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HYDRIDE ADDITION AND RELATED REACTIONS OF CYCLO-OCTA-1,5-DIENE(TETRACARBONYL)MANGANESE(I).

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SUMMARY

The cations $[M(CO)_4(cod)]^+$ (M = Mn or Re; cod = cyclo-octa-1,5-diene) have been isolated as their tetrafluoroborate salts. The manganese compound reacts with sodium tetrahydroborate to afford initially (1,4-5-η-cyclo-octenyl)(tetracarbonyl)manganese which isomerises to (1-3-η-cyclo-octenyl)(tetracarbonyl)manganese. Both complexes react with triphenylphosphine or trimethylphosphite to give the compounds $[\textit{fac}\text{-}Mn(CO)_3(L)(1,4\text{-}5\text{-}\eta\text{-}C_8H_{13})]$ (L = Ph_3P or $(MeO)_3P$). Reaction of $[Mn(CO)_4(cod)][BF_4]$ with methoxide, azide, cyanide or iodide ions, and with 1,8-bis(dimethylamino)naphthalene are also described.

INTRODUCTION.

Transition metal complexes containing cyclo-octa-1,5-diene(cod) as a ligand are exceedingly numerous and include, for example, the species $[M(CO)_4(cod)]$ (M = Cr [1], Mo or W [1-3]), $[M(CO)_3(cod)]$ (M = Fe or Ru [4-6]), $[M(cod)(\eta^5\text{-}C_5H_5)]$ (M = Co [7-9], Rh [10,11] or Ir [12]), and $[M(cod)_2]$ (M = Ni [13], Pd [14,15] or Pt [14,16]). Many of these compounds are important precursors in organometallic synthesis, and in this context it is surprising that no cyclo-octa-1,5-diene complexes of manganese or rhenium seem to have been reported. Herein we describe the tetracarbonyl(cyclo-octa-1,5-diene)-manganese and -rhenium salts

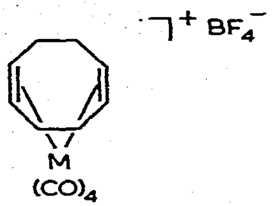
$[M(CO)_4(cod)][BF_4]$ (M = Mn or Re), and some reactions of the former with nucleophiles.

RESULTS AND DISCUSSION.

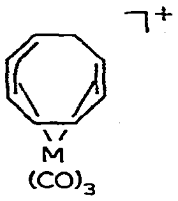
In view of the synthesis [17] of the cations $[Mn(CO)_5(C_2H_4)]^+$ and $[Re(CO)_4(C_2H_4)_2]^+$ from chloro(pentacarbonyl)-manganese or -rhenium complexes, aluminium trichloride, and ethylene under pressure, it seemed likely that the cations $[M(CO)_4(cod)]^+$ (M = Mn or Re) could be similarly prepared using cyclo-octa-1,5-diene in place of ethylene. This proved to be the case and the two cations were isolated in about 80% yield as their tetrafluoroborate salts.

The two compounds $[M(CO)_4(cod)][BF_4]$ (I; M = Mn or Re) were characterised by analysis, and by their spectroscopic properties. Thus the manganese complex showed four carbonyl stretching bands in its infrared spectrum at 2 112m, 2 056 sh, 2 039s and 2 024sh cm^{-1}, typical of a cis-$M(CO)_4L_2$ species and with the high wave numbers characteristic of a cationic carbonyl complex [18]. The ^1H n.m.r. spectrum of $[Mn(CO)_4(cod)][BF_4]$ (Ia) showed two multiplets of relative intensity 1:2 at τ 4.82 (:CH) and 7.35 (CH_2), typical of those observed in the spectra of cyclo-octa-1,5-diene complexes [6, 14].

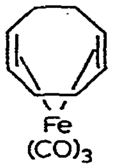
Reactions between cationic cyclic polyolefin complexes of transition metals and nucleophiles, especially hydride ion, have been extensively studied [6, 19, 20]. Previous work [6] has shown that the isomeric cationic (1-3,5-6-η-cyclo-octadienylium)-iron and -ruthenium complexes (II) behave in a different manner when treated with sodium tetrahydroborate. Whereas the iron compound yields two complexes (III) and (IVa), the ruthenium cation gives (IVb) exclusively. Complexes containing the $C_8H_{13}^+$ ligand can undergo similar proton shifts. Thus the rhodium cation (V) formed by protonation of $[Rh(cod)(\eta^5-C_5H_5)]$ with trifluoroacetic acid undergoes prototropic shifts to yield (VII) via (VI) [21]. In view of these results with iron, ruthenium and rhodium complexes it was of interest to examine the effect of hydride addition on the manganese compound (Ia).



