Ferrocene Derivatives. 23.[1] Isocyanoferrocene and Isothiocyanatoferrocene†

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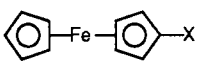
Aminoferrocene has been converted into formamidoferrocene, which exists in solution as an equilibrium mixture of two rotational isomers, a monomeric cis form and a dimeric (or oligomeric) trans form. Variable-temperature ^1H and $^{13}C\{^1H\}$ NMR spectra have been used to measure $\Delta G^{\ddagger}$ for the hindered internal rotation about the C-N bond. Dehydration of formamidoferrocene yields isocyanoferrocene, which has been characterized by complex formation with iron and molybdenum carbonyls. A high-yield conversion of aminoferrocene into isothiocyanatoferrocene is described.

Introduction

Some 35 years after the discovery of ferrocene[2] and its aromaticity,[3] the organic chemistry of this iron complex continues to attract attention.[4] Initially much research was directed toward the preparation of simple derivatives after it was found that conventional methods of electrophilic substitution, appropriate for benzene analogues, often caused oxidation of diamagnetic ferrocene to the electrophile-resistant paramagnetic ferrocenium cation. Some functionally substituted ferrocenes have been prepared directly[5] from appropriately substituted cyclopentadienides, and more recently, this technique has been exploited with considerable success by Rausch and coworkers, and others, to produce a wide variety of metallocene,[6] cyclopentadienylmetal carbonyl[7] and cyclopentadienylmetal carbonyl nitrosyl[8] derivatives. However, to prepare the ferrocene analogues of, for example, aniline and phenol, circuitous procedures are required that are multistage and usually uneconomical. Consequently the organic chemistry of, for example, hydroxyferrocene[9] has been little explored, although the reactions of nitrogen-substituted ferrocenes have attracted some recent interest with the preparation of nitrosoferrocene and some ferrocenylamines being described by Herberhold,[10] Stahl,[5e] and co-workers. This paper describes the preparation of two other simple nitrogen-substituted ferrocenes, namely isocyanoferrocene, FcNC,[38] and isothiocyanatoferrocene, FcNCS, and some related chemistry.

Results and Discussion

Alkyl and aryl isocyanides have been extensively employed as ligands in organometallic chemistry since they are analogous to, but more basic than, carbon monoxide.[11] Aryl isocyanides are better π-acceptors than alkyl isocyanides.[12] A wide range of substituted aryl isocyanides is now readily accessible, due to the development by Ugi and co-workers[13] of substituent-tolerant formamide dehydration procedures that are more versatile than the historically interesting carbylamine reaction.[14] Surprisingly, isocyanoferrocene has not been described, although it might be expected to be a stronger σ-donor but a slightly weaker π-acceptor[14] than isocyanobenzene. Each of the isocyanide syntheses developed by Ugi et al. utilizes arylamines as precursors. Aminoferrocene (**1**) and its simple



X = NH_2 (**1**), NHLi (**2**), NHCHO (**3**), NC (**4**), N$\equiv$CHN(*i*-Pr)$_2$ (**5**), CN (**6**), NCS (**7**), SCN (**8**), CH_2NCS (**9**), (NC)Fe(CO)$_4$ (**10**)

derivatives have been prepared by a number[5c,10b,15b,16] of

† Dedicated to Professor Lord Tedder on the occasion of his retirement.

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(15) (a) Fc is slightly electron donating compared with Ph (Nagy, A.; Toma, S. *J. Organomet. Chem.* **1985**, *282*, 267). (b) Aminoferrocene is 20 times as strong a base as aniline (Nesmeyanov, A. N.; Perevalova, E. G.; Golovnya, R. V.; Shilovtseva, L. S. *Dokl. Akad. Nauk SSSR* **1955**, *102*, 353), while measurement of the Hammett σ_p function shows Fc to be a stronger electron donor than CH_3 (Nesmeyanov, A. N.; Perevalova, E. G.; Gubin, S. P.; Grandberg, K. I.; Kozlovosky, A. G. *Tetrahedron Lett.* **1966**, 2381).

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Table I. Osmometric Molecular Weight Measurements[a] for 3[b]

concn, mmol/mL	measd mol wt	concn, mmol/mL	measd mol wt
0.003 955	231	0.015 55	263
0.012 54	258	0.029 26	298

[a] All measurements in toluene solution at 312.7 K. [b] $C_{10}H_9FeNHCHO$ requires formula weight 229.

