CONVERSION OF μ-ALKYLIDYNEDIIRON COMPLEXES TO NITRILES *

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Summary

The reaction of the diiron μ-propylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_3)^+$ PF_6^- (3) with Me_3SiN_3 in CD_2Cl_2 under a CO atmosphere produced 64% (NMR) propanenitrile, 33% $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)_2$ (2) and 16% $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C=CHCH_3)$ (4). Treatment of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C\text{-}n\text{-}C_4H_9)^+$ PF_6^- (6) under similar conditions produced pentanenitrile in 51% (NMR) yield, 2 in 20% yield and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C=CHCH_2CH_2CH_3)$ (7) in 22% yield. Similarly, $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4\text{-}p\text{-}CH_3)^+$ BF_4^- (5) reacted with Me_3SiN_3 under a CO atmosphere to produce $p\text{-}CH_3C_6H_4CN$ in 64% isolated yield and 2 in 71% isolated yield.

Introduction

The hydrocarbation reaction in which the methylidyne C–H bond of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$ (1) adds across the carbon–carbon double bond of a variety of alkenes to form bridging alkylidyne complexes provides a new mode of C–C bond formation [1]. In conjunction with Rosenblum's earlier synthesis of cationic μ-alkylidyne compounds from the reaction of RLi with $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)_2$ (2) followed by strong acid work-up [2], a wide range of diiron alkylidyne cations are readily available.


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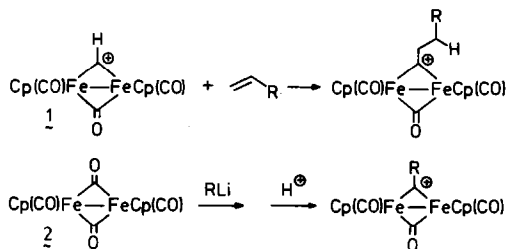
* Dedicated to Professor Jean Tirouflet on the occasion of his retirement.

In order to realize the full synthetic potential of these two processes, it is desirable to release the organic fragment from the diiron center with the newly formed C–C bond still intact [3]. This requires the delivery of three new valences and a negative charge to the bridging carbon of the alkylidyne ligand and poses a difficult and unusual synthetic challenge. A further complication involves the ease of deprotonation of cationic μ-alkylidyne complexes to form neutral alkenylidene compounds [4].
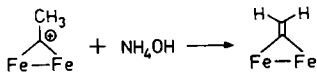
Early work with mononuclear carbyne and carbene complexes suggested that azide would be a promising reagent provided that its basicity would not be a problem. Fischer showed that treatment of a chromium carbyne complex with $[n\text{-}Bu_4N]^+ \, N_3^-$ readily afforded a nitrile complex [5]. This reaction presumably involves nucleophilic attack of azide at the carbyne carbon to form an intermediate azidocarbene complex. Subsequent loss of N_2 and migration of chromium from carbon to nitrogen produces the nitrile complex.
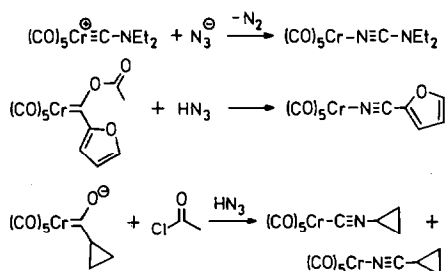
Similarly, Connor has demonstrated that reaction of HN_3 with an (acetoxy)(2-furyl)carbene chromium complex yields a coordinated 2-furonitrile [6]. The intermediacy of an azidocarbene complex was also inferred in this case. When HN_3 was added to a mixture of a cyclopropylacyl anion complex and acetylchloride in CH_2Cl_2, a 20/1 mixture of the isonitrile and nitrile complexes formed [7].
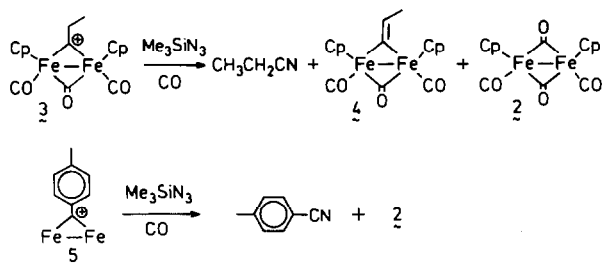
We report here that the reaction of azides with selected cationic μ-alkylidynediiron complexes produces nitriles in moderate yields.

