An Investigation of the Reaction Between [{Fe(η^5–C_5H_5)(CO)$_2$}$_2$] and Aryl Isonitriles †

By **Neil J. Coville** * and **Michel O. Albers**, Department of Chemistry, University of Witwatersrand, Johannesburg, 2001, South Africa
Eric Singleton, National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria 0001, South Africa

The direct reaction between [{Fe(η^5-C_5H_4X)(CO)$_2$}$_2$] (X = H, Me, or COOMe) and aryl isonitriles RNC (R = 2,6-$Me_2C_6H_3$ or C_6H_5) in refluxing toluene readily yields the tetrasubstituted derivatives [{Fe(η^5-C_5H_4X)(RNC)$_2$}$_2$]. The intermediate derivatives [Fe_2(η^5-C_5H_5)$_2$(CO)$_{4-n}$(RNC)$_n$] (n = 1 or 2) can be prepared by the exchange reaction between [{Fe(η^5-C_5H_5)(RNC)$_2$}$_2$] and [{Fe(η^5-C_5H_5)(CO)$_2$}$_2$]. Reaction rates for the substitution of [{Fe(η^5-C_5H_5X)(CO)$_2$}$_2$] by RNC are dependent on both the nature of R and X, and increase with both the nucleophilicity of R and the electron-withdrawing power of X. An alternative route to [Fe_2(η^5-C_5H_5)$_2$(CO)$_{4-n}$(RNC)$_n$] (n = 1 or 2) is *via* the reaction between Na[Fe(η^5-C_5H_5)(CO)$_2$] and 2,6-$Me_2C_6H_3NC$ in the presence of $C_7H_7^+BF_4^-$. The isonitrile complexes have been characterized by i.r. and n.m.r. spectroscopy.

As part of our current program on the investigation of the catalytic behaviour of metal dimers [1,2] we have found it necessary to synthesize complexes of the type [Fe_2(η^5-C_5H_5)$_2$(CO)$_{4-n}$(RNC)$_n$] (RNC = isonitrile, n = 1—4). Complexes with n = 1—3, R = alkyl group, can readily be synthesized by the direct reaction between [{Fe(η^5-C_5H_5)(CO)$_2$}$_2$] (1) and RNC.[3-7] Surprisingly, the corresponding reaction between (1) and aryl isonitriles has been reported to yield at most the disubstituted product [{Fe(η^5-C_5H_5)(CO)(RNC)}$_2$] (2) and then in poor yield [*e.g.* for R = C_6H_5, yields of <1% of (2) have been reported [8]]. An indirect method starting from [Fe(η^5-C_5H_5)(CO)$_{3-n}$(C_6H_5NC)$_n$]$^+$ (n = 1—3) has, however, allowed for the synthesis of [Fe_2(η^5-C_5H_5)$_2$(CO)$_{4-n}$(C_6H_5NC)$_n$] (n = 1, 2, or 4) in moderate to good yields.[9,10]

We thus decided to investigate the direct reaction between (1) and aryl isonitriles and our results are reported herein.

EXPERIMENTAL

Phenyl isocyanide was prepared by the literature method [11] and 2,6-dimethylphenyl isocyanide was purchased from Fluka A.G. The compound [{Fe(η^5-C_5H_5)(CO)$_2$}$_2$] was purchased from Strem Chemicals and [{Fe(η^5-C_5H_4X)(CO)$_2$}$_2$] (X = Me or COOMe) prepared by the literature method [12] from [Fe(CO)$_5$] and $C_{10}H_{10}Me_2$ or C_5H_5COOMe [13] in octane. Tropylium tetrafluoroborate was prepared from C_7H_8 and $(C_6H_5)_3C^+BF_4^-$.[14] Reactions were routinely carried out under nitrogen in purified solvents.

I.r. spectra were recorded on a Pye Unicam SP 300 spectrophotometer, ^{1}H n.m.r. spectra on a Bruker WP80 spectrometer. Elemental analyses were carried out by the Microanalytical Laboratories, C.S.I.R.