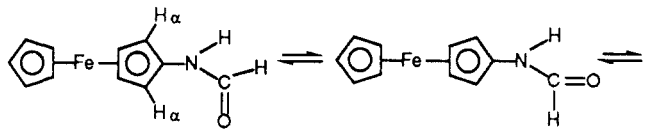
alternative routes, but the Kocheshkov reaction using *O*-benzylhydroxylamine and lithiated ferrocene is possibly the most economical and convenient[17] route for obtaining multigram quantities. In the time since this synthesis of aminoferrocene was first described by Nesmeyanov et al.,[15b] optimum procedures[18] for the lithiation of ferrocene have been described, and the lithiation products have been characterized.[19] However, when we applied the more recent lithiation procedures to the preparation of aminoferrocene, we were unable to obtain yields consistently improved over those of the Nesmeyanov procedure. The best yields of aminoferrocene (**1**) (approximately 12%) were obtained under conditions that are known to result in extensive dilithiation, but 1,1′-diaminoferrocene[5c] was never detected among the products. Although it is possible that the intermediate 1-amino-1′-lithioferrocene is resistant to further amination, we suggest that intermolecular or, more likely, rapid intramolecular lithium–hydrogen exchange occurs to give *N*-lithioferrocenylamine (**2**, eq 1), which suppresses diamine formation.

$$(1,1'\text{-}Li_2)C_{10}H_8Fe \rightarrow (1\text{-}Li)C_{10}H_8Fe(1'\text{-}NH_2) \rightleftharpoons \underset{\mathbf{2}}{C_{10}H_9FeNHLi} \quad (1)$$

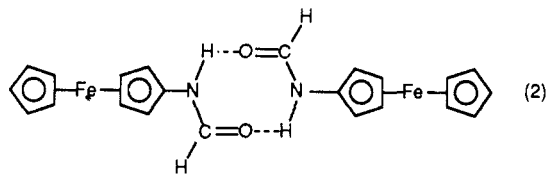
Aminoferrocene dissolves readily in dilute mineral acids, but it suffers concomitant cleavage of the amino group to give ferrocene. Consequently, it cannot be purified by repeated acid extraction–alkali precipitation cycles. This unusually facile protodeamination reaction thus parallels earlier observations, where more severe conditions were employed, on the proton-catalyzed removal of MeO[20] and Cl groups[1] from ferrocene.

Conversion of aminoferrocene into the formamide **3** occurred smoothly in refluxing ethyl formate, but parallel cleavage of the amino group sometimes depressed the yield of **3**. Lithiation of aminoferrocene at −30 °C with *n*-butyllithium, presumably to give **2**, followed by treatment with ethyl formate, gave a marginal improvement in yield of **3**.

During the process of routine characterization it was discovered that (formylamino)ferrocene (**3**) was not a single, simple substance. After chromatographic purification and repeated recrystallization from a single solvent it was always obtained as a microcrystalline or apparently amorphous orange solid with a constant melting point. IR spectra were consistent with a formamide structure, and mass spectrometry gave a molecular ion and fragment ions consistent with the expected monomeric composition. However, solution molecular weight determinations indicated partial association of monomeric units, the observed molecular weight values being concentration dependent (Table I). From variable-temperature and variable-concentration ^1H and ^{13}C NMR spectroscopy experiments (see below) it was concluded that, in solution, **3** exists as an equilibrium mixture (eq 2) of monomers and oligomer(s).



3a **3b**



3c (2)

Isocyanoferrocene (**4**) was obtained in variable, nonreproducible (25–90%) yields as a pungent, orange, volatile solid, mp 76–77 °C, when **3** was treated with $POCl_3$ in diisopropylamine.[13c] Fission of the N–C bond yielded ferrocene as a byproduct and a trace amount of an orange-red crystalline solid, $C_{17}H_{24}FeN_2$, which was identified spectroscopically as the imine **5**.

Dehydration of **3** with use of dicyclohexylcarbodiimide was also investigated, but the conversion to **4** was consistently inferior to the $POCl_3$ method. Reaction between CNBr and lithiated ferrocene failed to give **4** or **6**.

Isocyanoferrocene, FcNC, is characterized by an intense IR peak at 2125 cm^{-1}, while for the isomeric cyanoferrocene[21] (FcCN, **6**) ν(CN) is at 2220 cm^{-1}. For comparison the value for PhNC is 2138 cm^{-1} and for EtNC ν(NC) is 2160 cm^{-1}.[22] Differences between ^1H and ^{13}C NMR spectra (Table I) of **4** and **6** are described later. Mass spectrometry does not allow easy differentiation between **4** and **6**, the cracking patterns and ion abundances being very similar except for more intense $(M + 1)^+$ ions in the spectrum of **4** and more intense $C_{10}H_8Fe^+$ ions in the spectrum of **6**. The TLC behavior of the two isomers is also different, **4** having a larger R_f value than **6** in petroleum ether and in ether on silica and alumina plates. Although somewhat air sensitive, especially in solution, **4** is thermally stable and does not dimerize[23] or rearrange to **6**.

