Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

REACTION BETWEEN METHYLPENTACARBONYLMANGANESE AND HEXAFLUORO-1,3-BUTADIENE

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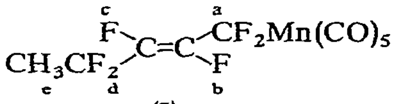
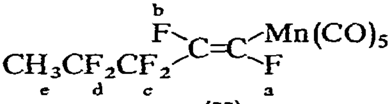
(Received December 29th, 1967)

Hydridopentacarbonylmanganese adds readily to tetrafluoroethylene on warming giving $HCF_2CF_2Mn(CO)_5$[1]. Recently we have shown[2] that reaction between the hydride and hexafluoro-1,3-butadiene at 0° affords several pentacarbonylmanganese complexes, however, those involving 1,4-addition predominate. In a parallel investigation we have studied the reaction between methylpentacarbonylmanganese and hexafluoro-1,3-butadiene. It is known[3] that methylpentacarbonylmanganese reacts with tetrafluoroethylene yielding $CH_3CF_2CF_2Mn(CO)_5$. Since reactions involving methylpentacarbonylmanganese are less facile than those involving the hydride but are promoted by ultra-violet irradiation[3], this technique was used in the present work, and in this manner two crystalline 1 : 1 adducts (I) and (II) were obtained. Sublimation and repeated crystallisation of the reaction mixture, which contained both compounds, gave pure (I) which isomerised to (II) on standing in solution.

The infrared spectra of (I) and (II) both showed four terminal carbonyl stretching bands characteristic of a pentacarbonylmanganese group to which an asymmetric fluorocarbon side-chain is attached[4]. In addition, the spectra showed bands at 1701 cm^{-1} (I) and at 1597 cm^{-1} (II), assignable to double bonds of the groups $CF{=}CF{-}CF_2{-}Mn$ and $CF_2{-}CF{=}CF{-}Mn$, respectively[2,5].



(I)



(II)

The NMR spectra of the two complexes establish the structure of the fluorocarbon ligands, including the stereochemistry around the double bonds. The ^{19}F spectrum of (I) consisted of four multiplets with relative intensities 2:2:1:1, increasing to high field. The two multiplets at 152.5 and 166.4 ppm[**] of relative intensity 1 had a large doublet coupling of 130 c/s as their principal feature, indicating a *trans*-vinylic group $-CF{=}CF-$[6-8]. The multiplet of intensity 2 at 93.3 ppm was basically a quartet with $J(H-F) = 18.8$ c/s, a coupling typical of a CH_3CF_2 group[3,9]. This was

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[**] ^{19}F chemical shifts are relative to CCl_3F (0.0 ppm) increasing to high field.

confirmed by the proton spectrum which was a triplet with splitting also 18.8 c/s. The other multiplet with intensity 2 at 59.5 ppm may be firmly assigned on the basis of its chemical shift to a CF_2 group bonded to a manganese pentacarbonyl group[10,11].

The ^{19}F spectrum of isomer (II) had four multiplets with relative intensity 1 : 2 : 2 : 1 at 93.3, 110.3, 117.5 and 153.5 ppm. The multiplets with relative intensity 1 again had a large coupling constant [J(F–F) = 129.0 c/s)]. In *trans*-$HCF_2CF_2CF{=}CFMn(CO)_5$ the coupling of the vinylic fluorine nuclei is 126.5 c/s (ref. 2), and in *trans*-$CF_2{=}CFCF{=}CFMn(CO)_5$ the corresponding coupling constant is 130 c/s (ref. 5). The quartet splitting of the resonance at 110.3 ppm in the ^{19}F spectrum of (II) and the corresponding triplet in the proton spectrum are consistent with a CH_3CF_2 group. The multiplet of intensity 2 at 117.5 ppm had doublet splittings consistent with a $CF_2CF{=}CF$ group[2].

The NMR spectra, therefore, confirm the illustrated structures for (I) and (II).