Results

Reactions with azides

When the μ-propylidyne complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CCH_2CH_3)^+ \, PF_6^-$ (3) was treated with NaN_3 in CD_3CN under CO, a 19% NMR yield (14% by GC) of propanenitrile was observed after 3 d. No μ-propylidyne complex 3 remained. The majority of μ-propylidyne complex 3 was deprotonated to produce the μ-1-propenylidene complex $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C=CHCH_3)$ (4) in 57% NMR yield. The domination of this acid-base reaction can be easily understood since μ-al-

kylidyne cations are very acidic [4,8].

$$\begin{array}{c}
\underset{3}{\overset{\oplus}{Cp\text{-}Fe\text{-}Fe\text{-}Cp}} \xrightarrow[CO]{Me_3SiN_3} CH_3CH_2CN + \underset{4}{\overset{}{Cp\text{-}Fe\text{-}Fe\text{-}Cp}} + \underset{2}{\overset{O}{Cp\text{-}Fe\text{-}Fe\text{-}Cp}}
\end{array}$$

$$\underset{5}{\overset{\oplus}{Fe\text{-}Fe}} \xrightarrow[CO]{Me_3SiN_3} \quad \text{—}\langle\bigcirc\rangle\text{—CN} + \underset{\sim}{2}$$

When the reaction of a μ-alkylidyne complex containing no acidic hydrogens was studied, a higher yield of nitrile was observed. Reaction of $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}CC_6H_4\text{-}p\text{-}CH_3)^+$ BF_4^- (5) with NaN_3 in acetone-d_6 under CO produced p-tolunitrile in 65% GC yield and $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)_2$ (2) in 73% NMR yield.

The reaction of μ-propylidyne complex 3 with NaN_3 was carried out in the presence of added acid in the hope that the deprotonation to 4 could be reversed and that improved yields of nitrile would be obtained. Indeed, a mixture of 3, NaN_3, and trifluoroacetic acid (TFA) in CD_3CN under CO resulted in an increased yield of propanenitrile (39% by NMR, 37% by GC after 21 h). Correspondingly, the amount of μ-propenylidene complex 4 obtained by deprotonation decreased to 7%.

Similar yields of propanenitrile were obtained from the reaction of 3 with NaN_3 and trifluoroacetic acid in acetone-d_6. When the reaction was carried out under CO for 24 h, 33% propanenitrile and 20% deprotonation product 4 were observed by ^1H NMR. After 34 h, the NMR yield of nitrile increased to 42% and 11% $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)_2$ 2 was observed. When no CO was used in this reaction, only 3% 2 was produced while 42% of propanenitrile and 57% of 4 were observed by NMR after 24 h.

Although it is clear that addition of acid to the reaction mixtures increased the yield of nitrile, a substantial amount of deprotonation of the alkylidyne was still occurring. Since Me_3SiN_3 is often an effective substitute for hydrazoic acid [9], we examined its effectiveness in producing propanenitrile from 3. When 3 was treated with Me_3SiN_3 in CD_3CN under CO, propanenitrile (24% by NMR), deprotonation product 4 (3%) and 2 (25%) were observed.

Slightly better nitrile yields were obtained in acetone-d_6 solvent. After 23 h, the reaction of 3 with Me_3SiN_3 in acetone-d_6 under CO led to the formation of propanenitrile (34%), 2 (11%) and propenylidene complex 4 (34%). When the same reaction was run without CO for 23 h, propanenitrile (36%), propenylidene complex 4 (51%), and ferrocene (7%) were observed by NMR.

The highest yields of propanenitrile were obtained in CD_2Cl_2. For example, treating 3 with Me_3SiN_3 in CD_2Cl_2 under CO for 120 h resulted in a 64% NMR yield of propanenitrile (61% by GC). In addition, 33% 2 and 16% 4 were observed. No starting propylidyne complex 3 remained.