The ligand properties of **4** were investigated briefly; reaction with $Fe_2(CO)_9$ gave the complex $(FcNC)Fe(CO)_4$ (**10**) as a low-melting orange crystalline solid. The values of ν(CO) for this iron carbonyl derivative indicate that **4** is a marginally better donor than PhNC but poorer than alkyl isocyanides.[22] Reaction between **4** and $C_7H_8Mo(CO)_4$[24] gave orange crystalline *cis*-$(FcNC)_2Mo(CO)_4$, but

(16) Arimoto, F.; Haven, A. C. *J. Am. Chem. Soc.* **1955**, *77*, 6295. Hall, D. W.; Richards, J. H. *J. Org. Chem.* **1963**, *28*, 1549. Schlögl, K.; Mechtler, H. *Monatsh. Chem.* **1966**, *97*, 150. Abramovitch, R. A.; Azogu, C. I.; Sutherland, R. G. *J. Chem. Soc. D* **1971**, 134.

(17) It is difficult to compare the advantages of the different routes to $FcNH_2$. Although the Herberhold procedure[10b] is reasonably efficient, the preparation of multigram quantities of the intermediate FcNHAc is tedious, is multistage, and also requires the initial formation of lithioferrocenes.[18]

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(22) Cotton, F. A.; Parish, R. V. *J. Chem. Soc.* **1960**, 1440.

(23) At 100 °C phenyl isocyanide dimerizes to indigo dianil (Grundmann, C. J. *Chem. Ber.* **1958**, *91*, 1380).

(24) Following the procedure for preparing $(RNC)_2Mo(CO)_4$ described by: King, R. B.; Borodinsky, L. *Tetrahedron* **1985**, *41*, 3235.

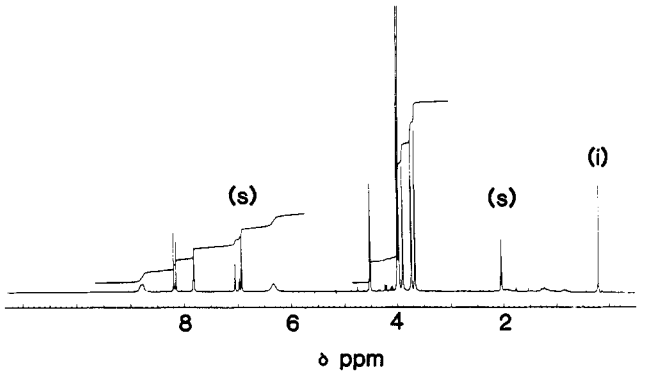

Figure 1. ^1H NMR spectrum of **3** (concentration ca. 0.2568 mmol/mL, $C_6D_5CD_3$, 295 K): (s) solvent; (i) impurity.

this complex was extremely labile in solution. Chromatography and/or attempted recrystallization gave mixtures containing *cis*- and *trans*-$(FcNC)_2Mo(CO)_4$ and an unidentified substance, which may be $(FcNC)_3Mo(CO)_3$.

Reaction between **4** and elemental sulfur gave some isothiocyanatoferrocene (FcNCS, **7**), but this was more conveniently prepared in high yield from aminoferrocene (**1**) via the ammonium salt of the dithiocarbamic acid (eq 3), by following the procedure described[25] for the prepa-

$$\underset{\mathbf{1}}{FcNH_2} + CS_2 + NH_3 \rightarrow FcNHCS_2NH_4 \xrightarrow{COCl_2} \underset{\mathbf{7}}{FcNCS} + COS + NH_4Cl + HCl \quad (3)$$

ration of PhNCS. Isothiocyanatoferrocene (**7**) was isolated as a volatile orange-red solid, mp 58 °C. A comparison of some of the spectral properties of **7** with those of the isomeric thiocyanatoferrocene[26] (FcSCN, **8**) and the previously reported[27] $FcCH_2NCS$ (**9**) is given in Table II. Apart from the position of the weak high-frequency peak, there is a striking similarity between ν_{asym}(NCS) values for **7** and **9**. The chemistry of **7** has not yet been investigated in detail, but it was observed that, as expected, the NCS group in **7** appears to be more resistant to hydrolysis than the oxygen analogue FcNCO, characterized by Schlögl et al.[28]

NMR Spectra. At 295 K the 250-MHz ^1H NMR spectrum of **3** in $C_6D_5CD_3$ (concentration approximately 0.3275 mmol/mL) exhibited *two* C_5H_5 singlets of approximately equal intensity at δ 3.90 and 3.95, four characteristic triplets identifiable with two A_2B_2 systems (δ 3.62, 3.69, 3.77, and 4.41), a broad N*H* signal at δ 5.19, a broad N*H* doublet (J = 11.3 Hz) at δ 7.92, a C*H*O doublet (J = 1.4 Hz) at δ 7.59, and a C*H*O doublet (J = 11.3 Hz) at δ 8.12. This spectrum is reproduced in Figure 1. Additionally, it was found that the spectrum was concentration-sensitive; at 313 K with concentrations of **3** in $C_6D_5CD_3$ similar to those used for the osmometric measurements (Table I) it was observed that the ratio of C_5H_5 signals (δ 3.85:δ 3.94) varied from 74.7:25.3 (concentration 0.004 010 mmol/mL) to 66.2:33.8 (concentration 0.029 26 mmol/mL). Furthermore, the chemical shift of the α- and β-protons of the substituted ring of the minor component(s) gradually coalesced to an apparent singlet and lost

