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Preliminary communication

THE SYNTHESIS OF CHLOROMETHYL COMPLEXES OF MANGANESE, RHENIUM AND RUTHENIUM AND THE REACTIONS OF SOME CHLOROMETHYL COMPLEXES WITH TRIPHENYLPHOSPHINE

CHERYL BOTHA, JOHN R. MOSS* and SIMON PELLING

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

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Summary

The syntheses of some new chloromethyl complexes are reported. The reactions of these and other chloromethyl complexes with triphenylphosphine have been investigated. $Fe(Cp)(CO)_2CH_2Cl$ and $W(Cp)(CO)_3CH_2Cl$ yield the cationic ylide complexes $[Fe(Cp)(CO)_2CH_2PPh_3]^+$ and $[W(Cp)(CO)_3CH_2PPh_3]^+$. Some new methoxymethyl complexes are also described.

Although haloalkyl complexes of main group metals are well-known [1,2] relatively few such complexes of the transition metals have been prepared and little is known of their chemistry.

Chloromethyl complexes of the transition metals are of interest since they may be useful sources of carbene and may also be versatile starting materials for the synthesis of several types of new complexes, for example: complexes containing the CH_2 ligand, binuclear complexes containing a CH_2 group bridging two metal atoms and for a range of complexes of the type L_nMCH_2Nu (where Nu is a nucleophile). An example of this latter type of complex is L_nMCH_2OH. Complexes derived from chloromethyl complexes may thus be important intermediates in catalytic reactions.

As part of a general study on haloalkyl complexes of the transition metals, we now report the synthesis and characterization of the chloromethyl complexes $Mn(CO)_5CH_2Cl$, $Re(CO)_5CH_2Cl$ and $Ru(Cp)(CO)_2CH_2Cl$ ($Cp = \eta^5\text{-}C_5H_5$) and the reactions of these complexes and $Fe(Cp)(CO)_2CH_2Cl$, $Mo(Cp)(CO)_3CH_2Cl$ and $W(Cp)(CO)_3CH_2Cl$ with triphenylphosphine (see Scheme 1).

The complexes $Mn(CO)_5CH_2Cl$ (I) and $Re(CO)_5CH_2Cl$ (II) have been men-

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*To whom correspondence should be addressed.

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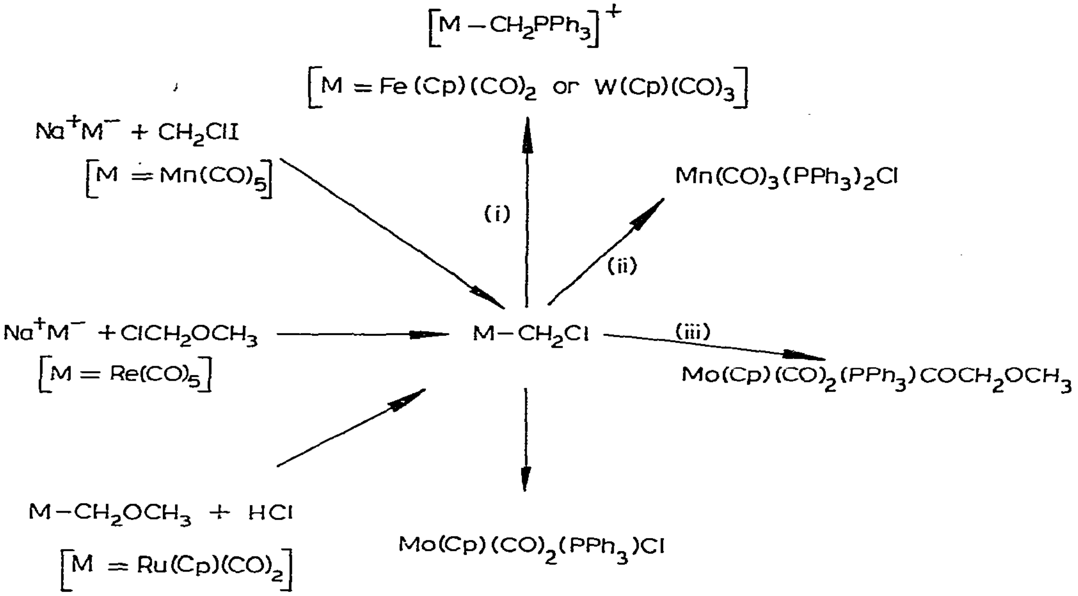

SCHEME 1. (i) PPh_3, reflux methanol 3—4 h; (ii) PPh_3, room temperature, acetonitrile 2 days; (iii) PPh_3, reflux methanol 30 minutes.

tioned previously as the products of the reaction of HCl with $M(CO)_5CH_2OCH_3$ (M = Mn or Re), but were not fully characterized [3]. Since then, several attempts to prepare I have been reported [4,5]. We find that the reaction of $Na[Mn(CO)_5]$ with CH_2ClI at –20°C yields $Mn(CO)_5CH_2Cl$ (I) as almost colourless prisms in 50% yield. (I)* is air stable, m.p. 44—45°C; ν(CO)(cyclohexane) 2118w, 2057w, 2022s, 2000s cm^{-1}; ^1H NMR (CCl_4) δ 3.52 ppm (singlet); ^{13}C NMR ($CDCl_3$) (proton decoupled) δ –210.05 (broad) (CO), δ –28.15 ppm (s), (CH_2Cl). $Re(CO)_5CH_2Cl$ (II) was obtained in 20% yield as one of the products of the reaction of $Na[Re(CO)_5]$ with chloromethyl methyl ether; the other product of this reaction, $Re(CO)_5CH_2OMe$ (III) was obtained in 24% yield. II is a white crystalline solid m.p. 62–65°C ν(CO)(cyclohexane) 2064vw, 2044vw, 2023s, 1994m cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.59 ppm (singlet). III is a colourless oil ν(CO)(hexane) 2059vw, 2016s, 1988m cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.05 (singlet, 2H), δ 3.28 ppm (singlet, 3H).