Treating $[(C_5H_5)(CO)Fe]_2(\mu\text{-}CO)(\mu\text{-}C\text{-}n\text{-}C_4H_9)^+$ PF_6^- (6) under similar conditions produced 51% (NMR) pentanenitrile (48% by GC) after 14 h. The starting μ-pentylidyne complex 6 was completely destroyed. The deprotonation product, μ-1-pentenylidene complex 7 (22%) and 2 (20%) were also observed by NMR. Pentanenitrile was isolated from a larger scale reaction using preparative GC.

The best yields of nitrile were achieved in the reaction of the tolyl carbyne complex **5** with Me_3SiN_3 in acetone-d_6 under CO. An 82% GC yield of *p*-tolunitrile was observed. Using the same conditions on a larger scale, *p*-tolunitrile and **2** were isolated in 64% and 71% yields respectively.

Reactions of 3 with N_2O

Since N_2O is isoelectronic with N_3^-, the possibility that it might deliver an oxygen atom to the alkylidyne carbon of **3** to form a μ-η^1,η^2-acyl complex was examined. However, treatment of **3** in acetone-d_6 with 675 mmHg N_2O for 7 d resulted in approximately a 56/44 mixture of starting material **3**: deprotonation product **4** as monitored by ^{1}H NMR.
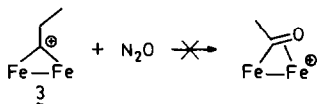

Discussion

A number of exploratory reactions were carried out using different solvents in which cationic μ-alkylidynediiron complexes were treated with either NaN_3, NaN_3 and trifluoroacetic acid, or Me_3SiN_3 as the azide source and in the presence or absence of a CO atmosphere (Table 1). In general, these reactions proceeded more cleanly and provided higher yields of **2** when carried out under an atmosphere of CO. While all of the azide sources produced nitriles, the best yields were obtained

TABLE 1

SUMMARY OF NMR YIELDS FROM THE REACTION OF DIIRON ALKYLIDYNE COM-PLEXES WITH AZIDES
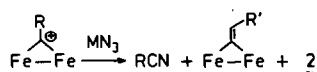
R	MN_3 [a]	Conditions	RCN (%)	$Fe_2(\mu$-C=CHR') (%)	2 (%)
Et	NaN_3	CD_3CN/CO/74 h	19	57	14
Et	NaN_3/TFA	CD_3CN/CO/21 h	39	7	6
Et	NaN_3/TFA	$(CD_3)_2CO$/CO/24 h	33	20	8
		34 h	42	23	11
Et	NaN_3/TFA	$(CD_3)_2CO$/24 h	42	57	3
Et	Me_3SiN_3	CD_3CN/CO/21 h	24	30	25
Et	Me_3SiN_3	$(CD_3)_2CO$/CO/23 h	34	34	11
Et	Me_3SiN_3	$(CD_3)_2CO$/23 h	36	51	0
Et	Me_3SiN_3	CD_2Cl_2/CO/120 h	64	16	33
Bu	Me_3SiN_3	CD_2Cl_2/CO/14 h	51	22	20
p-tolyl	NaN_3	$(CD_3)_2CO$/CO/168 h	65 (GC)	–	73
p-tolyl	Me_3SiN_3	$(CD_3)_2CO$/CO/72 h	82 (GC)	–	63

[a] Trifluoroacetic acid is abbreviated as TFA.