Preparations.—(*a*) [{Fe(η^5-C_5H_4X)(RNC)$_2$}$_2$] (X = H *or* Me, R = 2,6-$Me_2C_6H_3$ *or* C_6H_5; X = COOMe, R = 2,6-$Me_2C_6H_3$). The compounds [{Fe(η^5-C_5H_5)$_2$(CO)$_2$}$_2$] (0.5 mmol) and RNC (≈2.2 mmol) were added to either benzene or toluene (15 cm^3) and the solution brought to reflux. In toluene, the reactions take place rapidly (5—60 min) but in benzene they occur more slowly (15 min—8 h) and can readily be monitored by changes in the i.r. spectrum (2 200—1 600 cm^{-1}). At the end of the reaction, the solution which had turned green (2,6-$Me_2C_6H_3NC$) or brown (C_6H_5NC) was filtered through a cellulose column. Recrystallization from tetrahydrofuran (thf) or benzene–hexane gave the required product in >60% yield.

(*b*) [Fe_2(η^5-C_5H_5)$_2$(CO)$_{4-n}$(2,6-$Me_2C_6H_3NC$)$_n$] (n = 1 *or* 2). The salt Na[Fe(η^5-C_5H_5)(CO)$_2$] (≈20 mmol) was prepared from [{Fe(η^5-C_5H_5)(CO)$_2$}$_2$] (3.5 g, 10 mmol) and Na/Hg (1.10 g in 75 g) in thf (60 cm^3).[12] After the Hg had been separated by decantation under nitrogen, 2,6-$Me_2C_6H_3NC$ (10 mmol) and $C_7H_7^+BF_4^-$ (1.1 g, 10 mmol) were added to the reaction solution. Vigorous evolution of CO occurred. The solution was stirred for 10 min, decanted, and the solvent removed *in vacuo*. The crude reaction material was chromatographed on grade IV alumina (Merck) using initially dichloromethane–hexane (1 : 1) mixtures and finally CH_2Cl_2. Bitropylium [15] was eluted first. This was followed by [{Fe(η^5-C_5H_5)(CO)$_2$}$_2$], then [Fe_2(η^5-C_5H_5)$_2$(CO)$_3$(2,6-$Me_2C_6H_3NC$)] (≈30%), and finally [{Fe(η^5-C_5H_5)(CO)(2,6-$Me_2C_6H_3NC$)}$_2$] (≈10%). The reaction yield of the disubstituted product can be increased by increasing the amount of 2,6-$Me_2C_6H_3NC$ added to Na[Fe(η^5-C_5H_5)(CO)$_2$].

DISCUSSION

In contrast to earlier reports [7,8] we have found that the direct reaction between [{Fe(η^5-C_5H_4X)(CO)$_2$}$_2$] (*e.g.* X = H) and aryl isonitriles readily yields the complexes [{Fe(η^5-C_5H_4X)(RNC)$_2$}$_2$]. Thus, addition of four equivalents of RNC (R = C_6H_5 or 2,6-$Me_2C_6H_3$) to [{Fe(η^5-C_5H_4X)(CO)$_2$}$_2$] (X = H, Me, or COOMe) gives [{Fe(η^5-C_5H_4X)(RNC)$_2$}$_2$] (3), with reaction times dependent on both the nature of X and the isonitrile (Table 1) (see below). The reaction in benzene can readily be monitored by i.r. spectroscopy; the ν(μ-CO) absorption at ≈1 780 cm^{-1} provides a ready measure of product disappearance. The i.r. spectra indicate that (3) is formed immediately with little sign of intermediate product formation. This is exemplified by the reaction between (1) and 2,6-$Me_2C_6H_3NC$ (1 : 1). The i.r. spectrum after ≈20 min (benzene) indicates that only

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† Regarded as Part 4 in the series ' Metal Dimers as Catalysts '.[1]