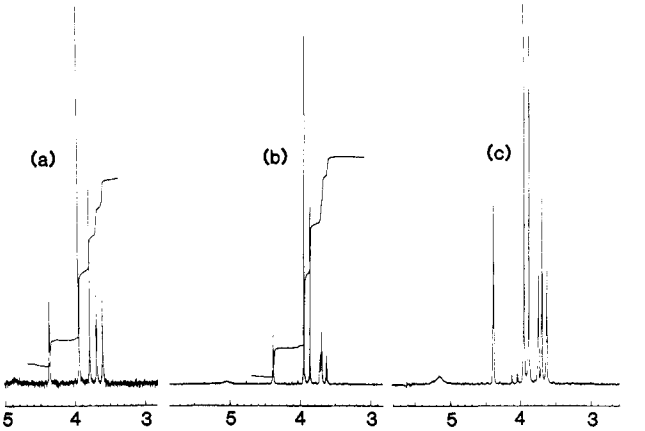

Figure 2. C_5H_5 and C_5H_4X region of the ^1H NMR spectrum of **3** (313 K, in $C_6D_5CD_3$): (a) concentration 0.004 010 mmol/mL; (b) concentration 0.029 26 mmol/mL; (c) concentration ca. 0.2568 mmol/mL.

their characteristic triplet structure as the solution was diluted (Figure 2 and Table III; Table III is supplementary material).

These observations are consistent with some monomer ⇌ dimer (or oligomer) equilibrium, suggested by the solution molecular weight measurements, but not consistent with a simple equilibrium of the type **3a** ⇌ **3b**. Selective decoupling revealed that the triplets at δ 3.69 and 4.41 constituted an interacting A_2B_2 system, and it is suggested that the lowest field triplet corresponds to the protons H_α in cis-rotamer **3a**, deshielded by the proximate C=O bond. By analogy with other systems[29] it is likely that the NH–CHO grouping with J = 11.3 Hz corresponds to a trans stereochemistry (**3b** and/or **3c**). Apart from differences in chemical shift and less well resolved N*H*–C*H*O signals, the ^1H NMR spectrum of **3** in $CDCl_3$ is broadly similar to that shown in Figure 1. The $^{13}C\{^1H\}$ NMR spectrum of **3** also indicated two different $C_{10}H_9Fe$ residues, approximately equally populated, and two different CHO groups.

When the temperature of a solution of **3** in $C_6D_5CD_3$ was raised incrementally from 273 to 353 K, several changes occurred in both the ^1H and ^{13}C NMR spectra corresponding to nonmutual site exchange. First, in the ^1H NMR spectrum the C_5H_5 signals coalesced at 353 K but reseparated as the solution was cooled; similar behavior was exhibited by the H_3 signals (Table IV, supplementary material). In the ^{13}C NMR spectra the C_2 signals coalesced at 293 K; in each case cooling caused reseparation of the signals (Table V, supplementary material).

Second, over the temperature range 273–343 K, from the ratio of the ^1H C_5H_5 signals the proportion of cis-rotamer **3a** increased from 55% to 66% for a concentrated solution.

Third, it was found that δ(NH-trans) for **3b** or **3c** was very sensitive to temperature, concentration, and even slight traces of impurities.

Together the NMR data are consistent with an equilibrium caused by restricted rotation about the amide C–N bond involving monomeric cis-rotamer **3a** and dimeric trans-rotamer **3c**; the values of $\Delta G^{\ddagger}$ at 293 and 323 K are close to those found for other amides.

A comparison between the $^{13}C\{^1H\}$ NMR spectra of **4** and **6** is interesting. The –C≡N resonance of the cyanide **6**

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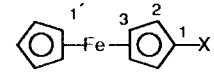
(27) (a) Nesmeyanov, A. N.; Perevalova, E. G.; Shilovsteva, L. S.; Ustynyuk, Yu. A. *Dokl. Akad. Nauk SSSR* **1959**, *124*, 331. (b) Uher, M.; Toma, S. *Zb. Pr. Chemickotechnol. Fak. SVST* **1971**, 49.
(28) Schlögl, K.; Seiler, H. *Naturwissenschaften* **1958**, *45*, 337.
(29) Trans protons NH–CHO commonly exhibit coupling in the range 11–14 Hz; the value for the corresponding cis protons falls in the range 1.7–2.3 Hz.
(30) Calculated from the Eyring equation; see e.g.: Ōki, M. *Applications of Dynamic N.M.R. Spectroscopy to Organic Chemistry*; VCH: New York, 1985.