The formation of (II) from (I) clearly involves a 1,3-fluorine shift[12], and is analogous to the formation of *trans*-$HCF_2CF_2CF{=}CFMn(CO)_5$ and *trans*-Me_3Ge-$CF_2CF_2CF{=}CFMn(CO)_5$ by addition of $HMn(CO)_5$[2] and $Me_3GeMn(CO)_5$[5] to $CF_2{=}CFCF{=}CF_2$, respectively. It is interesting that conversion of (I) into (II) is stereospecific, a result consistent with an S_N2' mechanism.

EXPERIMENTAL

NMR spectra were recorded using Perkin–Elmer R 10 (^{19}F) and Varian A60 (1H) spectrometers. Carbonyl and carbon–carbon double bond stretching frequencies were measured in cyclohexane solution, using a Perkin–Elmer 257 spectrometer.

The synthesis of complexes (I) and (II)

Methylpentacarbonylmanganese (1.09 g, 5.2 mmoles), hexafluoro-1,3-butadiene (3.03 g, 18.7 mmoles) in pentane (5 ml) were sealed *in vacuo* in a Pyrex tube. The latter was irradiated (60 h) with UV light (250 watt high pressure lamp). On opening the reaction vessel, solvent was removed *in vacuo*, and the residue sublimed ($45°/10^{-3}$ mm). The yellow semi-solid sublimate was crystallised (3 ×) from pentane to give (I) (300 mg, 15.6%). [Found: C, 32.2; H, 0.9; F, 30.5; mol. wt. (benzene, Mechrolab osmometer) 379. $C_{10}H_3F_6MnO_5$ calcd.: C, 32.3; H, 0.8; F, 30.6%; mol. wt., 372.] IR data: ν_{max} 2126 m, 2065 w, 2034 s, 2013 s [ν(CO)], 1701 [ν(C=C)] cm^{-1}. The ^1H NMR spectrum had a single absorption at 8.05 τ (multiplet, $J_{ed} = 18.8$, $J_{ec} = 2.6$, $J_{eb} = 2.6$ c/s). The ^{19}F NMR spectra had absorptions at 59.5 ppm (two fluorines F_a: multiplet, $J_{ab} = 20.0$, $J_{ac} = 33.5$, $J_{ad} = 3.2$ c/s), 93.3 ppm (two fluorines F_d: multiplet, $J_{dc} = 13.5$, $J_{da} = 3.2$ c/s), 152.5 ppm (one fluorine, F_b: multiplet, $J_{bc} = 132.2$, $J_{ba} = 20.0$ c/s), 166.4 ppm (one fluorine F_c: multiplet, $J_{ca} = 33.5$, $J_{cb} = 132.2$, $J_{cd} = 13.5$ c/s).

A sample (100 mg, 2.69 mmoles) of (I) was dissolved in chloroform (5 ml). Solvent was removed *in vacuo* after standing at a temperature of 30° for 1 h. The residue was recrystallised from pentane to give (II) (60 mg, 60%) [Found: C, 32.5; H, 0.9; F, 30.4; mol. wt. (dichloromethane), 367. $C_{10}H_3F_6MnO_5$ calcd.: C, 32.3; H, 0.8; F, 30.6%; mol. wt., 372.] IR data: ν_{max} 2122 m, 2064 w, 2037 s, 2012 s [ν(CO)]; 1597 [ν(C=C)] cm^{-1}. The ^1H NMR spectrum had a single absorption at 8.27 τ (multiplet, $J_{ed} = 18.2$, $J_{ec} = 2.4$, $J_{eb} = 2.6$ c/s). The ^{19}F NMR spectrum had absorptions at 93.3 ppm (one fluorine F_a: multiplet, $J_{ab}=129.0$, $J_{ac}=25.8$, $J_{ad}=5.5$ c/s), 110.3 ppm (two fluorines F_d: multiplet, $J_{da}=5.5$, $J_{db}=5.5$ c/s), 117.5 ppm (two fluorines F_c: multiplet, $J_{ca}=25.8$, $J_{cb}=12.9$ c/s), 153.5 ppm (one fluorine F_b: multiplet, $J_{ba}=129.0$, $J_{bc}=12.9$, $J_{bd}=5.5$ c/s).

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