Reaction of $Na[Ru(Cp)(CO)_2]$ with chloromethylmethyl ether at –78°C yields $Ru(Cp)(CO)_2CH_2Cl$ (IV) but the main product of this reaction is $Ru(Cp)(CO)_2CH_2OCH_3$ (V). Reaction of V with HCl yields IV. IV was obtained as sticky yellow needles; ν(CO)(hexane) 2035s, 1978s cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.39 (singlet, 2H), δ 5.37 ppm (singlet, 5H). Satisfactory microanalytical data for the new compound (V) have not yet been obtained but it was characterized by the following data: ν(CO)(cyclohexane) 2026s, 2017vs, 1965s, 1956vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.23 (singlet, 3H) δ 4.97 (singlet, 2H), δ 5.31 ppm (singlet, 5H); a parent ion is observed in the mass spectrum with the expected isotope pattern. The four bands in the ν(CO) region of the

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*Satisfactory microanalytical data have been obtained for all new compounds unless otherwise stated.

infrared spectrum of V are indicative of rotational isomerism as has been observed for some related complexes [6] and as we have observed for $Fe(Cp)(CO)_2CH_2OMe$ [7].

We have investigated the reactions of a series of chloromethyl complexes with triphenylphosphine. We find that allowing $Fe(Cp)(CO)_2CH_2Cl$ to stand with PPh_3 in acetonitrile in the dark for 5 days, or refluxing $Fe(Cp)(CO)_2CH_2Cl$ with PPh_3 in methanol for 3 h yields the cation $[Fe(Cp)(CO)_2CH_2PPh_3]^+$, which was isolated as the BPh_4^- and PF_6^- salts. The PF_6^- salt VI was obtained as yellow platelets m.p. 202—205°C decomp.); $\nu(CO)(CH_2Cl_2)$ 2028s, 1976s cm^{-1}, ^1H NMR (CD_2Cl_2) δ 1.80 (doublet, $^2J(PH)$ 10.0 Hz, 2H), δ 4.93 (singlet, 5H), δ 7.66 ppm (multiplet, 15H). The BF_4^- salt of this cation has recently been reported as the product of the reaction of $[Fe(Cp)(CO)_2(THF)]^+$ with CH_2PPh_3 [8]. The reaction of $W(Cp)(CO)_3CH_2Cl$ with PPh_3 in acetonitrile for one month in the dark yields the cation $[W(Cp)(CO)_3CH_2PPh_3]^+$ isolated as yellow needles of the BPh_4^- salt VII, m.p. 192—198°C; $\nu(CO)(CH_2Cl_2)$ 2036s, 1952(sh), 1933s cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.81 (doublet, $^2J(PH)$ 15.5 Hz, 2H), δ 5.24 (singlet, 5H) δ 6.93, 7.53 ppm (multiplets, 35H). The reaction of $W(Cp)(CO)_3CH_2Cl$ with PPh_3 in refluxing methanol for 4 h yielded $[W(Cp)(CO)_3CH_2PPh_3]^+Cl^-$ (VIII) in 35% yield as yellow needles m.p. 173—180°C. Satisfactory microanalytical data have not been obtained for VIII but the compound was characterized by the following: $\nu(CO)(CH_2Cl_2)$ 2030s, 1940(sh), 1926s cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.80 (doublet, $^2J(PH)$ 16.0 Hz, 2H), δ 5.97 (singlet, 5H), δ 7.64 ppm (multiplet, 15H). In contrast, the reaction of $Mo(Cp)(CO)_3CH_2Cl$ with PPh_3 in acetonitrile in the dark for 28 days at room temperature yields $Mo(Cp)(CO)_2(PPh_3)Cl$ in 71% yield, whereas in refluxing methanol for 30 minutes, $Mo(Cp)(CO)_2(PPh_3)COCH_2OCH_3$ (X) is obtained as an orange solid m.p. 119—126°C $\nu(CO)(CH_2Cl_2)$ 1940m, 1857s, 1627w cm^{-1}; ^1H NMR (CD_2Cl_2) δ 3.34 (singlet, 3H), δ 4.24 (singlet, 2H), δ 5.02 (singlet, 5H), δ 7.46 ppm (multiplet, 15H). Reaction of $Mn(CO)_5CH_2Cl$ with PPh_3 in acetonitrile or methanol in the dark at room temperature over several days gives $Mn(CO)_3(PPh_3)_2Cl$, whereas no reaction was observed between $Re(CO)_5CH_2Cl$ and PPh_3 under similar conditions in acetonitrile. In contrast to the reaction of $Fe(Cp)(CO)_2CH_2Cl$ with PPh_3, the ruthenium analogue shows only the formation of $Ru(Cp)(CO)_2CH_2OCH_3$ on refluxing with PPh_3 in methanol for 5 days.

We are at present investigating the reactions of these and other haloalkyl-transition metal complexes with a series of nucleophiles and attempting to elucidate the mechanisms of the reactions reported above.

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