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Substitution Reactions of Dicarbonyl Cyclopentadienyliron Azide

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Introduction

Previous kinetic and synthetic studies [1,2] showed that the dicarbonylcyclopentadienyliron halides, η^5-$CpFe(CO)_2X$ (X = Cl, Br, I), undergo nucleophilic substitution by a number of pathways. Carbonyl substitution occurs by a dissociative S_N1 mechanism involving attack at the metal atom [1] but as the ionic character of the metal–halogen bond increases in the sequence I < Br < Cl, substitution may also occur by displacement of the halogen and formation of the ionic compounds $[CpFe(CO)_2L]^+X^-$. In this latter case, if L is a tertiary phosphite then phosphonate derivatives, $CpFe(CO)_2[P(O)(OR)_2]$, are also formed [2]. To date, no substitution reactions of the halides involving direct attack at a carbonyl carbon atom have been reported. We now report such an example for the analogous azide, $CpFe(CO)_2N_3$.

Experimental

Dicarbonylcyclopentadienyliron azide was prepared according to the method of Dombek and Angelici [3]. Infrared spectra in the region 2300–1900 cm^{-1} were recorded in CH_2Cl_2 solutions on a Perkin Elmer 237 spectrophotometer. ^1H nmr spectra were obtained in $CDCl_3$ on a Perkin Elmer R12B. Microanalyses were performed in the Microanalytical Laboratories of this department.

π-$CpFe(CO)(NCO)P(OPh)_3$

π-$CpFe(CO)_2N_3$ (1.09 g, 5 mmol) in CH_2Cl_2 (*ca.* 100 ml) was stirred under N_2 at room temperature with $P(OPh)_3$ (1.60 g, 5.3 mmol–1.4 ml) for 4 hours. After filtering and removing the solvent by the water aspirator vacuum pump, the dark red product was washed with pet. ether (40–60 °C). Crystallisation from CH_2Cl_2 was effected by adding pet. ether followed by cooling in an ice-salt mixture. The red crystalline product (yield 1.83 g, 75%) melts at 123 °C (decomp.). *Anal.* $C_{25}H_{20}FeNO_5P$ calc. C 59.88, C 3.99, N 2.79; found C 59.76, H 3.91, N 3.17. ν_{assym} (NCO) 2233s, ν (CO) 1985s, 2037w; τ 5.70 (C_5H_5), 2.60 (C_6H_5).

π-$CpFe(CO)(NCO)PPh_3$

Following the same procedure π-$CpFe(CO)_2N_3$ (1.09 g, 5 mmol) was treated with PPh_3 (1.38 g, 5.25 mmol). The brownish red crystals (yield 1.62–75%) obtained from CH_2Cl_2–pet. ether melt at 129 °C (decomp,). $C_{25}H_{20}FeNO_2P$ calc. C 66.20, H 4.42, N 3.09; found C 66.17, H 4.64, N 3.17. ν_{assym} (NCO) 2231s, ν (CO) 1953s; τ 5.40 (C_5H_5), 2.52 (C_6H_5).

π-$CpFe(CO)(NCO)P(n\text{-}Bu)_3$

In a similar manner $P(n\text{-}Bu)_3$ 1.06 g, 5.25 mmol) was reacted with π-$CpFe(CO)_2N_3$ (1.09 g, 5 mmol). The dark red oil obtained after removing the solvent and washing with pet. ether was dissolved in benzene (*ca.* 5 ml). The product was precipitated by adding pentane and passing a slow stream of nitrogen. The red product (yield 1.22 g, 62%) melts at 84 °C (decomp.). *Anal.* $C_{19}H_{32}NO_2P$ calc. C 58.02, H 8.14, N 3.56; found C 57.94, H 8.37, N 3.80. ν_{assym} (NCO) 2231s, ν (CO) 1943; τ 5.40 (C_5H_5), 9.07–8.43 complex pattern (C_4H_9).

Results

Microanalytical and spectral data support the formulation $CpFe(CO)(NCO)L$ [L = $P(OPh)_3$, PPh_3, $PnBu_3$] for these compounds. In the case L = $P(OPh)_3$ the presence of two carbonyl stretching modes is consistent with the presence of two conformers in solutions as we reported previously for analogous compounds [4]. There have been two previous reports of $CpFe(CO)(NCO)(PPh_3)$ [5, 6]; the first [5] involved iodine oxidation of the mixed carbanoyl carbonyl complex, $CpFe(CO)(CONH_2)(PPh_3)$ and gave low yields (8%) whilst the second [6] involved azide attack on $[CpFe(CO)_2(PPh)_3]PF_6$. Our method gives good yields and promises to be generally applicable. Attempts to prepare the above series by direct ligand substitution of $CpFe(CO)_2NCO$ proved unsuccessful.

The formation of $CpFe(CO)(NCO)L$ is presumed to occur by initial ligand substitution of the "pseudohalogen" azide group followed by attack of the displaced azide onto a carbonyl carbon atom of the intermediate $[CpFe(CO)_2L]^+$ cation (A) [6] and a subsequent Curtius rearrangement to form an iso-

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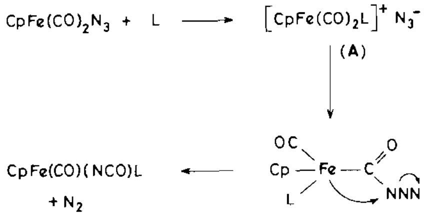
cyanate group, analogous to that occurring in the substitution of the hexacarbonyl metals by azide ion [7].



Support for this mechanism is provided by the isolation of $[CpFe(CO)_2PPh_3]^+BPh_4^-$ when the reaction is carried out in the presence of $NaBPh_4$ and a trace of methanol; however, under these conditions there is no trace of the isocyanato band during reaction, probably because NaN_3 precipitates out of the solvent. If this mechanism is correct, substitution by tertiary phosphites should not lead to the formation of phosphonates despite the initial displacement of the azide (X) because *i*) the azide ion subsequently attacks a carbonyl carbon atom and *ii*) formation of phosphonate is presumed to involve elimination of RX [2] which is unlikely to occur for azides. Kinetic studies of the substitution reaction of $CpFe(CO)_2N_3$ are in progress in these laboratories.

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