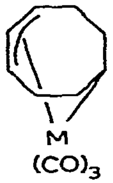
(Ia, M = Mn)
(Ib, M = Re)



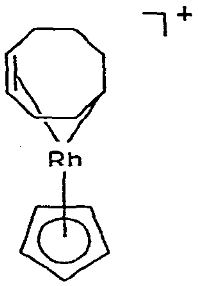
(II, M = Fe or Ru)



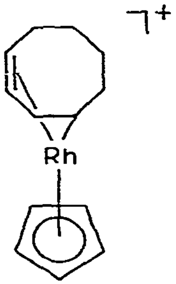
(III)



(IVa, M = Fe)
(IVb, M = Ru)



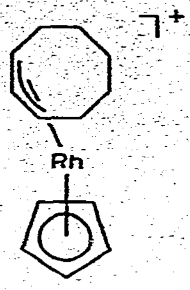
(V)



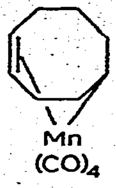
(VI)

Treatment of (Ia) with sodium tetrahydroborate in acetone at -80°C followed by warming to room temperature afforded a complex (VIII), the infrared spectrum of which showed bands at 2 061m, 1 985m, 1 969vs and 1 949s cm^{-1} indicative of a cis-tetracarbonyl species. The shift to lower frequency of these bands, compared with those in (Ia), clearly corresponded to the formation of a neutral species. Complex (VIII) proved to be very air-sensitive but it was possible to record its mass spectrum, which showed a parent ion (m/e 276) followed by successive loss of four carbonyl groups. The ^1H n.m.r. spectrum of (VIII) showed resonances at τ 5.33 (m, 1 H, :CH), 6.12 (m, 1 H, :CH) and 8.4 (m br, 11 H, $5CH_2$ + CHMn), similar to those of the C_8H_{13} ring in (V) [21] except that the :CH signals in (VIII) resolve into separate peaks. Accordingly, on the basis of these data complex (VIII) is formulated as (1,4-5-η-cyclooctenyl)(tetracarbonyl)manganese.

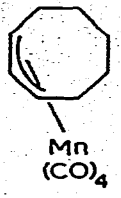
If complex (VIII), dissolved in hexane, is allowed to stand at room temperature, new carbonyl stretching infrared bands appear in the spectrum



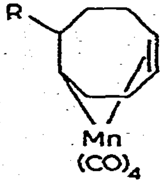
(VII)



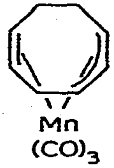
(VIII)



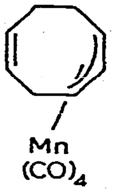
(IX)



(XIII, R = OMe)
(XIV, R = N_3)



(XV)



(XVI)

at 1 975 and 1 959 cm^{-1}. The band at 1 949 cm^{-1} in the spectrum of (VIII) is correspondingly reduced in intensity. After one to two hours the spectrum in the carbonyl region showed that (VIII) had converted into another cis-tetracarbonylmanganese species with bands at 2 061m, 1 985m, 1 969vs and 1 959s cm^{-1}. The process is accompanied by the initial appearance and subsequent disappearance of the band at 1 975 cm^{-1}.

The new product (IX) was also extremely air-sensitive but the mass spectrum (parent ion at m/e 276, followed by peaks corresponding to loss of four CO ligands) revealed that it was an isomer of (VIII). The mass spectrum also showed a peak at m/e 109 corresponding to the fragment $C_8H_{13}^+$. The ^1H n.m.r. spectrum of (IX) had resonances at τ 6.37 (m, 3 H, CH) and 8.20 (m, 10 H, CH_2), these chemical shifts being virtually identical with the η^3-CH and the CH_2 protons observed in the C_7-complex $[Mn(CO)_4(1\text{-}3\text{-}\eta\text{-}C_7H_{11})]$ [22], a complex which is also of very limited stability. On the basis of the available evidence, compound (IX) is formulated as (1-3-η-cyclo-octenyl)(tetracarbonyl)manganese.