Table II. Summary of IR, ^{1}H NMR, and ^{13}C NMR Spectra[a]



compd	X	IR ν(X), cm^{-1}	^{1}H NMR,[b] ppm $H_{1'}$	H_2	H_3	X	^{13}C NMR,[b] ppm $C_{1'}$	C_1	C_2	C_3[c]	X	ref
1	NH_2		4.12	3.99	3.85	2.6 (br)	68.7	105.5	58.7	63.2	...	10b
		3418 m, 3330 m[d]	4.10	3.98	3.83	2.5 (br)						*e*
3	NHCHO	3425 w, 3390 w sh (N—H) 1685 vs (C=O)[d]			*f*				*f*			*e*
4	N≡C	2125 vs[g]	4.27	4.50	4.08	...	70.63 (J_{CH} 176.6)	*h*	66.76 (J_{CH} 179.5)	66.76	163.92 (J_{NC} 5.6)	*e*
5	N=CHN(*i*-Pr)$_2$	1620 vs[d]	4.10	4.08	3.94	7.97 (1 H) 2.23 d (12 H) 2.40 mt (2 H)	...	...	...	...	...	*e*
6	C≡N	2220 s[d]	4.32	4.62	4.36	...	70.47 (J_{CH} 176.6)	51.8	70.82 (J_{CH} 178.5)	71.59 (J_{CH} 182.6)	119.97	*e*
							70.1	51.4	71.2	70.4	119.4	33
7	N=C=S	2215 w, 2135 vs, 2100 sh, 2078 sh[d] 2218 w, 2130 vs, 2080 sh[i]	4.23	4.36	4.0[j]	...	70.00 (J_{CH} 176.6)	85.14	65.78 (J_{CH} 182.2)	66.19 (J_{CH} 176.7)	ca. 131.7 br	*e*
8	S—C≡N	2158 m[g]	4.27	4.51	4.35	...	70.19	30.17	70.58	73.13	111.36	*e*, *l*
							69.9	*h*	70.5	72.19	*h*	33
9	CH_2—N=C=S	2196 w, 2136 vs, 2083 vs[k]										
10	NCFe(CO)$_4$	2180 m, 2158 sh (NC)[i] 2060 vs, 1994 s, 1958 m (CO)[i]										

[a] Abbreviations: br = broad; m = medium; w = weak; vs = very strong; sh = shoulder; s = singlet; d = doublet; mt = multiplet. [b] $CDCl_3$ solution; ϵ values relative to TMS; J values in Hz. [c] Resonance signals assigned according to ref 33. [d] $CHCl_3$ solution. [e] This work. [f] See Tables III–V (supplementary material). [g] Petroleum ether. [h] Not located. [i] Neat. [j] δ values concentration dependent. [k] CCl_4 solution. [l] C_6D_6 solution.

appears as a sharp singlet at δ 119.97, but the –N≡*C* resonance of the isocyanide **4** appears as a triplet centered at δ 163.92, due to ^{14}N–^{13}C coupling ($^1J_{NC}$ = 5.6 Hz). Comparable behavior is exhibited[31] by the isomeric pairs PhCN and PhNC ($^1J_{NC}$ = 5.2 Hz) and MeCN and MeNC ($^1J_{NC}$ = 5.8 Hz); the appearance of ^{14}N–^{13}C coupling in the isocyanides has been ascribed to a more symmetrical electron distribution around the nitrogen atom. Similar to the case for PhNCS, the isothiocyanate **7** exhibited a broad ^{13}C signal for the –N=*C*=S group at δ 131.7 (PhNCS, δ 135.2)[32] while the isomer **8**, FcSCN, exhibited a sharp singlet at δ 111.36 for –S–*C*≡N.

In keeping with other investigations the C_1 ^{13}C resonance signal exhibited large variation (δ 30–205 ppm) with the substituent X; only for isocyanide **4** was the C_1 resonance obscured by other resonances. Signals due to C_2 and/or C_3 have been assigned (Table II) by following the ordering pattern suggested by Nesmeyanov et al.[33] Compounds **4** and **7** also exhibited long-range interannular ^1H–^{13}C coupling, in each case the ^{13}C resonance signal for the unsubstituted ring carbons, $C_{1'}$, appearing as a doublet of quintets ($^1J_{CH}$ = 176.6 Hz, $^3J_{CH}$ = 6.5 Hz). Similar behavior has been noted previously[34] for acetylferrocene, for example.

Experimental Section

General Data. All experiments were conducted under an atmosphere of oxygen-free dry nitrogen. Neutral alumina was prepared by exposing active alumina to ethyl acetate for at least 10 days, washing (EtOH, H_2O), and reactivating at 150 °C for 18 h. Precoated "Polygram" silica gel (0.25-mm layer) and aluminum oxide (0.2-mm layer) TLC plates were obtained from Macherey-Nagel and Co. Solvent petroleum ether fractions were redistilled before use. Solution molecular weight measurements were obtained with a Hitachi-Perkin-Elmer molecular weight apparatus, Model 115. NMR spectra were obtained with a Bruker WM-250 instrument equipped with a B-VT-1000 variable-temperature facility, using TMS as an internal standard. IR spectra were obtained with a Perkin-Elmer Model 397 instrument. Mass spectra were recorded on an AEI (Kratos) MS9 mass spectrometer. Melting points were determined in unsealed capillaries, unless otherwise stated, and are uncorrected.

