^{-1}) [a]				^{1}H NMR (δ ppm) [b]
$CpRu(CO)_2CH_2Cl$	I	2035s	1978s [c]			4.39 (s, 2H) 5.37 (s, 5H)
$CpRu(CO)_2CH_2OMe$	II	2026s	2017vs	1965s	1956vs	3.23 (s, 3H) 4.97 (s, 2H) 5.31 (s, 5H)
$Re(CO)_5CH_2Cl$	III	2063vw	2044vw	2023s	1994m	3.59 (s)
$Re(CO)_5CH_2OMe$	IV	2014s	1986m			3.28 (s, 3H) 4.05 (s, 2H)
$Mn(CO)_5CH_2Cl$	V	2118w	2057w	2022vs	2000s	3.52 (s) [d]
$Mn(CO)_4(PPh_3)CH_2Cl$	VI	2069m	1999s	1979vs	1950vs [e]	3.25 {d, 2H; ^3J(PH) 5.25 Hz} 7.45 (m, 15H)
$CpFe(CO)_2CH_2OMe$		2016m	2006s	1961m	1949s	3.26 (s, 2H) 4.81 (s, 5H) 4.87 (s, 2H)

[a] Cyclohexane solution unless otherwise stated; s strong, m medium, w weak. [b] $CDCl_3$ solution unless otherwise stated; s singlet, d doublet, m multiplet. [c] n-Hexane solution. [d] CCl_4 solution. [e] CH_2Cl_2 solution.

presumably as a result of the IR spectrum being recorded as a neat oil which resulted in the broadening of the bands [5]. Rotational isomers have previously been postulated to account for the IR spectra of complexes $CpFe(CO)_2CH_2R$ (R = phenyl, naphthyl or $SiMe_3$) [19].

Reaction of $Na[Re(CO)_5]$ with chloromethyl methyl ether gave a mixture of $Re(CO)_5CH_2Cl$ (III) and $Re(CO)_5CH_2OMe$ (IV) which were separated by fractional crystallisation. Complexes III and IV have been briefly mentioned previously [20] but their full characterisation has not been reported. We obtained III as a white crystalline solid and IV as a colourless oil. These complexes showed large differences in their solubilities in hexane. Although chloromethyl methyl ether has previously been found to give methoxymethyl complexes in anion reactions, we find that both methoxymethyl- and chloromethyl-metal complexes can be products of such reactions.

King and Braitsch [6] reported that several halomethyl metal complexes could be prepared by the reaction of a metal carbonyl anion with dihalomethanes. Thus complexes $CpM(CO)_3CH_2Cl$ (M = Mo or W) were prepared in good yield from $Na[CpM(CO)_3]$ and CH_2ClI. The reaction of $Na[Mn(CO)_5]$ with CH_2ClI however, was reported to give $Mn_2(CO)_{10}$ instead of the expected product $Mn(CO)_5CH_2Cl$ (V) [6]. Other attempts to prepare V have been made by thermal and photochemical decompositions of $Mn(CO)_5COCH_2Cl$ however, these attempts were not successful [21]. V had previously been briefly mentioned along with the rhenium analogue but not fully characterised [20]. We find that the reaction of $Na[Mn(CO)_5]$ with CH_2ClI at —20°C gives V as very pale yellow prisms in nearly 50% yield; V is an air-stable, volatile, crystalline solid which is soluble in most common organic solvents. In contrast, we did not isolate any of the compound $Re(CO)_5CH_2Cl$ from the reaction of $Na[Re(CO)_5]$ and CH_2ClI. We have however synthesized the complex *cis*-$[Mn(CO)_4(PPh_3)CH_2Cl]$ (VI) by the reaction of $Na[Mn(CO)_4(PPh_3)]$ with CH_2ClI.

The mass spectra of the complexes $M—CH_2X$ (where M = $CpFe(CO)_2$, $CpRu(CO)_2$, $Mn(CO)_5$, $Re(CO)_5$; X = Cl or OMe) and of $CpMo(CO)_3CH_2Cl$ have been determined as part of their characterization. For the methoxymethyl complexes, parent ions $[M]^+$ were observed for $Re(CO)_5CH_2OMe$ and $CpRu(CO)_2CH_2OMe$ whereas the highest m/e ion for $CpFe(CO)_2CH_2OMe$ corresponded to $[M - CO]^+$ and that for $Mn(CO)_5CH_2OMe$ was $[M - H_2O]^+$. A characteristic peak at m/e 45 which may be assigned to $[C_2H_5O]^+$ is observed in the mass spectra of the $M—CH_2OMe$ complexes. For the chloromethyl complexes, parent ions were observed for all the complexes investigated except $CpMo(CO)_3CH_2Cl$ where $[M - CO]^+$ was seen. There was competitive loss of CO and CH_2Cl from the parent ion (Mn or Re complexes) or from $[M - CO]^+$ (Fe or Ru). Three interesting fragmentation patterns were observed for the $M—CH_2Cl$ group viz. loss of Cl to give fragments of the type $[M(CO)_nCH_2]^+$ (M = Mn or Re), loss of HCl to give fragments of the type $[MCH]^+$ (M = Mn, Fe or Ru) and α-transfer of Cl to the metal to give $[MCl]^+$ (for Mn and Fe). Further evidence for α-transfer of Cl is found in some reactions of $M—CH_2Cl$ complexes which result in M—Cl complexes [18] and this process is common for main group metal haloalkyl compounds which behave as useful sources of carbenes [2].

