A New Reaction of Alk-2-ynyl Complexes of Iron with *N*-Thionylaniline

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Summary The reactions of $C_5H_5Fe(CO)_2CH_2C{\equiv}CR$ [R $=$Me, $CH_2Fe(CO)_2(C_5H_5)$, or Ph] with *N*-thionylaniline afford novel metal vinyl complexes

$$C_5H_5Fe(CO)_2\overline{C{=}C(R)S(O)N(Ph)CH_2}$$

which contain a 1,2-thiazine 1-oxide cyclic system.

THE electronic and structural similarity between sulphur dioxide and *N*-thionylamines extends also to certain aspects of their chemistry; *e.g.*, both exhibit extensive dienophilic properties.[1] In view of the known behaviour of SO_2 towards transition-metal–carbon σ-bonds,[2,3] it appeared of interest to examine analogous reactions of PhNSO.

Storage of a solution of $C_5H_5Fe(CO)_2CH_2C{\equiv}CMe$ in neat, dry PhNSO at 25° for several days resulted in the separa-

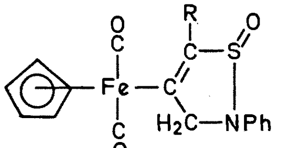
Pertinent i.r.[a] *and* ^{1}H *n.m.r.*[b] *data*

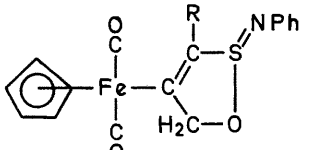
Compound	ν_{CO} (cm^{-1})	ν_{S-O}, ν_{S-N} (cm^{-1})	^{1}H n.m.r. signals (τ)
$C_5H_5Fe(CO)_2C_4H_5,SO_2$ (II)	2024, 1968	1094, 900 m	7·60 (CH_3) 4·80 (C_5H_5) 4·81, 4·45 (CH_2)
$C_5H_5Fe(CO)_2C_4H_5$,PhNSO (I; R = Me)	2022, 1974	1052, 925 m	7·64 (CH_3) 4·92 (C_5H_5) 5·52, 5·18 (CH_2)
$[C_5H_5Fe(CO)_2]_2C_4H_4$,PhNSO [I; R = $CH_2Fe(CO)_2(C_5H_5)$]	2029, 1994 mw, 1967, 1953	1068, 925 m	
$C_5H_5Fe(CO)_2C_9H_7$,PhNSO (I; R = Ph)	2023, 1967	1070, 933 m	

[a] Measured as Nujol mulls. All bands strong unless otherwise indicated.

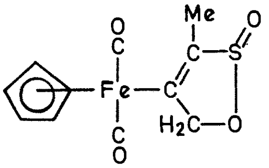
[b] Measured in $CDCl_3$ solution with Me_4Si as reference. The CH_2 protons are magnetically nonequivalent.

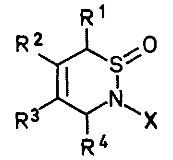
tion of a yellow precipitate. Recrystallization of this solid from toluene–pentane afforded in *ca.* 20% yield a pure complex of empirical formula $C_5H_5Fe(CO)_2C_4H_5$,PhNSO (I; R = Me), m.p. 97—98° (dec.), and of monomeric constitution, as deduced from its mass spectrum.


(Ia)


(Ib)

R = Me, $CH_2Fe(CO)_2(C_5H_5)$, Ph


(II)


(III) X = Ar, SO_2R

The pertinent i.r. absorption bands and ^{1}H n.m.r. signals for (I; R = Me) are listed in the Table. The corresponding data for $C_5H_5Fe(CO)_2C_4H_5,SO_2$, its SO_2-containing counterpart of known structure (II),[3] are provided for comparison.

The close similarity between the ^{1}H n.m.r. spectra of (I; R = Me) and (II) strongly supports analogous structures for these compounds. Of the two most likely structures (Ia and Ib; R = Me), we favour the former, although the latter cannot be unequivocally rejected. The i.r. band at 1052 cm^{-1} in the spectrum of (I; R = Me) matches well the absorptions found at *ca.* 1080 cm^{-1} for various 1,2-thiazine 1-oxides (III)[4,5] and at 1068 cm^{-1} for *N*-phenyl-*N'N'*-dimethylthionyldiamidotrimethylstannane, $Me_3SnN(Ph)SO\cdot NMe_2$.[6] This band is best assigned to $\nu_{S=O}$, while another strong absorption, at 925 cm^{-1}, may be attributed to ν_{S-N}. The S–N stretching frequency for a series of sulphinamides, $R_2NSO\cdot R$,[6,7] and sulphonamides, $R_2NSO_2\cdot R$,[8] occurs in the range 930—870 cm^{-1}. Further support, albeit also not definitive, is provided by the observed resistance of the compound to hydrolysis. A species having the structure (Ib) is expected, by analogy with the behaviour of PhNSO, to be readily attacked by H_2O yielding (II) and aniline.

The reaction of PhNSO with other alk-2-ynyl iron complexes—$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_2Fe(CO)_2(C_5H_5)$ and $C_5H_5Fe(CO)_2CH_2C{\equiv}CPh$—leads to the formation of similar products. Some pertinent spectral data for these compounds [I; R = $CH_2Fe(CO)_2(C_5H_5)$ and Ph] are given in the Table. We are currently examining the behaviour of *N*-thionylamines towards transition-metal alkyl complexes in order further to develop comparison between SO_2 and RNSO as reagents in organometallic chemistry.

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