

1,3-Dipolar Cycloaddition to the Fe—N=C Fragment. 14.¹ Aromatic Isothiocyanates as Dipolarophiles. Reversible Formation of Novel [3.2.2] Bicyclic Double Isocyanide Insertion Products. Thermodynamics of Isocyanide Deinsertion Reactions

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The 1,3-dipolar cycloaddition reaction of $\text{Fe}((2,6\text{-xylyl})\text{NC})_3(i\text{-PrDAB})$ (**7**) with para-substituted phenyl isothiocyanates ($\text{R}''\text{C}_6\text{H}_4\text{NCS}$; $\text{R}'' = \text{H}$ (**a**), Me (**b**), OMe (**c**), NO_2 (**d**)) is followed by one or two isonitrile insertions. Depending on the solvent and type of isothiocyanate used, [2.2.2] and [3.2.2] bicyclic products (**10** and **11**) are isolated. Crystals of **10a**, $\text{C}_{51}\text{H}_{57}\text{N}_7\text{SFe}$, are monoclinic, space group $I2/a$, with cell constants $a = 24.041(2)$ Å, $b = 12.095(2)$ Å, $c = 36.161(6)$ Å, $V = 10502(3)$ Å³, $Z = 8$, and $R = 0.109$ for 2918 observed reflections with $I > 2.5\sigma(I)$. Compounds **11** undergo a unique reversible isocyanide deinsertion reaction when warmed in toluene. The equilibria $11\text{a-d} \rightleftharpoons 10\text{a-d} + 2,6\text{-xylyl-NC}$ have been studied by ¹H NMR. The equilibrium constants at various temperatures ($303 \text{ K} \leq T \leq 368 \text{ K}$) have been determined from which for the first time ΔG° (**a**, 16.2 ± 2.7 ; **b**, 22.7 ± 1.6 ; **c**, 23.2 ± 1.9 ; **d**, 24.7 ± 1.1 kJ/mol), ΔH° (**a**, 61.6 ± 6.3 ; **b**, 74.5 ± 3.3 ; **c**, 65.5 ± 2.0 ; **d**, 86.9 ± 2.5 kJ/mol), and ΔS° (**a**, 152 ± 29 ; **b**, 174 ± 14 ; **c**, 142 ± 12 ; **d**, 208 ± 11 J/(mol·K)) values could be calculated for isocyanide deinsertion. These values provide an explanation for the observed product selectivities in different solvents. The reactions $7 \rightleftharpoons 10$ are also reversible; however equilibrium constants could not be determined because at the required temperatures compound **7** is itself too labile.

Introduction

In the last decade one focal point of our interest has been the properties and reactivity of $\text{M}(\text{CO})_3(\text{CNR})_n$ (R'DAB)² ($\text{M} = \text{Fe}, \text{Ru}$; $n = 0, 1$, and 3) complexes with unsaturated substrates (e.g., activated alkynes,³ alkenes,⁴ and heteroallenes⁵) involving C—C and C—N bond formation leading to interesting heterocycles (see Scheme 1).

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(1) Part 13: van Wijnkoop, M.; Siebenlist, R.; Ernsting, J. M.; de Lange, P. P. M.; Frühauf, H.-W.; Vrieze, K.; Horn, E.; Spek, A. L. *J. Organomet. Chem.*, in press.

(2) The 1,4-diaza-1,3-dienes of formula $\text{R}'\text{N}=\text{CH}-\text{CH}=\text{NR}'$ are abbreviated as R'DAB .

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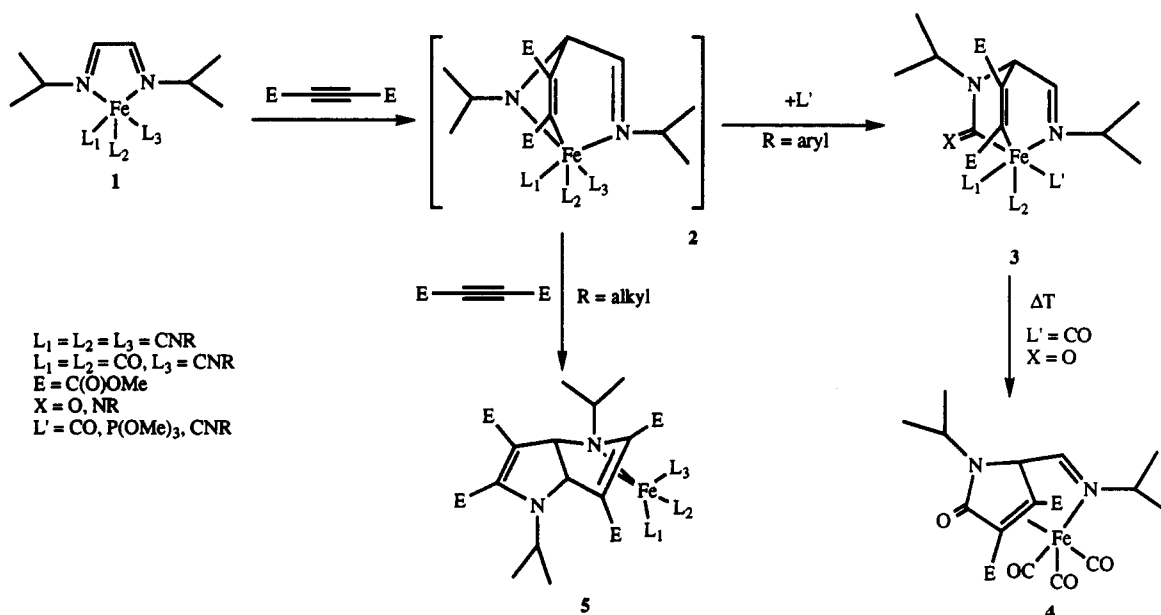
The initial step in these reactions consists of an oxidative 1,3-dipolar cycloaddition reaction of the dipolarophile, e.g., an electron deficient alkyne, across the 1,3-dipolar $\text{M}-\text{N}=\text{C}$ fragment resulting in the formation of a [2.2.1] bicyclic intermediate (**2**). This intermediate can intramolecularly react further by insertion of one of the CO or CNR ligands attached to the iron center followed by the uptake of an additional ligand L' leading to a stable [2.2.2] bicyclic compound (**3**) or **2** reacts further intermolecularly with a second dipolarophile to give a double cycloaddition product (**5**). For the formation of **5** it is necessary that at least one of the three terminal ligands in complex **1** be an aliphatic isocyanide, which is more σ -donating/worse π -accepting than CO.⁶ In the case that the three ligands **L** in **1** are CO ligands, complex **3** can undergo a reductive elimination leading to the formation of a 1,5-dihydropyrrol-2-one complex **4**.

