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THE REACTION OF σ-ALLYLPENTACARBONYLMANGANESE WITH SOME STRONG PROTON ACIDS

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The protonation of metal–σ-allyl systems of iron[1], molybdenum[2] and cobalt[3] has been shown to form π-ethylenic metal derivatives. Here we describe some related reactions of σ-allylpentacarbonylmanganese (I) with acids. The products of the reaction are shown to depend on the acid used although in all cases, as would be expected, there appears to be initial formation of a π-propene complex.

RESULTS

Protonation with perchloric acid

Treatment of the σ-allyl complex (I) with anhydrous perchloric acid in benzene gives a pale yellow crystalline complex which analysis and conductivity show to have the stoicheiometry $[C_8H_6O_5Mn]ClO_4$ (II). The salt (II) is soluble in, but very rapidly decomposed by, donor solvents such as tetrahydrofuran and acetone. Aqueous solutions rapidly decompose evolving a gas. Solutions in liquid sulphur dioxide, however, are more stable and may be used for recrystallisation. The pure salt (II) is unstable to oxidation, decomposing within hours.

Treatment of the compound (II) with excess triphenylphosphine in vacuum at 80° evolves a gas which the infrared spectrum showed to be a mixture of carbon monoxide and propene. From the solid products may be isolated, in good yields, a complex which the evidence discussed below shows to be a phosphine complex of stoicheiometry $[(Ph_3P)_2Mn(CO)_4]^+ClO_4^-$. The infrared spectrum of the salt (II) is very similar to that of the π-ethylene complex $[\pi\text{-}C_2H_4Mn(CO)_5]^+BF_4^-$. On the above evidence the complex (II) is formulated as the analogous π-propene cation $[\pi\text{-MeCH=CH}_2Mn(CO)_5]^+ClO_4^-$.

The stoicheiometry of the complex $[(Ph_3P)_2Mn(CO)_4]^+ClO_4^-$ was established by analysis and conductivity measurements. A compound of the same stoicheiometry but with a slightly different infrared spectrum has also been prepared by the reaction of the π-propene complex (II) with triphenylphosphine in acetone, and a tetrafluoroborate analogue has been prepared[4] from triphenylphosphine and $[\pi\text{-}C_2H_4Mn(CO)_5]^+BF_4^-$. The differences in the infrared spectra between the two perchlorate salts suggests that there are *cis* and *trans* isomers formed. Repeated recrystallisation of both perchlorate salts from a variety of solvents showed no changes

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in their respective infrared spectra. Finally, the spectra do not themselves unambiguously indicate whether either of the phosphine products are pure or are both a mixture of isomers.

Reactions with HCl, HNO_3, H_2SO_4 and CF_3COOH

Treatment of the pure σ-allyl complex (I) with hydrogen chloride immediately gives a yellow solid which rapidly evolves propene. The yellow residue was shown by its infrared spectrum to be mainly the well-known chloride $Mn(CO)_5Cl$. Similarly, treatment of the complex (I) with concentrated nitric acid gives a yellow precipitate which evolves propene. The residue was identified by analysis and the infrared spectrum as the previously[5] described nitrate complex $Mn(CO)_5ONO_2$. With trifluoroacetic acid the trifluoroacetate, $CF_3COOMn(CO)_5$, is similarly obtained. Finally with concentrated sulphuric acid the bisulphate derivative $(CO)_5MnOSO_3H$ is formed. The evidence for the latter formulation comes from analysis, equivalent weight and molecular weight determinations and the infrared spectrum; from the equivalent weight titration the p*K* of the acid was found to be 2.6–2.7. The infrared spectra of all new compounds are reported in the experimental section.

Studies on the thermal decomposition of the complexes $Mn(CO)_5R$, where $R = CF_3COO$, NO_3, or SO_3H showed that no binuclear complexes comparable to the bridging halide complexes $(Mn(CO)_4Cl)_2$ were formed. The main products of thermal decomposition were carbon monoxide, dimanganese decacarbonyl and manganese salts. The reaction of the compound (I) with hydrofluoric acid is briefly noted in the experimental section, the compound $Mn(CO)_5F$ could not be obtained despite several attempts to prepare it.

