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Several Insertion Reactions of $Fe(C_5H_5)(dpe)H$ and $Fe(C_5H_5)(dpe)CH_3$ with Acetylenes, CS_2 and SO_2

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The compound $Fe(C_5H_5)(dpe)H$ adds to the acetylenes $RC{\equiv}CR$ ($R = CF_3$, $COOMe$) to give the products $Fe(C_5H_5)(dpe)CR{=}CHR$. For $R = CF_3$, cis addition is established by ^{19}F nmr. Addition of the iron hydride complex to CS_2 gives a new S-bonded thioformate complex $Fe(C_5H_5)(dpe)S_2CH$. The compound $Fe(C_5H_5)(dpe)CH_3$ adds SO_2 to give $Fe(C_5H_5)(dpe)SO_2CH_3$, a S-bonded sulfinate complex.

Introduction

Reported here are initial results on the addition of the Fe–H bond in $Fe(C_5H_5)(dpe)H$ to acetylenes and to CS_2, and the insertion of SO_2 into the Fe–C bond in $Fe(C_5H_5)(dpe)CH_3$.

Experimental

The organometallic starting materials, $Fe(C_5H_5)(dpe)H$ and $Fe(C_5H_5)(dpe)CH_3$ were prepared from $[Fe(C_5H_5)(dpe)(CH_3CN)]Br$ by the published procedures [1]. Tetrahydrofuran was distilled from $LiAlH_4$ before use. All reactions were carried out under nitrogen.

Infrared spectra (KBr pellet) were recorded on Beckman IR–10 and Digilab FTS-20 spectrometers. Proton nmr spectra were recorded on a Brucker WH-270 spectrometer operating in the Fourier Transform mode, with TMS, $\delta = 0$, as an internal standard; ^{19}F nmr spectra were recorded on a Varian XL-100 spectrometer operating in the Fourier Transform mode with hexafluorobenzene as internal standard. Molecular weight determinations were made using a Mechrolab Osmometer, Model 301A. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Reaction of $Fe(C_5H_5)(dpe)H$ and $CH_3OCOC{\equiv}COOCH_3$

To a solution of $Fe(C_5H_5)(dpe)H$ (0.55 g, 1.06 mmol) in tetrahydrofuran (50 ml) was added dimethyl acetylenedicarboxylate (0.23 g, ~1.6 mmol). The solution was stirred for 2 hr at room temperature. The tetrahydrofuran was removed and the residue was extracted with dichloromethane/toluene (1:1) and chromatographed on neutral alumina. A large orange band was collected, and the solvent was removed at reduced pressure. The product was crystallized from chloroform and hexane as air stable, dark red crystals (0.35 g, 50%). The compound appeared to decompose between 180° and 190 °C, and the decomposition product melted at 200–201.5 °C. *Anal*: Calcd. for $C_{37}H_{36}FeO_4P_2$: C, 67.08; H, 5.48, P, 9.35; mol. wt. 662. Found: C, 66.69; H, 5.48; P, 9.24; mol. wt. 646. *IR*: $\nu_{C=O}$ 1693s $\nu_{C=C}$ 1514 ms. *^1H nmr (C_6D_6)*: 6.8–7.8 δ (m, C_6H_5), 4.76 δ (s, H), 4.23 δ (s, C_5H_5), 3.61 δ (s, OCH_3), 2.63 δ and 2.19 δ (m, PCH_2CH_2P).

Reaction of $Fe(C_5H_5)(dpe)H$ and $CF_3C{\equiv}CCF_3$

Excess hexafluoro-2-butyne (1.0 g, 6.0 mmol) was bubbled into a solution of $Fe(C_5H_5)(dpe)H$ (0. 48 g, 0.92 mmol) in pentane. The reaction mixture was stirred for 1.5 h at room temperature. The product slowly precipitated out of solution as a red-brown powder. It was collected by filtration. The crude product was recrystallized from diethyl ether and hexane, giving air stable, red-purple crystals (0.3 g, 48%); mp, 174–177 °C. Anal: Calcd. For $C_{35}H_{30}F_6FeP_2$: C, 61.60; H, 4.43; P, 9.08; mol. wt. 682. Found: C, 61.77; H, 4.59, P, 9.19; mol. wt. 659. IR: KBr $\nu_{C=C}$ 1545w cm^{-1}. ^1H nmr (C_6D_6): 6.8–7.6 δ (m, C_6H_5), 4.84 δ (q, $J_{H-F} \simeq 10.3$ Hz, H), 4.24 δ (s, C_5H_5), 1.85–2.4 δ (m, CH_2). ^{19}F nmr ($(CD_3)_2CO$): 107.6 ppm (pseudo q, $J_{F,F} = 14$ Hz, CF_3 geminal to the iron, *trans* to H), 101.4 ppm (m, CF_3 geminal to H, *trans* to iron) (chemical shifts downfield from C_6F_6).

Reaction of $Fe(C_5H_5)(dpe)H$ and CS_2

Carbon disulfide (10 ml, excess) was added to $Fe(C_5H_5)(dpe)H$ (0.25 g, 0.48 mmol). The hydride initially dissolved, but the yellow solution rapidly became red. After standing for two hr., well formed, air stable, red-brown crystals of the product had precipitated. These were collected by filtration (0.22

g, 77%). The crystals were washed with hexane. The compound decomposes at 105 °C, and the decomposition product melts at 155 °C. *Anal.* Calcd. for $C_{32}H_{30}FeP_2S_2$: C, 64.43; H, 5.07; P, 10.38; S, 10.75; mol. wt. 597. Found: C, 63.24; H, 5.01; P, 10.25; S, 10.35; mol. wt. 645. *IR*: $\nu_{SC(S)H}$ 1240m, 985s, cm^{-1}. *^1H nmr (C_6D_6)*: 11.01 δ (s, –SC(S)*H*), 7–7.6 δ (m, C_6H_5), 4.17 δ (t, J_{P-H} = 1.1 Hz, C_5H_5), 1.32–2.0 δ (m, PCH_2CH_2P).