with Me_3SiN_3. These results are consistent with the silyl azide serving as a mild source of N_3^-.
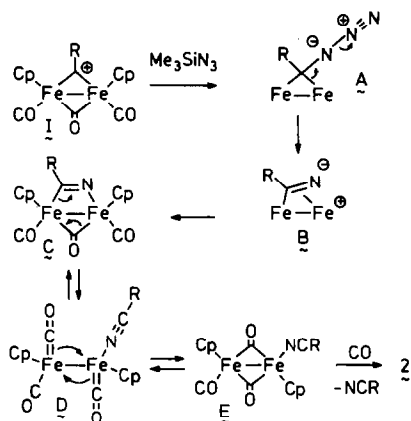
In accord with the earlier work of Fischer [5] and Connor [6,7] on mononuclear complexes, it seems likely that the nitrile forming process in the diiron system also proceedes through an intermediate azidocarbene complex, **A**. Iron assisted loss of N_2 from **A** is suggested to produce a $\mu\text{-}\eta^1,\eta^2$-iminyl anion complex, **B**, analogous to $\mu\text{-}\eta^1,\eta^2$-alkenyl diiron complexes [10].
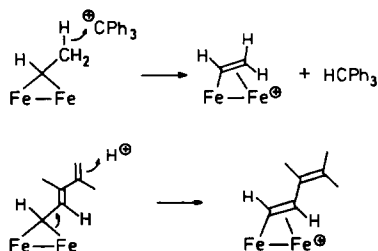
The formation of these μ-alkenyl complexes can be viewed as models for the formation of **B**. β-Hydride abstraction from a μ-ethylidenediiron complex using trityl cation produces the $\mu\text{-}\eta^1,\eta^2$-ethenyl complex [4]. Protonation of a dienyl carbene complex also yields a μ-alkenyl complex [11].
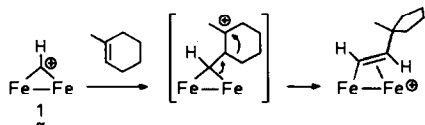
In the course of examining the scope of the hydrocarbation reaction, we discovered that several alkenes react with **1** to produce μ-alkenyl complexes rather than μ-alkylidyne complexes [12]. The mechanism for some of these reactions involve a carbocation rearrangement as illustrated for the reaction of **1** with 1-methyl-cyclohexene.
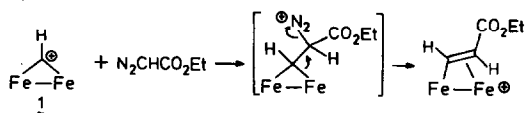
The closest analogy for the formation of **B** involves μ-alkenyl formation from the reaction of **1** with ethyl diazoacetate [8]. In this case the product forming step is likely to involve iron assisted loss of N_2 from a diazonium complex. The fact that the reaction of azides with diiron alkylidyne complexes preferentially forms nitriles instead of isonitriles suggests that the stability of **B** parallels that of μ-alkenyl complexes.

Experimental

General

All reactions were carried out in flame dried glassware. Acetone and acetone-d_6 were distilled from B_2O_3, CD_3CN was distilled from P_2O_5 then CaH_2, CH_2Cl_2 was distilled from CaH_2, and CD_2Cl_2 was distilled from P_2O_5. ^1H NMR spectra were obtained on a Bruker WP-270 spectrometer using a 30 s pulse delay between scans. Mass spectra were obtained on a Kratos MS-25 spectrometer. Infrared spectra were obtained on a Beckman IR-4230 spectrophotometer. Analytical GC was performed on a Hewlett-Packard 5890A gas chromatograph with a flame ionization detector, coupled to a Hewlett-Packard 3390A integrator. A 10 m $\times$ 0.53 mm methyl silicon capillary column at 200°C was used for p-tolunitrile analyses and a temperature program (30°C for 2 min, 40°C/min to 120°C) was used for propanenitrile and pentanenitrile analyses. Preparative GC was carried out on a Varian 90-P instrument with a thermal conductivity detector. A 20% SE-30 on 30-60 Chromosorb P column (20 ft $\times$ 3/8″) at 140°C was used to isolate pentanenitrile.

Reaction of alkylidynes with azides

The details outlined in the reaction of **3** with NaN_3 in CD_3CN were used in all subsequent exploratory procedures.

Reaction of [(C$_5$H$_5$)(CO)Fe] $_2$(μ-CO)(μ-CCH$_2$CH$_3$)$^+$ PF$_6^-$ (3) [1] with NaN$_3$ in CD$_3$CN under CO. CD_3CN (0.43 ml) was distilled into an NMR tube containing **3** (7.2 mg, 14.1 μmol), NaN_3 (1.3 mg, 20 μmol) and p-$C_6H_4(SiMe_3)_2$ (1.5 mg, 6.7 μmol, internal standard) at -78°C. CO (700 mmHg) was admitted, the tube was flame sealed and monitored periodically by ^1H NMR. Partial ^1H NMR after 74 h: CH_3CH_2CN δ 1.19 (t, J 7.5 Hz, CH_3), CH_2 obscured by CH_3 signal of deprotonation product **4**; **4** δ 7.11 (q, J 7 Hz, =CH) 4.91 (s, C_5H_5), 4.82 (s, C_5H_5), 2.33 (d, J 7 Hz, CH_3); [(C$_5$H$_5$)(CO)Fe]$_2$(μ-CO)$_2$ (2) δ 4.85 (s, C_5H_5); (C$_5$H$_5$)Fe(CO)$_3^+$ PF$_6^-$ δ 5.72 (s, C_5H_5). GC analysis was carried out on 250 μl of the volatiles which were vacuum transferred at -196°C from the NMR tube. 10 μl of a 0.193 M cyclohexanone solution was added as an internal standard. Extraction of the solid residues in the NMR tube with Et_2O, filtration of the resulting solution, and evaporation of the solvent under reduced pressure produced 5 mg of a red solid consisting of a 62/6/32 mixture of **4**/**2**/p-$C_6H_4(SiMe_3)_2$.