Although isomerisation of (VIII) to (IX) could be observed by infrared spectroscopy attempts to follow the prototropic shift by n.m.r. failed because of line-broadening as a result of decomposition. Conversion of (VIII) into (IX) is similar to the transformation of (V) into (VII) and presumably occurs via a similar pathway. In this event the infrared band at 1 975 cm^{-1} initially observed in the isomerisation may be due to a species $[Mn(CO)_4(1\text{-}\sigma,3\text{-}4\text{-}\eta\text{-}C_8H_{13})]$ (X), corresponding in metal-ring bonding mode to (VI). It was observed that addition of acid to a solution of (VIII) did not effect the rate of isomerisation, indicating an intramolecular pathway involving 1,2-proton shifts.

If the reduction of (Ia) with sodium tetrahydroborate in acetone at -80°C is followed by addition of triphenylphosphine or trimethylphosphite to the mixture the yellow crystalline compounds $[\underline{fac}\text{-}Mn(CO)_3(L)(1,4\text{-}5\text{-}\eta\text{-}C_8H_{13})]$ $[L = Ph_3P$ (XI) or $(MeO)_3P$ (XII)$]$ are formed. The n.m.r. spectra of these complexes revealed a chemical shift pattern corresponding to a σ,π attachment of the C_8H_{13} ligand as in (VIII). Surprisingly compounds (XI) and (XII) were also formed by reacting pure (IX) with triphenylphosphine and trimethylphosphite, respectively. It is interesting that the $1\text{-}3\text{-}\eta\text{-}C_8H_{13}$-metal bonding mode is preferred for the $Mn(CO)_3$ group but not for the $Mn(CO)_2L$ moiety.

Reactions between the salt (Ia) and methoxide or azide ions produced the compounds (XIII) and (XIV), not obtained in a pure state due to their extreme air- and thermal-instability. They are formulated only on the basis of their mass and infrared spectra, and by analogy with earlier studies involving attack of these nucleophiles on $[Fe(CO)_3(1\text{-}3,6\text{-}7\text{-}\eta\text{-}C_8H_{11})]^+$ [23]. Reaction of (Ia) with iodide ion affords $[MnI(CO)_4]_2$. Removal of an organic group with this reagent has been previously observed [19, 21, 24].

The compound 1,8-bis(dimethylamino)naphthalene is remarkably basic, and is a very effective "proton sponge" in certain organic reactions [25]. Moreover, it has been shown [26] that 1,8-bis(dimethylamino)naphthalene promotes attack of weak nucleophiles such as $C_6F_5NH_2$ or C_6F_5SH on the salt $[Mn(CO)_3(1\text{-}6\text{-}\eta\text{-}C_7H_8)][BF_4]$ to yield compounds $[Mn(CO)_3(1\text{-}5\text{-}\eta\text{-}C_7H_8R)]$ (R = C_6F_5NH or C_6F_5S). Hence a study of the effect of bis-1,8-dimethylaminonaphthalene on compound (Ia) was of interest. In acetone at 0°C the infrared spectrum of the reaction mixture initially showed carbonyl stretching bands at 2 061m, 1 985m, 1 969vs and 1 960s cm^{-1}, indicative of the presence of an $Mn(CO)_4$ complex. However, after ten minutes these bands were replaced by others at 2 013s, 1 935s and 1 929s cm^{-1}, corresponding to an $Mn(CO)_3$ complex. Work up of the reaction mixture afforded the known [22] compound $[Mn(CO)_3(1\text{-}3,5\text{-}6\text{-}\eta\text{-}C_8H_{11})]$ (XV), identified by its ^1H n.m.r. spectrum. It is suggested, therefore, that initially bis-1,8-dimethylaminonaphthalene removes a proton from (Ia) to give (XVI) which releases CO to give (XV). As expected, carbonyl bands in the infrared assigned to the former transient species are virtually identical to those found in the spectrum of (IX). Interestingly, compound (XV) is also the final product of the reaction of (Ia) with cyanide ion. Initially at 0°C in acetone a very air sensitive complex is formed, believed to be $[Mn(CO)_4(1,5\text{-}6\text{-}\eta\text{-}C_8H_{12}\text{-}2\text{-}CN)]$ (XVII) [ν_{CO} 2 065m, 1 996m, 1 973vs and 1 961s cm^{-1}]. Although the mass spectrum of (XVII) showed a weak parent ion (<u>m/e</u> 301) the major peaks corresponded to those of (XV). On warming (XVII) in hexane it converts to (XV) presumably by release of CO and HCN. Two pathways are possible. Loss of HCN from the ring could give a tetracarbonyl complex $[Mn(CO)_4(1,5\text{-}6\text{-}\eta\text{-}C_8H_{11})]$, containing an unco-ordinated double bond which would bond to the metal, following loss of CO, to yield (XV). Alternatively, migration of the ring-attached CN group to the metal [24] could lead to loss of CO giving $[Mn(CN)(CO)_3(cod)]$. Elimination of HCN from the latter would then produce (XV). Removal of ring hydrogen in this way has precedent in the loss of trimethylgermane from the cyclo-octa-1,5-diene complex $[Ru(GeMe_3)_2(CO)_2(cod)]$ to give the tetrahydropentalenyl compound $[RuGeMe_3(CO)_2(C_8H_9)]$ [27].