Experimental

^1H NMR spectra were recorded on a Varian XL 100 instrument using tetramethyl silane as internal reference standard. IR spectra were recorded on a Perkin—Elmer 180 spectrophotometer. Mass spectra were recorded on a VG Micromass 16F spectrometer operating at 70 eV ionizing voltage and using the direct probe with source temperature of about 80° C.

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. All reactions were carried out under an atmosphere of nitrogen using Schlenk tube techniques. Tetrahydrofuran (THF) and hexane were distilled from lithium aluminium hydride under nitrogen. The following complexes were prepared by published procedures $[CpRu(CO)_2]_2$ [22], $Mn_2(CO)_8(PPh_3)_2$ [23], $CpFe(CO)_2CH_2X$ (X = Cl or OMe) [5], $Mn(CO)_5CH_2OMe$ [24] and $CpMo(CO)_3CH_2Cl$ [5,6]. Column chromatography was carried out using Merck silica gel (30—70 mesh). Microanalyses were performed by the microanalytical laboratories at the University of Cape Town or F. and P. Pascher, Bonn, Germany.

Preparation of $CpRu(CO)_2CH_2Cl$ (I)

Dry HCl gas was bubbled through a hexane solution of $CpRu(CO)_2CH_2OMe$ (II) prepared (as below) from $[CpRu(CO)_2]_2$ (1.40 mmol) for 7 min. The resulting cloudy yellow solution was filtered and cooled to —78° C at which temperature I crystallized. The product was recrystallized from hexane at —78° C to give I as sticky yellow needles (0.12 g, 15%) (Found: C, 35.70; H, 2.65; Cl, 12.54. $C_8H_7ClO_2Ru$ calcd.: C, 35.37; H, 2.60; Cl, 13.05%).

Preparation of $CpRu(CO)_2CH_2OMe$ (II)

A dark brown solution of $Na[CpRu(CO)_2]$ (prepared by stirring a THF solution of $[CpRu(CO)_2]_2$ (1.40 mmol) with sodium amalgam) was added dropwise with stirring to a solution of $ClCH_2OMe$ (8.10 mmol) in THF (5 ml) at —78° C. The mixture was allowed to warm to room temperature and stirred for 3 h. The solvent was removed and the residue extracted with hexane (4×20 ml), filtered and the hexane removed under reduced pressure to give the product as a red-brown oil (crude yield >90%). The product was further purified by molecular distillation using a modified Hickman still, however it could not be completely separated from an unidentified colourless oil. (Found: C, 43.80; H, 4.65. $C_9H_{10}O_3Ru$ calcd.: C, 40.45; H, 3.77%); a parent ion was observed in the mass spectrum with the expected isotope pattern. An IR spectrum of the crude product showed the presence of traces of another compound with ν(CO) bands in identical positions to those shown by I.

Reaction of $Na[Re(CO)_5]$ with chloromethyl methyl ether

A reddish solution of $Na[Re(CO)_5]$ (prepared by stirring a solution of $Re_2(CO)_{10}$ (2.35 mmol) in THF with sodium amalgam) was added dropwise with stirring to a solution of $ClCH_2OMe$ (13.40 mmol) in THF (5 ml) at —78°C. The reaction mixture was allowed to warm up to room temperature and stirred for 2 h. The solvent was removed and the residue extracted with hexane (50 ml) to give a yellow oily solid. This product was sublimed (40°C/0.5 mmHg) onto a cold (0°C) probe. The sublimate was dissolved in hexane and cooled to —78°C when $Re(CO)_5CH_2Cl$ (III) precipitated as a white crystalline solid (0.33 g, 20%), m.p. 62—65°C. (Found: C, 19.18; H, 0.58; Cl, 9.51. $C_6H_2ClO_5Re$ calcd.: C, 19.18; H, 0.56; Cl, 9.44%). After precipitation of III, the mother liquors were evaporated to give $Re(CO)_5CH_2OMe$ (IV) as a colourless oil (0.41 g, 24%). (Found: C, 22.95; H, 1.40. $C_7H_5O_6Re$ calcd.: C, 22.65; H, 1.35%).