Reaction of [(C$_5$H$_5$)(CO)Fe] $_2$(μ-CO)(μ-CC$_6$H$_4$-p-CH$_3$)$^+$ PF$_6^-$ (5) [2] with NaN$_3$. Acetone-d_6 (0.36 ml) was distilled into an NMR tube containing **5** (8.6 mg, 16.7 μmol) and NaN_3 (1.4 mg, 21.5 μmol) at -78°C. CO (680 mmHg) was admitted, the tube was flame sealed and monitored periodically by ^1H NMR. After 7 d, partial ^1H NMR: p-$CH_3C_6H_4CN$ δ 7.65 (d), 7.40 (d), 2.42 (s, CH_3); **2** δ 4.94 (C_5H_5).

Reaction of 3 with NaN$_3$ and TFA in CD$_3$CN under CO. The amount of reagents used were **3** (7.5 mg, 14.7 μmol), NaN_3 (1.7 mg, 26.2 μmol), TFA (15 mmHg, 29 ml,

23°C), CO (700 mmHg), p-$C_6H_4(SiMe_3)_2$ (0.8 mg, 3.6 μmol), and CD_3CN (0.37 ml).

Reaction of 3 with NaN_3 and TFA in acetone-d_6 under CO. 3 (7.5 mg, 14.7 μmol), NaN_3 (1.1 mg, 16.9 μmol), TFA (12 mmHg, 29 ml, 26°C), CO (700 mmHg), p-$C_6H_4(SiMe_3)_2$ (1.2 mg, 5.4 μmol), and acetone-d_6 (0.37 ml) were used.

Reaction of 3 with NaN_3 and TFA in acetone-d_6 with no CO. 3 (7.6 mg, 14.8 μmol), NaN_3 (1.2 mg, 18.5 μmol), TFA (12 mmHg, 29 ml, 26°C), p-$C_6H_4(SiMe_3)_2$ (1.4 mg, 6.3 μmol), and acetone-d_6 (0.36 ml) were flame sealed in an NMR tube at −78°C under vacuum.

Reaction of 3 with Me_3SiN_3 in CD_3CN under CO. The amounts used were 3 (6.7 mg, 13.1 μmol), Me_3SiN_3 (41 mmHg, 29 ml, 23°C, 64.4 μmol), p-$C_6H_4(SiMe_3)_2$ (0.9 mg, 4.0 μmol), CO (744 mmHg), and CD_3CN (0.36 ml).

Reaction of 3 with Me_3SiN_3 in acetone-d_6 under CO. 3 (7.1 mg, 15.4 μmol), Me_3SiN_3 (43 mmHg, 29 ml, 26°C, 66.8 μmol), CO (700 mmHg), p-$C_6H_4(SiMe_3)_2$, and acetone-d_6 (0.37 ml) were flame sealed in an NMR tube.

Reaction of 3 with Me_3SiN_3 in acetone-d_6 without CO. A mixture of 3 (7.3 mg, 14.3 μmol), Me_3SiN_3 (37 mmHg, 29 ml, 26°C, 57.5 μmol), and acetone-d_6 (0.39 ml) at −78°C was flame sealed under vacuum. After 23 h a yellow precipitate had formed.

Reaction of 3 with Me_3SiN_3 in CD_2Cl_2 under CO. The amounts of reagents used were 3 (7.2 mg, 14.1 μmol), Me_3SiN_3 (37 mmHg, 29 ml, 19°C, 58.9 μmol), CO (700 mmHg), p-$C_6H_4(SiMe_3)_2$ (1.2 mg, 5.4 μmol), and CD_2Cl_2 (0.39 ml).

