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Preliminary communication

LINKAGE ISOMERISM IN 5-*exo* THIOCYANATE AND ISOTHIOCYANATE SUBSTITUTED TRICARBONYL(η-CYCLOHEXA-1,3-DIENE)IRON AND TRICARBONYL(η-CYCLOHEPTA-1,3-DIENE)IRON

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Summary

Nucleophilic addition to the tricarbonyl(η-cyclohexadienyl)iron cation and the tricarbonyl(η-cycloheptadienyl)iron cation by the thiocyanate ion forms initially the 5-*exo*-isothiocyanate (NCS) isomers, $C_6H_7NCSFe(CO)_3$ and $C_7H_9NCSFe(CO)_3$, both of which isomerise to the corresponding 5-*exo* thiocyanate isomers $C_6H_7SCNFe(CO)_3$ and $C_7H_9SCNFe(CO)_3$ on exposure to air.

Linkage isomerism involving bonding of the thiocyanate group either via the sulphur or nitrogen atom to a transition metal is well known and generally follows the correlation of sulphur bonding to soft metals and nitrogen to hard metals [1]. In contrast with a carbon centre the S atom is the more nucleophilic whilst the N atom is more basic so although S bonded thiocyanates are formed initially, they rearrange rapidly to the more stable N-bonded isothiocyanates [2]. In this note we report the isolation of 5-*exo* ring substituted isothiocyanate isomers of tricarbonyl(η-cyclohexa-1,3-diene)iron and tricarbonyl(η-cyclohepta-1,3-diene)iron by nucleophilic attack of the thiocyanate ion on the corresponding tricarbonyl(cyclodienyl)iron cation. In contrast to previous behaviour at a carbon centre these ring substituted N-bonded isothiocyanates rearrange to the corresponding ring substituted S-bonded thiocyanate isomers. Nucleophilic substitution of cyclic diene metal carbonyl complexes involves attack at either the dienyl ring [3], the metal [3] or the carbonyl group [4] but in the present example direct ring attack by NCS^- appears the most likely reaction pathway since no intermediates were observed in contrast to attack by azide ion [5] and alkoxide ion [6].

The yellow 5-*exo* isothiocyanate was obtained by adding ammonium thiocyanate in a dichloromethane/water mixture to a suspension of

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TABLE 1

Complex	IR frequencies (cm^{-1})			Integrated intensity ($A \times 10^{-4}$ M^{-1} cm^{-2})
	ν_{as} (NCS)	ν(CO)		ν_{as} (NCS)
$C_6H_7NCSFe(CO)_3$ (I)	2154.5	2048.4	1973.6 1964.2	2.90
$C_6H_7SCNFe(CO)_3$ (II)	2110.4	2050.3	1976.6	0.80
$C_7H_9NCSFe(CO)_3$ (III)	2130.0	2044.0	1981.0	2.40
$C_7H_9SCNFe(CO)_3$ (IV)	2109.0	2045.6	1980.0	0.78

$[C_6H_7Fe(CO)_3]BF_4$ in the same solvent mixture with rapid formation of a yellow colour. After 20 min the dichloromethane layer was separated and washed with (3 × 30 ml) portions of water, dried over powdered anhydrous $MgSO_4$, filtered and evaporated to leave a yellow oil. The yellow oil was dissolved in deoxygenated n-pentane and crystallized at –78°C to give good yields of the 5-*exo* N-bonded isothiocyanate $C_6H_7NCSFe(CO)_3$ (I). However, in both solution and the solid state and especially on exposure to air, I rearranges to the red isomer $C_6H_7SCNFe(CO)_3$ (II) and this was confirmed from spectral data; thus the mass spectrum of I showed a parent ion peak at m/e 277 and major peaks at 249 $[M - CO]^+$, 217 $[M - CO - S]^+$, 189 $[M - 2CO - S]^+$ and 134 $[M - 3CO - NCS - H]^+$; the intense peak at 217 indicates bonding of the NCS group via the N atom rather than the S atom. In contrast II gave a parent ion peak at 277 and major peaks at 249 $[M - CO]^+$, 221 $[M - 2CO]^+$, 191 $[M - CO - SCN]^+$ and 134 $[M - 3CO - SCN - H]^+$ with no peak at 217. Both the positions and integrated intensities of the asymmetric CN mode (ν_{as}(NCS)) given in Table 1 support the above formulation of I and II as the N-bonded and S-bonded isomers respectively by comparison with previous studies of both organic thiocyanates and isothiocyanates [7—9] and metal bonded thiocyanates and isothiocyanates [7]. The ^1H NMR spectra ($CDCl_3$) of I and II are identical and typical of 5-*exo* substituted cyclic diene metal carbonyl complexes [10] with multiplets at 5.54 H(2,3), 4.16 H(5), 3.10 H(1,4), 2.33 H(6 *exo*), and 1.71 H(6 *endo*) with respect to TMS ($\delta = 0$). Comparison of decoupled spectra with computer-simulated spectra gave coupling constants, $J_{5.6\ endo}$ 2.93 and $J_{5,6\ exo}$ 10.25 Hz for both complexes which confirm the 5-*exo* configuration.

Analogous isomers $C_7H_9NCSFe(CO)_3$ (III) and $C_7H_9SCNFe(CO)_3$ (IV) were obtained by treating $[C_7H_9Fe(CO)_3]BF_4$ with NH_4NCS in CH_2Cl_2/H_2O mixtures, as above. Again, although the yellow 5-*exo* N-bonded isothiocyanate III formed initially, it rearranged rapidly on exposure to air to the red 5-*exo* S-bonded thiocyanate isomer IV. The positions and integrated intensities of ν_{as}(NCS) of III and IV (Table 1) support their formulation as N-bonded and S-bonded ring isomers respectively as in the analogous case of the six-membered ring isomers I and II. The ^1H NMR spectrum of III showed multiplets at 5.45 H(2,3), 4.06 H(5), 3.04 H(1,4), 2.04 H(6 *exo*, 7 *exo*) and 1.69 H(6 *endo*, 7 *endo*) and that of IV at 5.38 H(2,3), 4.06 H(5), 3.03 H(1,4), 1.98 H(6 *exo*, 7 *exo*) and 1.62 H(6 *endo*, 7 *endo*) with respect to TMS ($\delta = 0$). Comparison of decoupled spectra with computer-simulated spectra gave values of $J_{5,6\ endo}$ 4.39 and $J_{5,6\ exo}$ 11.30 Hz for both isomers. These spectra are typical of 5-

exo substituted tricarbonyl(η-cyclohepta-1,3-diene)iron complexes [11] and confirm their structure. Unfortunately, the mass spectra of III and IV were very similar and cannot be used to distinguish the mode of bonding as in I and II.

The rearrangement of the N-bonded isomers I and III to the corresponding S-bonded isomers II and IV is in marked contrast to the normal rearrangement of S-bonded organic thiocyanates to the more stable N-bonded isothiocyanates and the mechanism of the rearrangement in these organometallic systems is under further investigation. Analogous reactions occur between the seleno-cyanate ion ($SeCN^-$) and the $[C_6H_7Fe(CO)_3]^+$ and $[C_7H_9Fe(CO)_3]^+$ cations. Again initial formation of the yellow 5-*exo* N-bonded isomers occurs with rapid rearrangement to the dark-brown S-bonded isomers but accompanying decomposition precluded isolation of pure products.

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