EXPERIMENTAL.

All reactions were carried out under an atmosphere of dried, oxygen-free nitrogen gas. Infrared spectra were measured with a Perkin-Elmer 257 spectrophotometer. Carbonyl bands were recorded in dichloromethane or in hexane solution. ^{1}H n.m.r. spectra ($CDCl_3$ solution) were recorded on a Varian HA100 spectrometer, and mass spectra, used to establish molecular weights, were measured with an AEI MS 902 spectrometer operating at 70 eV. All solvents were freshly distilled prior to use.

Formation of the salts $[M(CO)_4(cod)][BF_4]$ (M = Mn or Re).

Pentacarbonyl(chloro)manganese (2.0 g, 8.6 mmol), aluminium trichloride (2.0 g, 15 mmol) and cyclo-octa-1,5-diene (6 cm^3) in cyclohexane (100 cm^3) were refluxed for 2 h. The mixture was cooled (0°C), distilled water (30 cm^3) added, and the solution stirred for a further 2 h. The water layer was then removed, washed with toluene (50 cm^3) and light petroleum (50 cm^3; 30-40°C b.pt.), and cooled (0°C). The mixture was acidified with HBF_4 (15 cm^3, 30% solution) and the precipitate removed and washed with diethyl ether. After drying over P_2O_5 overnight, the product was recrystallised from acetone-diethyl ether as yellow crystals of $[Mn(CO)_4(cod)][BF_4]$ (Ia) (2.64 g, 84%). Analysis: Found: C, 39.2; H, 3.6. $C_{12}H_{12}BF_4MnO_4$ calcd.: C, 39.8; H, 3.3%. For spectroscopic properties see Results and Discussion.

The rhenium compound (Ib) was similarly prepared (75% yield, magnolia crystals from acetone-diethyl ether). Analysis: Found: C, 28.6; H, 2.7. $C_{12}H_{12}BF_4O_4Re$ calcd.: C, 29.2; H, 2.4%.

Infrared spectrum: ν_{CO}(max) 2 128m, 2 060sh, 2 048s and 2 016m cm^{-1}. ^{1}H n.m.r. spectrum: τ, 4.70 (m, 4 H, :CH) and 7.30 (m, 8 H, CH_2).

Reactions of the salt $[Mn(CO)_4(cod)][BF_4]$ (Ia).

(a) $NaBH_4$. Compound (Ia) (0.5 g, 1.4 mmol) was dissolved in acetone (25 cm^3) and the solution cooled to -80°C. Sodium tetrahydroborate (0.1 g, 2.6 mmol) was added and the mixture stirred for 10 min. After warming to 0°C, solvent was removed in vacuo and the red-orange solid product (VIII) recovered from the residue by extraction with hexane (0°C). It was identified spectroscopically (see Results and Discussion).

When (VIII) is warmed in hexane for 5 min, or dissolved in this solvent for about 90 min at room temperature, it is converted into orange-red crystals of (IX) which is also very air sensitive and thermally unstable.

(b) NaOMe. The salt (Ia) (0.25 g, 0.68 mmol) in methanol (25 cm^3) was treated with NaOMe (0.05 g, 0.94 mmol) and the mixture stirred for 10 min at room temperature. Solvent was removed in vacuo and the residue extracted with hexane (10 cm^3). Filtration and removal of solvent gave yellow micro-crystals of $[Mn(CO)_4(1,5\text{-}6\text{-}\eta\text{-}C_8H_{12}\text{-}2\text{-}OMe)]$ (XIII). A mass spectrum showed a parent ion at m/e 306. Infrared spectrum: ν_{CO}(max) 2 035m, 1 973vs and 1 961s cm^{-1}.

(c) NaN_3. The salt (Ia) (0.25 g, 0.68 mmol) was treated with NaN_3 (0.125 g, 1.7 mmol) in acetone (25 cm^3) at room temperature for 1 h. Solvent was removed in vacuo and the residue extracted with hexane (10 cm^3). Evaporation of hexane gave orange micro-crystals of $[Mn(CO)_4(1,5\text{-}6\text{-}\eta\text{-}C_8H_{12}\text{-}2\text{-}N_3)]$ (XIV), identified from its mass spectrum (parent ion at m/e 317) and infrared spectrum [ν_{CO}(max) 2 059m, 1 987m, 1 969s and 1 950s cm^{-1}]. This extremely air-sensitive complex decomposed even in vacuo.