Reaction of $[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-C-n-$C_4H_9)^+ PF_6^-$, 6 [1] with Me_3SiN_3. 6 (6.5 mg, 12.0 μmol), Me_3SiN_3 (31 mmHg, 29 ml, 26°C, 48.2 μmol), p-$C_6H_4(SiMe_3)_2$ (1.6 mg, 7.2 μmol), and CD_2Cl_2 (0.35 ml) were flame sealed under 700 mmHg of CO. Partial ^1H NMR after 14 h: $CH_3CH_2CH_2CH_2CN$ δ 2.33 (t, CH_2CN), 1.67 (m, CH_2), 1.47 (m, CH_2), 0.95 (t, CH_3); $[(C_5H_5)(CO)Fe]_2(\mu$-$CO)(\mu$-C=-$CHCH_2CH_2CH_3)$ (7) δ 7.10 (t, =CH), 4.84 (s, C_5H_5), 4.77 (s, C_5H_5), 2.81 (m, CH_2), 2.66 (m, CH_2), 1.06 (t, CH_3); 2 δ 4.80 (C_5H_5).

Isolation of pentanenitrile. Under an atmosphere of CO, 6 (1.50 g, 2.78 mmol) and Me_3SiN_3 (0.74 ml, 5.59 mmol) were stirred in freshly distilled CH_2Cl_2 (65 ml) for 14 h. The reaction mixture was concentrated to 2 ml by distillation of CH_2Cl_2 at atmospheric pressure. The remaining volatiles were then vacuum transferred at −196°C through a short path tee. Pentanenitrile (18 mg, 8%) was isolated by preparative GC. ^1H NMR (270 MHz, CD_2Cl_2) δ 2.33 (t, CH_2CN), 1.63 (m, CH_2), 1.47 (m, CH_2), 0.94 (t, CH_3); IR (CH_2Cl_2) 2248 cm^{-1}; HRMS showed major peak for protonated pentanenitrile; Found: 84.0808. $C_5H_{10}N$ calc: 84.0813.

Reaction of 5 with Me_3SiN_3. Me_3SiN_3 (30 mmHg, 8.96 ml, 23°C, 14.6 μmol) was condensed into an NMR tube containing 5 (5 mg, 9.7 μmol) and acetone-d_6 (0.37 ml) at −78°C. CO (680 mmHg) was admitted and the tube was flame sealed.

Isolation of tolunitrile. Me_3SiN_3 (0.55 ml, 4.1 mmol) and 5 (1.01 g, 1.96 mmol) were stirred in acetone (50 ml) under a CO atmosphere for 5 d. Acetone was removed under reduced pressure and the residues were extracted with pentane. Pentane was removed from the organic fraction under reduced pressure and the remaining portion was distilled at 13 mmHg to yield p-tolunitrile (147 mg, 64%). ^1H NMR (270 MHz, acetone-d_6) δ 7.64 (d, aryl H), 7.40 (d, aryl H), 2.42 (s, CH_3); IR (CH_2Cl_2) 2230 cm^{-1}; HRMS Found: 117.0573. C_8H_7N calc: 117.0577. The residues from the pentane extracts were passed down a 6 cm Al_2O_3 column with

CH_2Cl_2 to yield **2** (0.49 g, 71%). ^1H NMR (270 MHz, acetone-d_6): δ 4.94 (s, C_5H_5); IR (CH_2Cl_2): 2000s, 1956m, 1773s cm^{-1}; HRMS Found: 353.9276. $C_{14}H_{10}Fe_2O_4$ calc: 353.9274.

Reaction of 3 with N_2O. Acetone-d_6 (0.38 ml) was condensed into an NMR tube containing **3** (8 mg, 15.6 μmol), N_2O (675 mmHg) was admitted and the tube was flame sealed. The reaction was monitored periodically by ^1H NMR. Partial NMR: **3** δ 5.67 (s, C_5H_5) 1.81 (t, CH_3); **4** δ 7.12 (d, *J* 7 Hz, =CH), 4.97 (s, C_5H_5), 4.89 (s, C_5H_5), 2.34 (d, *J* 7 Hz, CH_3).

Acknowledgement

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