TABLE 1

Reaction times [a] and analytical data for the dimeric iron isonitrile complexes

Complex [b]	Reaction time (min)		Analytical data (%) [c]		
	Benzene	Toluene	C	H	N
$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(RNC)]$			58.4 (57.8)	4.15 (4.20)	3.10 (3.05)
$[\{Fe(\eta^5\text{-}C_5H_5)(CO)(RNC)\}_2]\cdot 0.5C_6H_6$			65.6 (66.1)	5.20 (5.20)	4.30 (4.60)
$[\{Fe(\eta^5\text{-}C_5H_5)(RNC)_2\}_2]$	90	5	72.1 (72.8)	6.65 (6.05)	7.55 (7.30)
$[\{Fe(\eta^5\text{-}C_5H_4Me)(RNC)_2\}_2]$	240 (70%) [d]	40	72.6 (73.4)	6.75 (6.35)	7.60 (7.05)
$[\{Fe(\eta^5\text{-}C_5H_4COOMe)(RNC)_2\}_2]$	15		68.9 (68.1)	5.95 (5.70)	6.45 (6.35)
$[\{Fe(\eta^5\text{-}C_5H_5)(C_6H_5NC)_2\}_2]$	120 (80%) [d]	25	70.8 (69.8)	4.85 (4.60)	9.00 (8.55)
$[\{Fe(\eta^5\text{-}C_5H_4Me)(C_6H_5NC)_2\}_2]$	450	60	70.9 (70.4)	5.25 (5.00)	8.45 (8.20)

[a] For the reaction $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2] + RNC \longrightarrow [\{Fe(\eta^5\text{-}C_5H_5)(RNC)_2\}_2]$. [b] $R = 2,6\text{-}Me_2C_6H_3$. [c] Calculated values are given in parentheses. [d] Extent of reaction.

the starting material (1) (≈75%) and $[\{Fe(\eta^5\text{-}C_5H_5)(2,6\text{-}Me_2C_6H_3NC)_2\}_2]$ (≈25%) are present. Further heating (≈15 h) results in the slow formation of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_{4-n}(2,6\text{-}Me_2C_6H_3NC)_n]$ ($n = 1$ or 2) as detected by i.r. spectroscopy. Since equimolar solutions of (1) and $[\{Fe(\eta^5\text{-}C_5H_5)(2,6\text{-}Me_2C_6H_3NC)_2\}_2]$ also yield the intermediate products ($n = 1$ or 2) on being heated together (benzene) the appearance of these intermediate products must arise from secondary reactions, after rapid formation of (3).

Our qualitative results thus suggest that the intermediate products react more rapidly than (1), with RNC,[16,*] a phenomenon which has precedent in the substitution reactions of other complexes containing metal–metal bonds.[17,18]

The intermediate derivatives $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_{4-n}(2,6\text{-}Me_2C_6H_3NC)_n]$ ($n = 1$ or 2) can also be prepared in moderate yields by indirect methods. Thus, the reaction of $Na[Fe(\eta^5\text{-}C_5H_5)(CO)_2]$, $C_7H_7^+BF_4^-$, and $2,6\text{-}Me_2C_6H_3NC$ (2 : 1 : 1 ratio) yields the products $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(2,6\text{-}Me_2C_6H_3NC)]$ (≈30%) and $[\{Fe(\eta^5\text{-}C_5H_5)(CO)(2,6\text{-}Me_2C_6H_3NC)\}_2]$ (≈10%). The mechanism of product formation presumably involves radical formation as suggested for the corresponding reaction between $[Mn(CO)_5]^-$ and $P(C_6H_5)_3$ in the presence of $(C_6H_5)_3C^+Br^-$.[19] These derivatives ($n = 1$ or 2) also react with further isonitrile to give $[\{Fe(\eta^5\text{-}C_5H_5)(2,6\text{-}Me_2C_6H_3NC)_2\}_2]$.