Reaction of Fe(C_5H_5)(dpe)CH_3 and SO_2

Sulfur dioxide was slowly bubbled through a solution of $Fe(C_5H_5)(dpe)CH_3$ (0.5 g, 0.9 mmol) in hexane (40 ml) and dichloromethane (5 ml) at –72 °C. After 10 min no color change had occurred, and so the dry ice bath was removed and the reaction mixture was allowed to slowly warm to room temperature. A rapid color change from orange to black occurred at approximately –20 °C. The solvent was removed on a rotary evaporator. A crude yellow product was collected and washed with hexane. The yellow product was then chromatographed on a short, neutral alumina column (1.5 X 6.0 cm) with acetone/methanol (9:1) as eluent. The single yellow band was collected. The solvent was removed and the product was obtained from the residue as small orange crystals, and recrystallized from dichloromethane/diethyl ether (0.2 g, 35%) decomposes 158–159 °C. *Anal*: Calcd. for $C_{32}H_{32}FeO_2P_2S$. C, 64.22, H, 5.39; P, 10.35, mol. wt. 698. Found: C, 63.95; H, 5.48; P, 9.51; mol. wt. 600. *IR*: KBr ν_{SO} 1142m, 1020s cm^{-1}. ν_{S-CH_3} 930 w cm^{-1}. *^1H nmr*: C_6D_6 6.7–8.1 δ (m, C_6H_5), 4.31 δ (t, J_{P-H} unresolved, C_5H_5), 1.7–2.0 δ (m, PCH_2CH_2P), 2.17 δ (s, $S(O)_2CH_3$).

Results and Discussion

The addition of the Fe–H unit in $Fe(C_5H_5)(dpe)H$ to the acetylenes RC≡CR (R = CF_3, COOMe) is facile, giving a single product in moderate yield:

$$Fe(C_5H_5)(dpe)H + RC{\equiv}CR \rightarrow Fe(C_5H_5)(dpe)CR{=}CHR$$

(R = CF_3, COOMe)

Both compounds are air stable, red crystalline compounds.

In the case of the product obtained from $CF_3C{\equiv}CCF_3$ the stereochemistry of addition is *cis*. This was ascertained from the J_{F-F} coupling constant in this compound, 14 Hz. It is found that *cis* CF_3 groups have coupling constants near to this value [2, 3] while *trans* CF_3 groups have J_{F-F} values of about 2 Hz [4, 5]. The stereochemistry of the single isomer from MeOCOC≡CCOOMe could not be determined.

A related compound, *cis*-$Fe(C_5H_5)(CO)_2C(CF_3){=}CHCF_3$, was obtained as a minor product from reactions of several $Fe(C_5H_5)(CO)_2$(allyl) compounds with $CF_3C{\equiv}CCF_3$ [3]. The *trans* isomer of this species has been made as a minor product in the reaction of $Fe(C_5H_5)(CO)_2SnMe_3$ with this acetylene [5]. Related reactions between $CF_3C{\equiv}CCF_3$ and both $Ru(C_5H_5(L)C(CF_3) = C(CF_3)C(CF_3){=}CHCF_3$ (L = CO, have also been reported, with the products, *trans*-$Ru(C_5H_5)(CO)_2C(CF_3){=}CHCF_3$ and *cis*-$Ru(C_5H_5)(PPh_3)_2C(CF_3){=}CHCF_3$, respectively, being obtained. Interestingly, in each reaction a second product, a 1:2 adduct of metal complex and acetylene, was also obtained. These adduct had the formulas $Ru(C_5H_5(L)C(CF_3) = C(CF_3)C(CF_3){=}CHCF_3$ (L = CO, PPh_3). Failure to form a related product in the $Fe(C_5H_5)(dpe)H$ reaction is probably a consequence of the reluctance of the complex toward displacement of one end of the chelating dpe ligand.

Dissolution of $Fe(C_5H_5)(dpe)H$ in CS_2 gave a yellow solution which rapidly changed to red. The product, a 1:1 adduct of these reactants, precipitates from this solution as dark-red crystals. An infrared spectrum for this product showed two absorptions not observed for the parent complex at 1240 m and 985 s cm^{-1}. The absorptions may be assigned to ν(CS) and δ(C–H) vibrations for the structure $Fe(C_5H_5)(dpe)S_2CH$, having a sulfur bonded thioformate ligand. In accord with this structural assignment is the nmr spectra data which includes a singlet resonance, intensity = 1, of the S_2CH proton at 11.01 δ. It is noted that this type of product has several analogues in $M(CO)_3(dpe)S_2CH$ (M = Mn, Re) [6] and *trans*-$Pt(PCy_3)_2(H)S_2CH$ [7], prepared in similar addition reactions of metal-hydrides.

The low temperature (–20 °C) reaction of $Fe(C_5H_5)(dpe)CH_3$ with SO_2 gave a single product $Fe(C_5H_5)(dpe)SO_2CH_3$. This product was characterized as the S-sulfinate isomer by the presence of two infrared absorptions at 1142 and 1020 cm^{-1}. Similar reactions of $Fe(C_5H_5)(CO)(L)R$ with SO_2 have been reported [8, 9].

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