Cyanoferrocene was prepared by dicyclohexylcarbodiimide dehydration of the mixed oximes of ferrocenecarboxaldehyde.[21] Thiocyanatoferrocene was prepared from diferrocenylmercury.[26]

Preparation of Ferrocenylamine. *O*-Benzylhydroxylamine, the starting material for the preparation of ferrocenylamine, was prepared by hydrolysis of *O*-benzylacetoxime with use of the following modification of the procedures described by Janny[35] and by Behrend.[36]

Acetoxime (85 g, 1.16 mol) followed by benzyl chloride (146.74 g, 133.4 mL, 1.16 mol) was added to a solution of sodium ethoxide (prepared from sodium (26.68 g, 1.16 mol) and EtOH (500 mL)), and the mixture was heated on a steam bath for 1 h, causing formation of a white precipitate. The contents of the flask were added to H_2O (1000 mL) and extracted into Et_2O (5 × 100 mL), and the Et_2O extracts containing EtOH and H_2O were evaporated. The residual oil was redissolved in Et_2O (200 mL), and the Et_2O solution was washed with H_2O (50 mL), dried (Na_2SO_4), and evaporated to yield crude *O*-benzylacetoxime as a pale yellow oil (146.8 g, 77%), which was used without further purification (^1H NMR ($CDCl_3$): δ 1.80 (s, 3 H), 1.82 (s, 3 H), 5.05 (s, 2 H), 7.26 (m, 7 H)).

Crude *O*-benzylacetoxime (20 mL) and concentrated hydrochloric acid (50 mL) were mixed in a two-necked flask fitted with a gas inlet tube, reflux condenser, and stirring magnet. A slow stream of air was passed into the mixture, which was heated to reflux for 15 min and then cooled. The resulting semicrystalline mass was filtered, the white crystalline *O*-benzylhydroxylamine hydrochloride was retained, and the filtrate together with fresh *O*-benzylacetoxime (10 mL) was returned to a two-necked flask set up for distillation. The mixture was reheated in a slow stream of air until most of the volatile material had been removed. The flask was cooled, the crystalline hydrochloride filtered off, and the filtrate together with the distillate returned to the flask. The contents were heated to reflux for a further 4 h and then cooled. If a precipitate formed at this stage, it was collected and the filtrate was rejected. Typically an accumulated yield of *O*-benzylhydroxylamine hydrochloride was about 5–6 g; mp 230–260 °C dec.

A bulk sample of *O*-benzylacetoxime (132 g) was divided into six portions and hydrolyzed with concentrated hydrochloric acid (300 mL) according to the above procedure.[39] The combined yield of *O*-benzylhydroxylamine hydrochloride was 63.7 g (49%).

O-Benzylhydroxylamine hydrochloride (79.7 g, 0.498 mol) was added to Na_2CO_3 (26.4 g, 0.249 mol) in H_2O (300 mL) and the mixture stirred until the solid had dissolved. The aqueous mixture was saturated with NaCl and extracted with Et_2O (5 × 100 mL). The extracts were dried (Na_2SO_4) and evaporated, and the residue was distilled to give *O*-benzylhydroxylamine (39.95 g, 67%) as a colorless liquid, bp 124–126 °C (20 mm). The ^1H NMR spectrum ($CDCl_3$) δ 4.61 (s, 2 H), 5.18 (br, 2 H), 7.26 (br, 5 H)) confirmed the purity of the product.

Ferrocenylamine. Method A.[15b] Ferrocene (6.67 g, 0.036 05 mol) was added to a solution of *n*-butyllithium (30.67 mL, 2.6 M in *n*-hexane, 0.079 74 mol, Aldrich) in anhydrous Et_2O (250 mL). The mixture was refluxed for 6 h, allowed to stand at room temperature overnight, and then cooled to –20 °C before *O*-benzylhydroxylamine (7.99 g, 0.064 95 mol) was added dropwise. Stirring was continued for a further 15 min at –20 °C and for 30 min as the mixture was warmed to room temperature. Dilute hydrochloric acid (20 mL) was added dropwise with external cooling, and the Et_2O layer was separated, washed several times with dilute hydrochloric acid, dried, and evaporated to recover ferrocene. Ferrocenylamine (**1**), precipitated from the combined acid extracts by the addition of excess concentrated sodium hydroxide solution, was obtained as a brown solid, which was washed with H_2O, dried, and used without further purification. Four parallel experiments yielded 0.87–0.95 g of ferrocenylamine (12–13% yield).

Method B. Several experiments were performed with use of ferrocene lithiated according to the procedure of Bishop et al.[18] and employment of *N,N,N',N'*-tetramethylethylenediamine and *n*-butyllithium. Yields of ferrocenylamine were comparable with those recorded for method A.

