# Preliminary communication

# The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]^+$ salts with trifluoromethanesulphonic acid $(HOSO_2CF_3)$

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## Abstract

In a non-coordinating solvent such as chloroform the very strong acid $HOSO_2CF_3$ reacts unexpectedly with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$ ($[1][SO_3CF_3]$) to give $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$, which deprotonates readily to $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNMe)(\mu\text{-}CNMe_2)][SO_3CF_3]$, an isomer of [1] $[SO_3CF_3]$.

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The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ with $MeOSO_2CF_3$ gives two products, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$, ($[1][SO_3CF_3]$) and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CNME_2)_2][SO_3CF_3]_2$, ($[2][SO_3CF_3]_2$). However, $[1][SO_3CF_3]$ does not react with $MeOSO_2CF_3$ to give $[2][SO_3CF_3]_2$ even in the absence of a solvent. Furthermore, in both $[1]^+$ and $[2]^+$ there is no evidence for *cis-trans* interconversion or for ligand site exchange [1]. This implies that there is a very high barrier to $t\text{-}CNMe \rightarrow \mu\text{-}CNMe$ migration (which must be accompanied by $\mu\text{-}CO \rightarrow t\text{-}CO$) as once there the $\mu\text{-}CNMe$ ligand would be alkylated very readily to a $\mu\text{-}CNMe_2^+$ ligand (see below) (t = terminal).

Consequently, we were surprised to find that the addition of pure $HOSO_2CF_3$ (1.5 g, 10 mmol) to a solution of $[1][SO_3CF_3]$ (1.1 g, 2 mmol) in chloroform solution at room temperature converts the $t\text{-}CNMe$ ligand of the latter to a $\mu\text{-}CN(H)Me^+$ group and its $\mu\text{-}CO$ ligand to $t\text{-}CO$ in a reaction which is shown by NMR spectroscopy to be quantitative. The product $[Fe_2(\eta\text{-}C_5H_5)_2(CO_2)\{\mu - CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ ($[3][SO_3CF_3]_2$) [2a] is related to $[2][SO_3CF_3]_2$ except that one $\mu\text{-}CNMe_2^+$ ligand of the latter has been replaced by $\mu\text{-}CN(H)Me^+$, and indeed the two have very similar IR spectra in the 1550–2100 cm$^{-1}$ region [2a]. However, $[3][SO_3CF_3]_2$ may be identified unambigu-

ously by its $^1H$ NMR spectrum which, in acidified $CD_3CN$ solution, shows two equal resonances due to the distinguishable $\eta\text{-}C_5H_5$ groups, two unequal (ratio 3:6) Me resonances due to the $CN(H)Me^+$ and $CNMe_2^+$ ligands with $CN(H)CH_3$ coupling in the former and a broad singlet at $\delta = 11.70$ ppm due to the $\mu\text{-}CNMe$ proton. The spectroscopic data is that for the more important *cis*-$[3][SO_3CF_3]_2$ although it should be noted that its *trans* counterpart is also formed in the reaction but only with low yields. Different spectra are observed in the absence of excess acid and in different solvents owing to reversible $H^+$ dissociation from the $\mu\text{-}CN(H)Me^+$ ligand (see below).

The reaction is not completely general; it takes place with analogues of $[2][SO_3CF_3]$ in which the $\mu\text{-}CNMe_2^+$ ligand has been replaced by other $\mu\text{-}CN(R')R^+$ and the $t\text{-}CNMe$ ligand by $t\text{-}CNR''$ where R, R' or R'' = ethyl or 2,6-diethylphenyl, but it does not take place with $HOSO_2CF_3$ in coordinating solvents such as acetonitrile or with weaker acids such as $CF_3CO_2H$ even in chloroform. If it is carried out on $[Fe_2(\eta\text{-}C_5H_5)_2(CNR)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$, two products are possible. $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)\{\mu\text{-}CN(H)R\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ arises from migration of the CNR ligand, and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNR)\{\mu\text{-}CN(H)Me\}(\mu\text{-}CNMe_2)][SO_3CF_3]_2$ from migration of the CNMe ligand. Both are formed when R = Et and 2,6-diethylphenyl, but not in equal amounts.