Preparation of $Mn(CO)_5CH_2Cl$ (V)

A solution of $Na[Mn(CO)_5]$ (6.42 mmol) in THF (30 ml) was added dropwise with stirring to a solution of CH_2ClI (2.35 g, 13.32 mmol) in THF (3 ml) at —20°C over 10 min. The reaction mixture was stirred at 0°C for 1 h and the solvent removed under reduced pressure at this temperature. The residue was extracted with hexane (3 X 25 ml) and hexane reduced to a small volume. This solution was then chromatographed to remove $Mn_2(CO)_{10}$. Removal of the hexane eluant from the pale-yellow fraction gave the product as colourless prisms (0.70 g, 45%), m.p. 44—45°C. The product was further purified by sublimation (20°C/0.1 mmHg). Found: C, 29.34; H, 0.87; Cl, 14.15; M (cryoscopically in benzene 251). $C_6H_2ClMnO_5$ calcd.: C, 29.47; H, 0.83; Cl, 14.50; M, 244.5. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 210.05 (broad) CO, 28.15 (s) CH_2Cl ppm downfield of TMS.

Preparation of cis-[$Mn(CO)_4(PPh_3)CH_2Cl$ (VI)

A yellow-brown solution of $Na[Mn(CO)_4(PPh_3)]$ (prepared by stirring $Mn_2(CO)_8(PPh_3)_2$ (0.51 mmol) with sodium amalgam in THF) was added dropwise to a solution of CH_2ClI (3.75 mmol) in THF (5 ml) at —78°C. The reaction mixture was allowed to warm to room temperature and stirred for 1.5 h. Removal of the solvent and extraction of the residue with CH_2Cl_2 (50 ml) gave a viscous orange oil. This oil was purified by column chromatography; elution with diethyl ether (5%)/petroleum ether b.p. 60—80°C (95%) gave a yellow and an orange band. The solvent was removed from the orange band to give VI as an orange oily solid (0.29 g, 60%). This product was further purified by recrystallisation from hexane at —78°C. Found: C, 58.10; H, 4.20. $C_{23}H_{17}ClMnO_4P$ calcd.: C, 57.70; H, 3.58%.

Acknowledgements

We would like to thank the University of Cape Town, the C.S.I.R. and A.E.C.I. Ltd. for financial support.

References

1 J.R. Moss, J. Organometal. Chem., 231 (1982) 229.
2 D. Seyferth, Acc. Chem. Res., 5 (1972) 65, and references therein.
3 D. Seyferth, W. Tronich, W.E. Smith and S.P. Hopper, J. Organometal. Chem., 67 (1974) 341.
4 J. Barluenga, P.J. Campos, J.C. Garcia-Martin, M.A. Roy and G. Asensio, Synthesis, (1979) 893.
5 M.L.H. Green, M. Ishaq and R.N. Whiteley, J. Chem. Soc. (A), (1967) 1508.
6 R.B. King and D.M. Braitsch, J. Organometal. Chem., 54 (1973) 9.
7 T.C. Flood, F.J. Disanti and D.L. Miles, Inorg. Chem., 15 (1976) 1910.
8 C.E.L. Headford and W.R. Roper, J. Organometal. Chem., 198 (1980) C7.
9 R. Feser and H. Werner, Angew. Chem. Int. Ed. Engl., 19 (1980) 940.

10 H. Werner, R. Feser, W. Paul and L. Hofmann, J. Organometal. Chem., 219 (1981) C29.

11 J.A. Labinger, J.A. Osborn and N.J. Coville, Inorg. Chem., 19 (1980) 3236.

12 G.B. Young and G.M. Whitesides, J. Amer. Chem. Soc., 100 (1978) 5808.

13 C. Engelter, J.R. Moss, M.L. Niven, L.R. Nassimbeni and G. Reid, J. Organometal. Chem., 232 (1982) C78.

14 O.J. Scherer and H.J. Jungmann, J. Organometal. Chem., 208 (1981) 153.

15 N.J. Kermode, M.F. Lappert, B.W. Skelton, A.H. White and J. Holton, J. Chem. Soc. Chem. Commun., (1981) 698.

16 G. Henrici-Olivé and S. Olivé, Angew. Chem. Int. Ed. Engl., 15 (1976) 136.

17 K.H. Theopold and R.G. Bergman, J. Amer. Chem. Soc., 103 (1981) 2489 and references therein.

18 C. Botha, J.R. Moss and S. Pelling, J. Organometal. Chem., 220 (1981) C21.

19 K. Stanley and M.C. Baird, J. Amer. Chem. Soc., 97 (1975) 4292.

20 P.W. Jolly and R. Pettit, J. Amer. Chem. Soc., 88 (1966) 5044.

21 M. Dilgassa and M.D. Curtis, J. Organometal. Chem., 172 (1979) 177.

22 A.P. Humphries and S.A.R. Knox, J. Chem. Soc. Dalton, (1975) 1710.

23 A.G. Osborne and M.H.B. Stiddard, J. Chem. Soc. (1964) 634.

24 J.N. Cawse, R.A. Fiato and R.L. Pruett, J. Organometal. Chem., 172 (1979) 405.