(d) Bis-1,8-dimethylaminonaphthalene. Compound (Ia) (0.25 g, 0.68 mmol) in acetone (25 cm^3) at 0°C was stirred with bis-1,8-dimethylaminonaphthalene (0.145 g, 0.68 mmol) for 30 min. Solvent was removed in vacuo and the residue extracted with hexane (25 cm^3). Chromatography on alumina gave colourless crystals of $[Mn(CO)_3(1\text{-}3,5\text{-}6\text{-}\eta\text{-}C_8H_{11})]$ (XV)[22] (0.105 g, 62%). Analysis: Found: C. 54.1; H, 4.6%; mol.wt. 246. $C_{11}H_{11}MnO_3$ calcd.: C, 53.7; H, 4.5%; mol.wt. 246. Infrared spectrum: ν_{CO}(max) 2 013s, 1 935s and 1 929s cm^{-1}. ^1H n.m.r. spectrum: τ, 5.46 (d of d, 1 H, J 9.6 Hz), 5.91 (m, 1 H), 6.05 (t, 1 H, J 9 Hz), 6.43 (m br, 1 H) and 6.9-8.1 (m br, 7 H).

(e) KCN. Compound (Ia) (0.5 g, 1.36 mmol) and KCN (0.1 g, 1.53 mmol) were stirred in acetone (50 cm^3) for 1 h at $0^\circ C$. Removal of solvent in vacuo, followed by extraction with cold hexane (20 cm^3) gave, after evaporation of solvent, orange crystals of $[Mn(CO)_4(1,5\text{-}6\text{-}\eta\text{-}C_8H_{12}\text{-}2\text{-}CN)]$ (XVII) identified by infrared (see Discussion) and mass spectrum, the latter showing a parent ion at *m/e* 301.

Reactions of complexes (VIII) and (IX) with triphenylphosphine and trimethylphosphite.

(a) The salt (Ia) (0.5 g, 1.4 mmol) in acetone (25 cm^3) at $-80^\circ C$ was treated with $NaBH_4$ (0.1 g, 2.1 mmol), stirred (10 min) and warmed to $0^\circ C$. Solvent was removed and the residue extracted with cold hexane (25 cm^3) and the hexane solution treated with Ph_3P (0.54 g, 2.0 mmol) with stirring for 2 h. Chromatography on alumina and elution with hexane gave unreacted Ph_3P (0.25 g). Elution with 10% $CHCl_3$ - 90% hexane gave yellow crystals of $[Mn(CO)_3(Ph_3P)(1,4\text{-}5\text{-}\eta\text{-}C_8H_{13})]$ (XI) (0.12 g, 19%). Analysis: Found: C, 68.2; H, 5.8. $C_{29}H_{28}MnO_3P$ calcd.: C, 68.2; H, 5.5%. Infrared spectrum: ν_{CO}(max) 1 993s, 1 923s and 1 906s cm^{-1}. ^1H n.m.r. spectrum: τ, 2.55 (m, 15 H, Ph), 6.00 (m, 1 H), 6.70 (m, 1 H) and 7.80, 8.20 and 8.65 (br m, 11 H).

The same compound (XI) was obtained by reacting triphenylphosphine with (IX), the latter being prepared (spectroscopically pure) from (VIII).

(b) The above reaction was repeated using $(MeO)_3P$ (1 cm^3) instead of Ph_3P. Chromatography on alumina gave, on eluting with CH_2Cl_2-hexane, yellow crystals of $[Mn(CO)_3\{(MeO)_3P\}(1,4\text{-}5\text{-}\eta\text{-}C_8H_{13})]$ (XII) (0.15 g, 30%). Analysis: Found: C, 45.4; H, 6.2%; mol.wt. 372. $C_{14}H_{22}MnO_6P$ calcd.: C, 45.2; H, 5.9%; mol.wt. 372. Infrared spectrum: ν_{CO}(max) 2 003s, 1 937s and 1 911s cm^{-1}. ^1H n.m.r. spectrum: τ, 5.60 (m, 1 H), 6.44 (m, 1 H), 6.61 (d, 9 H, J 11 Hz) and 7.82, 8.28 and 8.60 (m br, 11 H).

The same compound was isolated from a reaction of (IX) with $(MeO)_3P$.

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