Reaction times for the reaction of $[\{Fe(\eta^5\text{-}C_5H_4X)(CO)_2\}_2]$ (X = H, Me, or COOMe) with C_6H_5NC and $2,6\text{-}Me_2C_6H_3NC$ are listed in Table 1. It is apparent from these data that $2,6\text{-}Me_2C_6H_3NC$ reacts more rapidly than C_6H_5NC, *i.e.* electron-donating groups on the isonitrile assist the reaction. The data reveal further that electron-withdrawing groups on the cyclopentadienyl ring also assist the reaction, *i.e.* the reaction rate follows the sequence $C_5H_4COOMe > C_5H_5 > C_5H_4Me$. The overall effects thus suggest that the substitution reaction is enhanced by attack of good nucleophiles at an electrophilic centre.

The ability of aryl isonitriles to substitute the CO groups on (1) to a greater degree than alkyl isonitriles is in agreement with the known electronic properties of the isonitrile ligand.[20] The previously reported poor yields for the reaction between (1) and aryl isonitriles [7,8] must therefore be a consequence of experimental product work-up procedures rather than the nature of the products [(3) rapidly decomposes on silica or alumina columns and plates].

The use of catalysts in the synthesis of substituted dimeric iron aryl isonitrile complexes, which prompted this study,[1,2] has to date been unsuccessful. Thus, the use of Pd/C, PdO, Pt/C, and activated carbon [21] have led to no detectable increase in the rate of substitution of CO by RNC in (1). (Further, the use of $CoCl_2$ as a potential catalyst [22] has resulted in reaction inhibition.) These results are in contrast to our finding that the reaction $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(Bu^tNC)] + Bu^tNC \longrightarrow [\{Fe(\eta^5\text{-}C_5H_5)(CO)(Bu^tNC)\}_2]$ is catalysed by PtO_2 (≈30% rate increase in refluxing benzene over 4 h).[23]

The dimeric iron isonitrile complexes have been characterized by i.r. spectroscopy (Table 2). The i.r. spectrum of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(2,6\text{-}Me_2C_6H_3NC)]$ is consistent with the RNC group adopting a terminal position,[4] *viz.* ν(NC) at 2 085 cm^{-1}. This is in contrast to the reported spectrum of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(C_6H_5NC)]$ which indicates that C_6H_5NC adopts a bridging position, *viz.* ν(NC) at 1 702 cm^{-1}.[8] The effect could arise from either steric or electronic factors,[4,7] *both* of which would favour the $2,6\text{-}Me_2C_6H_3NC$ adopting a terminal position relative to C_6H_5NC. The i.r. spectrum of $[\{Fe(\eta^5\text{-}C_5H_5)(CO)(2,6\text{-}Me_2C_6H_3NC)\}_2]$, by analogy with the spectra recorded for other disubstituted isonitrile derivatives,[7] is consistent with at least one of the $2,6\text{-}Me_2C_6H_3NC$ groups adopting a terminal position [ν(NC)

TABLE 2

I.r. data (cm^{-1}) [a]

$[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(RNC)]$ [b]	2 085m, 1 974m, 1 953s, 1 752s
$[\{Fe(\eta^5\text{-}C_5H_5)(CO)(RNC)\}_2]$	2 074s, 1 983w, 1 948w, 1 764m, 1 747m, 1 708ms
$[\{Fe(\eta^5\text{-}C_5H_5)(RNC)_2\}_2]$	2 025m, 1 992m, 1 670ms
$[\{Fe(\eta^5\text{-}C_5H_5)(C_6H_5NC)_2\}_2]$	2 070m, 1 987mw, 1 658ms
$[\{Fe(\eta^5\text{-}C_5H_4COOMe)(RNC)_2\}_2]$ [c]	2 074m, 1 998w, 1 720ms
$[\{Fe(\eta^5\text{-}C_5H_4Me)(RNC)_2\}_2]$	2 030m, 1 992m, 1 668ms
$[\{Fe(\eta^5\text{-}C_5H_4Me)(C_6H_5NC)_2\}_2]$	2 060m, 1 985mw, 1 655m

[a] Recorded in CS_2 unless otherwise stated. m = Medium, s = strong, and w = weak; $R = 2,6\text{-}Me_2C_6H_3$. [b] In C_6D_6. [c] ν(COOMe) 1 764 cm^{-1}.