***N*-Formylferrocenylamine (3). Method A.** Ferrocenylamine (1.2 g, 6 mmol) and freshly distilled ethyl formate (25 mL) were heated under reflux, the reaction being followed by TLC. After 5 h the formation of ferrocene was becoming significant, so the mixture was cooled and evaporated to dryness and the residue dissolved in Et_2O and extracted with dilute hydrochloric acid to remove unreacted ferrocenylamine (typically 50–60% recovery). The Et_2O solution was washed (H_2O), dried (Na_2SO_4), and evaporated to an oil, which was chromatographed on neutral alumina. Et_2O–petroleum ether (50:50) eluted ferrocene (0.10 g), and Et_2O eluted *N*-formylferrocenylamine (**3**; 0.38 g, 28% yield), which was obtained as an orange solid, mp 86–87 °C, after recrystallization from Et_2O. MS: *m/e* 229.0163 (M^+). Osmometric molecular weight measurements are reported in Table I. Anal. Calcd for $C_{11}H_{11}FeNO$ (M_r = 229.0190): C, 57.68; H, 4.84; N, 6.12. Found: C, 57.44; H, 5.09; N, 6.02.

Method B. *n*-Butyllithium in hexane (2.30 mL, 15% in hexane, 5.4 mmol) was syringed into a flask under dry nitrogen at –30 °C. Ferrocenylamine (0.5 g, 2.5 mmol) in dry Et_2O (15 mL) was added dropwise, causing the formation of **2** as an orange precipitate, and the mixture was stirred for a further 30 min. Ethyl formate (0.245

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mL, 0.185 g, 2.5 mmol) dissolved in anhydrous Et_2O (10 mL) was added slowly, and after 1 h the reaction mixture was allowed to warm to room temperature and stirred for a further 18 h. Water (15 mL) was added and the Et_2O layer separated, dried (Na_2SO_4), evaporated, and chromatographed on a column (60 cm, B14) of neutral alumina; Et_2O–petroleum ether (50:50) eluted a trace of ferrocene followed by *N*-formylferrocenylamine (**3**; 0.26 g, 46% yield).

Isocyanoferrocene (4). In a typical experiment *N*-formylferrocenylamine (**3**; 0.55 g, 2.4 mmol) was dissolved in a mixture of dry CH_2Cl_2 (10 mL) and freshly distilled diisopropylamine (0.91 mL, 0.66 g, 6.5 mmol) cooled to 0 °C under N_2. Phosphoryl chloride (0.02 mL, 0.034 g, 2.2 mmol) was added to the stirred solution from a syringe and the mixture allowed to warm to room temperature. After 18 h the flask was cooled in an ice bath and H_2O (20 mL) added dropwise to destroy the phosphoryl chloride, taking care to maintain the reaction temperature below 10 °C. The organic phase was separated with an additional volume (10 mL) of CH_2Cl_2, washed with H_2O (3 × 5 mL), dried (Na_2SO_4), and evaporated. The residual orange oil was chromatographed on a column (20 cm, B19) of neutral alumina. Petroleum ether eluted isocyanoferrocene (**4**; 0.45 g, 90% yield) as an orange band, which yielded orange crystals, mp 76–77 °C, after recrystallization from petroleum ether. MS: *m/e* 211.0080 (M^+). Anal. Calcd for $C_{11}H_9FeN$ (M_r = 211.0084): C, 62.59; H, 4.30; N, 6.64. Found: C, 62.25; H, 4.05; N, 6.44. From some experiments, which gave a lower yield of **4**, a very small second orange-red band was eluted with Et_2O. This yielded a red oil, which solidified in the refrigerator; the products from several experiments were combined and recrystallized from petroleum ether to give a small quantity of orange-red crystals, mp 46–47 °C, of the imine **5**. MS: *m/e* 312.1301 (M^+). Anal. Calcd for $C_{17}H_{24}FeN_2$ (M_r = 312.1288): C, 65.39; H, 7.75; N, 8.97. Found: C, 66.68; H, 8.48; N, 8.56. The preparation of **4** was not always reproducible, some experiments giving small amounts of ferrocene, recovered **3**, and yields of **4** as low as 46%.

Complexes of 4 with Metal Carbonyls. (a) (FcNC)Fe(CO)$_4$. Isocyanoferrocene (**4**; 90 mg, 0.43 mmol) and $Fe_2(CO)_9$ (172 mg, 0.473 mmol) were stirred together in air-free C_6H_6 (ca. 10 mL) under N_2 in a flask protected from sunlight. After 45 min the solution had changed from orange to dark red, and after 20 h TLC (SiO_2; Et_2O–petroleum ether) indicated that all of the isocyanide **4** had reacted. The mixture was filtered through Kieselguhr to remove insoluble material, evaporated, and chromatographed on a column (30 cm; B14) of neutral alumina with use of petroleum ether as eluant. A single, orange-red band was eluted to give a gummy solid (58 mg), which gave orange-red crystals, mp 40 °C, after two recrystallizations from petroleum ether (bp 40–60 °C). IR (neat): ν 2180 m, 2158 sh, 2060 vs, 1994 s, 1958 m cm^{-1}. Anal. Calcd for $C_{15}H_9Fe_2NO_4$: C, 47.54; H, 2.38; N, 3.69. Found: C, 47.59; H, 2.20; N, 3.74.