When complexes such as $[3][SO_3CF_3]_2$ are passed down an acetone–alumina column, they lose $H^+$ from

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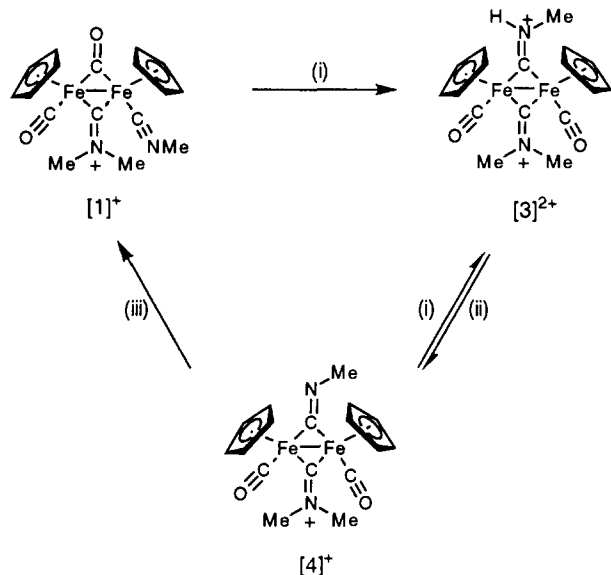
Scheme 1. (i) $HOSO_2CF_3$–$CHCl_3$ solution; (ii) $Al_2O_3$–acetone: (iii) $h\nu$–$CHCl_3$ solution.

the $\mu$-CN(H)Me$^+$ ligand to give high yields (greater than 90%) of derivatives such as [Fe$_2$($\eta$-C$_5$H$_5$)$_2$(CO)$_2$($\mu$-CNMe)($\mu$-CNMe$_2$)][SO$_3$CF$_3$] ([4][SO$_3$CF$_3$]) (Scheme 1) [2b] which shows no N($H$) resonance in its $^1$H NMR spectrum. This particular compound is an

isomer of [1][SO$_3$CF$_3$] and reverts to it on standing in solution in the presence of light, but the solid is indefinitely stable in the dark. It can be trapped by reaction with electrophiles, e.g. with $HOSO_2CF_3$ it reforms [3][SO$_3$CF$_3$]$_2$ (Scheme 1), and $EtOSO_2CF_3$ converts it to [Fe$_2$($\eta$-C$_5$H$_5$)$_2$(CO)$_2${$\mu$-CN(Et)Me}($\mu$-CNMe$_2$)]-[SO$_3$CF$_3$]$_2$.

### Reference and note

[1] G. Cox, C. Dowling, A.R. Manning, P. McArdle and D. Cunningham, *J. Organomet. Chem.*, *438* (1992) 143, and references cited therein.

[2] All compounds described herein have been isolated as analytically pure solids. (a) [3] [SO$_3$CF$_3$]$_2$: Anal. Found: C, 32.8; H, 3.0, N, 39.0. Calc.: C, 32.9; H, 2.9; N, 4.0%. Isolated yield, 85%. IR (KBr disc): $\nu$(CO) 2048, 2023; $\nu$($\mu$-CN) 1620 cm$^{-1}$. $^1$H NMR (CD$_3$CN–HOSO$_2$CF$_3$ solution): $\delta$ 5.64 (C$_5$H$_5$), 5.59 (C$_5$H$_5$), 4.11 (CN(C$H_3$)$_2$, 3.88 (doublet, $J_{HH}$ = 5.13 Hz, CN(H)C$H_3$), 11.70 {CN($H$)Me} ppm. (b) [4][SO$_3$CF$_3$]: Anal. Found: C, 39.6; H,3.3; N, 5.3. Calc.: C, 39.7; H, 3.5; N, 5.2%. Isolated yield, 90%. IR (KBr disc): $\nu$(CO) 2013, 1981, $\nu$($\mu$-CNMe) 1786; $\nu$($\mu$-CNMe$_2$) 1600 cm$^{-1}$. $^1$H NMR (CD$_3$CN solution): $\delta$ 5.09 (2C$_5$H$_5$), 4.22 (CN(C$H_3$)$_2$), 3.72 (CNC$H_3$) ppm. For the $^1$H NMR spectra the chemical shifts are given as downfield from tetramethylsilane as an internal standard with integrations as shown by the assignments.