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[*] See, however, the synthesis of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(C_6H_5NC)]$.[16]

2 074 cm^{-1}]. The band at 1 708 cm^{-1} is, however, consistent with at least one isomer containing a bridging 2,6-$Me_2C_6H_3NC$ group.

Thus, modification of the aryl isonitrile through substitution of the benzene ring is in agreement with the earlier definitive studies [4,5,7] on the effect of the modification of electronic and steric effects of alkyl isonitriles on the bridge/terminal RNC ratio.

The i.r. spectra of the tetrasubstituted derivatives (3) all show two terminal ν(NC) stretches of varying intensity and one broad ν(NC) bridging absorption. Although the presence of an electron-donating group on the η^5-C_5H_5 ring has little effect on the ν(NC) band positions, the effect of electron-withdrawing groups is more noticeable. The move to higher frequency is in keeping with the greater reactivity of the ester-substituted ring derivative (see above).

The ^1H n.m.r. spectrum of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_3(2,6\text{-}Me_2C_6H_3NC)]$ (benzene, 35 °C) shows singlet resonances for both the C_5H_5 ring and CH_3 groups (Table 3), thus suggesting that the molecule is fluxional at 35 °C. The disubstituted derivative shows broadened resonances for all the protons (35 °C) suggesting that the complex is close to the coalescence temperature for bridge–terminal CO–RNC interchange and/or *cis–trans* isomerism.[7] The ^1H n.m.r. spectra of the tetrasubstituted derivatives are complicated and will require a variable-temperature study for their complete interpretation. The n.m.r. spectrum of $[\{Fe(\eta^5\text{-}C_5H_5)(2,6\text{-}Me_2C_6H_3NC)_2\}_2]$, reported in Table 3, can however be tentatively assigned, using the Cotton–Adams rules,[24] as a mixture of *trans* (40%) and *cis* (60%) isomers.

TABLE 3

N.m.r. data [a]

	C_5H_5	Me
$[Fe_2(\eta^5\text{-}C_5H_5)(CO)_3(RNC)]$	4.40	2.21
$[\{Fe(\eta^5\text{-}C_5H_5)(CO)(RNC)_2\}_2]$	4.51	2.43, 2.22
$[\{Fe(\eta^5\text{-}C_5H_5)(RNC)_2\}_2]$	4.72,[b] 4.61 [c]	2.56,[c] 2.35,[b] 2.07 [c]

[a] Recorded in C_6D_6 (δ/p.p.m.) relative to $SiMe_4$. R = 2,6-$Me_2C_6H_3$. [b] *trans* isomer. [c] *cis* isomer.

Since the tetrasubstituted complexes (X = H) containing 2,6-$Me_2C_6H_3NC$ and C_6H_5NC have different i.r. spectra [terminal ν(NC) region] and further, have different colours, it was thought that these effects could result from the different steric and/or electronic properties of the different ligands. However, an *X*-ray structure determination [25] of $[\{Fe(\eta^5\text{-}C_5H_5)(2,6\text{-}Me_2C_6H_3NC)_2\}_2]$ has revealed that this complex and $[\{Fe(\eta^5\text{-}C_5H_5)(C_6H_5NC)_2\}]$ are similar in all respects. The bridging ligands adopt an ***anti-trans*** arrangement in both molecules and the Fe–Fe bond lengths are 2.518 Å (2,6-$Me_2C_6H_3NC$) and 2.525 Å (C_6H_5NC) [26] respectively.

The facile synthesis of the completely substituted complex (3) thus opens up the chemistry of these new complexes and present efforts are being extended to an understanding of the chemistry of the bridging isonitrile ligand.[27]

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