DISCUSSION

It seems reasonable that the reaction of metal–σ-allyl complexes, $M–C_3H_5$, with acids, HA, may in those cases where A can act as a ligand to the metal, provide a convenient route to the complexes M–A.

EXPERIMENTAL

Microanalyses were carried out in the Microanalytical Laboratory, Lensfield Road, Cambridge. Preparations and purification were performed under nitrogen or in vacuum. Infrared spectra were determined as mulls in Nujol and hexachlorobutadiene and were measured using either a Perkin–Elmer 221 or an Infracord 137 spectrometer. Proton magnetic resonance spectra were determined using a Perkin–Elmer permanent magnet instrument at 40 Mc/s.

Pentacarbonyl-π-propenemanganese perchlorate

A slight excess of redistilled pentacarbonyl-σ-allylmanganese (0.67 g) in benzene (20 ml) was treated with perchloric acid in benzene. [The latter solution was prepared by treating dry silver perchlorate (0.53 g) in benzene (20 ml) with anhydrous hydrogen chloride, removing excess hydrogen chloride by pumping on the solution, and finally filtering the solution to remove the silver chloride precipitate.] The white precipitate formed was separated by filtration and dissolved in liquid sulphur dioxide from which it was reprecipitated with ether. Yield 0.723 g. The compound is readily hydrolysed by water evolving propene and it decomposes in the solid state overnight. (Found: C, 28.6; H, 2.1; Mn, 16.1. $C_8H_6ClMnO_9$ calcd.: C, 28.2; H, 1.78; Mn, 16.3%.)

The infrared spectrum was: 3080 m, 3040 w, 2980 w, 2160 s, 2070 vs, 1543 w (C=C str.), 1463 m, 1439 m, 1418 m, 1383 m, 1100 vs, 1034 s, 1014 s, 948 w, 901 m, 778 m, 719 w.

Pentacarbonylmanganese nitratomanganese

Pentacarbonyl-σ-allylmanganese (0.79 g) in light petroleum (25 ml) was treated with a slight excess of concentrated nitric acid (0.5 ml) affording a bright yellow solid. The light petroleum was removed by decantation and the residue was kept under a vacuum at 45° until no more effervescence was observed. The product was washed with ether and dried. Yield 0.7 g. (Found: C, 23.5; N, 5.31. C_5MnNO_8 calcd.: C, 23.4; N, 5.45%.)

Pentacarbonyl(trifluoroacetate)manganese

Pentacarbonyl-σ-allylmanganese (1.5 g) in ether (50 ml) was treated with anhydrous trifluoroacetic acid (1 ml). The solvent was removed leaving a yellow solid which effervesced. (The gas evolved was identified as propene from its infrared spectrum.) The residue was heated at 45° in a vacuum for 30 min and then extracted with tetrahydrofuran (10 ml). Addition of light petroleum (40 ml) to the solution forms yellow crystals which were recrystallised from light petroleum/ether, m.p. 76.5–78°. Yield 1.2 g. (Found: C, 27.0; Mn, 17.7; CO, 45.9. $C_7F_3MnO_7$ calcd.: C, 27.3; Mn, 17.8; CO, 45.4%.)

The infrared spectrum was: 2170 sh, 2070 s, 2025 s, 1711 sh, 1687 s, 1645 sh, 1589 w, 1410 m, 1189 s, 1154 s, 852 m, 794 m, 732 m.

The compound is quite stable in air. It dissolves readily in solvents such as acetone or ether but is insoluble in light petroleum. Thermal decomposition studies showed that dimanganese decacarbonyl and carbon monoxide were amongst the decomposition products. No evidence for a dimeric acetatomanganese carbonyl complex was found in the decomposition products.

