

Preliminary communication

THE REACTION OF $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$ WITH ALKYL ISOCYANIDES; $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNR})_4]$ (R = Me OR Et)

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Summary

In boiling xylene $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$ reacts with RNC (R = Me, Et) to give $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNR})_2(\mu\text{-CNR})_2]$ complexes, which appear to exist as mixtures of non-interconverting isomers at room temperature and which have very basic N atoms in the $\mu\text{-CNR}$ ligands.

Recently it has been reported that $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$ reacts with aryl isocyanides in boiling toluene to give $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNAr})_4]$ [1]. This prompts us to report our similar studies on the reactions of alkyl isocyanides with $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$ and some of the properties of the derivatives thus obtained.

The reactions of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$ with MeNC (mole ratio 1/8) in boiling xylene ultimately gives a mixture of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})_3]$ and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})_4]$ (ca. 1/5) after ca. 3 h. The hot solution was filtered, and an equal volume of heptane added to the filtrate. On cooling, this mixture deposited black crystals and a light-brown powder, both of which analysed reasonably well as $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})_4]$. The combined yields were 50–60%. $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNEt})_4]$ was obtained similarly as a red oil. With PhCH_2NC , substitution proceeds no further than $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNCH}_2\text{Ph})_2]$. These reactions proceed via detectable amounts of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_{4-n}(\text{CNR})_n]$ ($n = 1-3$) as intermediates. In this respect they differ from the reaction of $o\text{-MeC}_6\text{H}_4\text{NC}$, which we have found to proceed directly to $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNC}_6\text{H}_4\text{Me-}o)_4]$. Identical behaviour has been observed for other aryl isocyanides by Albers et al. [1].

The IR spectrum of the black crystals of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})_4]$ shows intense absorption bands at 1640 and 2140 cm^{-1} due respectively to the $\nu(\text{CN})$ vibrations of bridging and terminal MeNC ligands of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})_2-$

(μ -CNMe)₂] molecules. In CHCl₃ solution, that at ca. 2200 cm⁻¹ has an asymmetric envelope which indicates that either a mixture of *cis*- and *trans*-isomers or just the *cis*-isomer is present. The ¹H NMR spectra discussed below support the second alternative.

The ¹H NMR of the black crystals of [Fe₂(η -C₅H₅)₂(CNMe)₄] in CDCl₃ solution (25°C) show singlet resonances at δ 2.96, 3.84, and 4.68 ppm (intensity ratio 6/6/10) attributable to t-MeNC, μ -MeNC and C₅H₅ protons, respectively. At lower temperatures (-50°C) the last broadens. These observations suggest that either the *cis*- or the *trans*-isomer only is present, that it does not undergo terminal-bridging MeNC exchange, and that it does not isomerise to the other isomer. The low temperature broadening may be due to inversion at the N atoms of the μ -ligands [2]. The possibility that both *cis*- and *trans*-isomers are present with coincident resonances is unlikely. The ¹H NMR spectrum of the brown powder form of [Fe₂(η -C₅H₅)₂(CNMe)₂] (CDCl₃, 25°C) shows the three resonances found for the black form together with two others at δ 3.53 and 4.60 ppm. It is tempting to suggest that these are due to the second isomer which does undergo fluxional terminal-bridging MeNC exchange without *cis/trans*-isomerism. On the basis of arguments put forward for [Fe₂(η -C₅H₅)₂(CO)₄] [3] we tentatively suggest that the black isomer is the *cis*-, and that the other is the *trans*-isomer.

The μ -MeNC ligands in [Fe₂(η -C₅H₅)₂(CO)_{4-n}(CNMe)_n] (*n* = 1-3) are basic and readily attacked by electrophiles. The same is true in our compound where *n* = 4. However whereas when *n* = 2 or 3 MeI alkylates only one μ -CNMe to give [Fe₂(η -C₅H₅)₂(CO)(CNMe)(μ -L)(μ -CNMe₂)]⁺ I⁻ (L = CO or CNMe) [4], [Fe₂(η -C₅H₅)₂(CNR)₄] give mono- or di-alkylated species depending on both R and the reagent. Thus when R = Me or Et the dimers react with one molar equivalent of R'I (R' = Me or Et) forming [Fe₂(η -C₅H₅)₂(CNR)₂(μ -CNR)-{ μ -CN(R)R'}]I and with an excess of R'I to give [Fe₂(η -C₅H₅)₂(CNR)₂{ μ -CN(R)R'}₂]I₂. This is consistent with the earlier observations that the basicity of μ -CNMe increases as *n* increases [2]. On the other hand when R = *o*-MeC₆H₄ the μ -CNR ligands are far less basic and MeI will only alkylate one of them, but both may be alkylated by MeSO₃F.

References

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