(b) (FcNC)$_2$Mo(CO)$_4$. Isocyanoferrocene (**4**; 90 mg, 0.43 mmol) and freshly sublimed tetracarbonyl(norbornadiene)molybdenum[37] (58.6 mg, 0.195 mmol) were stirred overnight at room temperature in *n*-hexane (5 mL). An orange crystalline precipitate (77 mg) was identified as *cis*-$(FcNC)_2Mo(CO)_4$, mp 104 °C. IR (petroleum ether): ν 2130 (ν(NC)), 2090, 2075 sh, 2015, 1950, 1935 cm^{-1}. Anal. Calcd for $C_{26}H_{18}Fe_2MoN_2O_4$: C, 49.56; H, 2.88; N, 4.44. Found: C, 49.56; H, 2.82; N, 4.02. Another similar preparation yielded an orange crystalline solid, mp 109–110 °C. Attempts were made to purify these materials by crystallization and chromatography, but solutions disproportionated, giving mixtures (TLC) from which a substance provisionally identified as *trans*-$(FcNC)_2Mo(CO)_4$ was isolated as orange crystals, mp 90–92 °C (IR (petroleum ether): 2135 w (ν (NC)), 2060 w, 1962 vs cm^{-1}), together with an unidentified yellow solid.

Isothiocyanatoferrocene (7). Ferrocenylamine (0.5 g, 2.49 mmol) in dry toluene (10 mL) was stirred and cooled externally in an ice bath while dry (KOH) ammonia gas was bubbled into the solution. After 10 min CS_2 (0.89 mL, 1.124 g, 14.8 mmol) was added slowly, causing a dark red precipitate to form. After 30 min the NH_3 supply was stopped, the supernatant toluene was decanted, and the red residue was dissolved in dry THF (10 mL). The solution was stirred, purged with a rapid stream of dry N_2, and cooled in an acetone–solid carbon dioxide bath, and a 12% solution of phosgene in toluene (2.39 mL) was added dropwise. After 30 min the mixture was warmed to room temperature, purged with dry N_2 for 1 h to remove excess phosgene, and evaporated. The residue was extracted with dry Et_2O, leaving a blue-gray H_2O-soluble residue. The red Et_2O extracts were filtered and evaporated to give a red oil (0.4 g). TLC analyses (silica plates, 50:50 Et_2O–petroleum ether) showed that the reaction mixture contained a trace of ferrocene, ferrocenylamine, and two substances of intermediate R_f values. The red oil was chromatographed on silica gel with use of petroleum ether to elute a trace of ferrocene followed by a major orange-red band, which yielded compound **7** as an orange-red oil (0.14 g; 32% crude yield): ether eluted ferrocenylamine (**1**; 0.14 g, 28% recovery). Isothiocyanatoferrocene (**7**) was obtained as an orange-red solid, mp 58 °C, after vacuum distillation (bath temperature 85 °C/0.001 Torr) of the orange-red oil. In the mass spectrum the molecular ion of this substance could not be identified due to coincidence with a reference ion. (Found for ^{13}C isotope peak of molecular ion, *m/e* 243.9875, which corresponds to a molecular ion *m/e* 242.9842; calcd for $C_{11}H_9FeNS$, *m/e* 242.9804. Intense fragment ions *m/e* 211.0070 [$(M - S)^+$], 199.0003 [$(M - CS)^+$], 185.0025 [$(M - NCS)^+$] were also identified). Anal. Calcd for $C_{11}H_9FeNS$: C, 54.35; H, 3.73; N, 5.76. Found: C, 54.35; H, 3.74; N, 5.73.

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Registry No. 1, 1273-82-1; 2, 124201-63-4; 3, 118805-87-1; 4, 32993-35-4; 5, 124201-64-5; 6, 1273-84-3; 7, 36472-46-5; 8, 1293-80-7; 9, 12089-11-1; 10, 124201-65-6; Fe, 102-54-5; $Fe_2(CO)_9$, 15321-51-4; *cis*-$(FeNC)_2Mo(CO)_4$, 124201-66-7; $C_7H_8Mo(CO)_4$, 12146-37-1; *trans*-$(FeNC)_2Mo(CO)_4$, 124264-42-2; *O*-benzylacetoxime, 3376-36-1; acetoxime, 127-06-0; benzyl chloride, 100-44-7; *O*-benzylhydroxylamine hydrochloride, 2687-43-6; *O*-benzylhydroxylamine, 622-33-3; ethyl formate, 109-94-4.

Supplementary Material Available: NMR data for **3** (Tables III–V) (3 pages). Ordering information is given on any current masthead page.

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