Pentacarbonylbisulphatomanganese

Pentacarbonyl-σ-allylmanganese (1.0 g) in ether (10 ml) was treated with concentrated sulphuric acid (2 ml). The mixture was shaken and a yellow solid precipitated which was washed several times with ether to remove excess sulphuric acid. The yellow effervescing residue was heated under vacuum as described above, and then extracted into acetone (*ca.* 10 ml). Addition of a 1 : 1 light petroleum/ether mixture precipitated bright yellow crystals. Yield 0.6 g. (Found: C, 20.8; H, 0.5; Mn, 18.7; CO, 47.0. C_5HMnO_9S calcd.: C, 20.7; H, 0.3; Mn, 18.8; CO, 47.3%.)

The pure compound showed no melting point below 200°. Attempts to recrystallise the pure solid after a day showed that it was only partially soluble in acetone and therefore that reaction in the solid state had occurred. The compound is hygroscopic and readily soluble in water; potentiometric titration of an aqueous solution with standard base gave an equivalent weight of 315 [calculated for $(CO)_5MnSO_4H$, 292].

The infrared spectrum was: 3050 broad, 2170 sh, 2070 s, 2020 s, 1650 vw,b, 1600 vw,b, 1325 m, 1300 m, 1258 m, 1245 m, 1165 ms, 1145 ms, 1045 s, 900 m, 878 m, 770 w.

The reaction of pentacarbonyl-σ-allylmanganese with other acids

Treatment of the σ-allyl complex with glacial acetic acid, as above, gave no reaction. Orthophosphoric acid gave a yellow product, which was not further studied. Carefully dried hydrogen fluoride did not react with a light petroleum solution of the complex (I). However, hydrofluoric acid (40%) gave a bright yellow precipitate which slowly evolved propene. Ether extraction of the product left after propene evolution had ceased gave a yellow solution, from which a yellow crystalline product could be crystallised. Its infrared spectrum always showed bands assignable to both terminal carbonyl groups and O–H stretching frequencies. Qualitative analysis showed fluorine to be present in the product but consistent analyses for C, H, or Mn could not be obtained.

Reaction between pentacarbonyl-π-propenemanganese perchlorate with triphenylphosphine

Method A. The π-propene complex (II) (0.5 g) was placed in a bulb with excess triphenylphosphine (1.0 g) and the bulb was evacuated. The bulb was warmed to 85° for 2 h during which time a gas was evolved which was collected. The gaseous products were separated by fractional distillation and shown to consist of a 1 : 1.07 mixture propene/carbon monoxide. The involatile residue was dissolved in acetone, ether was added slowly and a yellow solid precipitated which was separated, dried and finally recrystallised from a sulphur dioxide/ether mixture. Yield 80%. (Found: 60.7; H, 4.5; Mn, 6.3. $C_{40}H_{30}ClMnO_8P_2$ calcd.: C, 60.8; H, 3.8; Mn, 6.96%.) Conductivity in nitromethane gave Λ 25° = 29.8 $ohm^{-1}cm^{-2}$. The proton magnetic resonance spectrum (liq. SO_2 soln.) showed a broad complex "doublet" band at $\tau = 2.37$, due to the protons of the Ph_3P groups. The infrared spectrum was: 3060 w, 2150 w, 206 m, 2005 vs; 4480 m, 1430, 1190 w, 1092 vs, 999 m, 929 w, 854 vw, 757 m, 746 s, 697 s.

Method B. A solution of the π-propene complex and excess triphenylphosphine in acetone was allowed to stand at room temperature for 6 h. The solvent was removed in vacuum and the residue was purified as described above. (Found: C, 59.8; H, 4.2%.) The infrared spectrum in the region 2200–1800 cm^{-1} was: 2145 vw, 2079 m, 2060 sh, 2005 vs, 1968 vs.

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SUMMARY

Treatment of σ-allylpentacarbonylmanganese with the acids HA gives the π-propene compound $[\pi\text{-}CH_3CH{=}CH_2Mn(CO)_5]^+A^-$ when $A^- = ClO_4^-$ and $(CO)_5MnA$, when A = Cl, NO_3, CF_3COO or SO_4H. The compound $(CO)_5MnO\text{-}SO_3H$ is a strong acid, $pK = 2.6$–2.7.

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