Earlier we described a unique reversible isocyanide temperature dependent deinsertion process⁴ and the reactivity of two dipolarophiles containing C=S bonds, namely COS and CS₂.⁵ In the present paper we again employ dipolarophiles with reactive C=S bonds, namely aryl isothiocyanates, $\text{R}''\text{C}_6\text{H}_4\text{NCS}$, which are also known

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Scheme 1. Reaction Steps in the Cycloaddition of DMAD to the Fe—N=C Fragment in Complexes $\text{Fe}(\text{CO})_{3-x}(\text{CNR})_x(\text{DAB})$ ($x = 0, 1, 3$)



for their usefulness as dipolarophiles in organic cycloaddition chemistry.⁷

Experimental Section

General Information. Reactions were performed in an atmosphere of dry nitrogen using standard Schlenk techniques. Silica gel for column chromatography (silanized Kieselgel 60, 70–230 mesh, E. Merck, Darmstadt) was activated before use. Solvents were freshly distilled from sodium benzophenone–ketyl. CH_2Cl_2 was distilled from CaCl_2 . Elemental analyses were carried out by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. 2,6-Xylyl isocyanide (Fluka) and isothiocyanates a–d (Fluka) were obtained commercially and used without purification. $\text{Fe}(\text{2,6-xylyl isocyanide})_3(i\text{-PrDAB})$ (7) was prepared in situ from $\text{Fe}(i\text{-PrDAB})_2$ (6) and 2,6-xylyl isocyanide according to published procedures.^{3i,8}

Synthesis of $\text{Fe}(\text{2,6-xylylNC})_3([\text{2.2.2}]\text{bic})$ (10a). A solution of $\text{Fe}(i\text{-PrDAB})_2$ (435 mg, 1.29 mmol) and 4 equiv of 2,6-xylyl isocyanide (680 mg, 5.17 mmol) in 30 mL of hexane was stirred for 30 min. To this solution was added a solution of 1 equiv of phenyl isothiocyanate (175 mg, 1.29 mmol) in 15 mL of hexane and 5 mL of Et_2O over a period of 30 min, and then the mixture was stirred for an additional 1 h. After filtration, the resulting yellow precipitate was washed twice with 20 mL of hexane and dried in vacuo. The yield of $\text{Fe}(\text{2,6-xylylNC})_3([\text{2.2.2}]\text{bic})$ (10a) is 90–95%. The product can be crystallized from a concentrated $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (5/1) solution at -20°C .

Synthesis of $\text{Fe}(\text{2,6-xylylNC})_3([\text{2.2.2}]\text{bic})$ (10a,b) and $\text{Fe}(\text{2,6-xylylNC})_3([\text{3.2.2}]\text{bic})$ (11a–d). To a solution of $\text{Fe}(i\text{-PrDAB})_2$ (416 mg, 1.24 mmol) and 5 equiv of 2,6-xylyl–NC (812 mg, 6.19 mmol) in 30 mL of THF was added at room temperature a solution of 1 equiv of the respective isothiocyanate in 20 mL of THF over 0.5 h followed by stirring for an additional 1 h. The solution was taken to dryness in vacuo, and the crude product was redissolved in 4 mL of CH_2Cl_2 and separated by column chromatography. Elution with hexane afforded a yellow fraction containing 11. Further elution with diethyl ether afforded a yellow fraction containing 10 in a yield of 5–10%. The hexane

fraction still contained traces of 2,6-xylyl–NC and free *i*-PrDAB. Therefore the product was redissolved in 4 mL of diethyl ether and rechromatographed. Again, elution with hexane gave a yellow fraction. After removal of the solvent a yellow powder resulted, which was identified as 11 in a yield of 90–95%. The product could be further purified by means of crystallization from a concentrated solution of hexane/ Et_2O (5/1).

Reaction of 10a/b with 1 equiv of 2,6-Xylyl–NC—Formation of 11a/b. A solution of 10a (11.8 mg, 13.6 μmol) (or 10b) and 1.0 equiv of 2,6-xylyl–NC (1.78 mg, 13.6 μmol) in 0.4 mL of C_6D_6 or toluene- d_8 at 303 K was continuously monitored by ^1H NMR for circa 2 h, showing a very fast formation of 11a,b. Complex 11b was formed in 100%, whereas 10b showed an equilibrium with 11b.

NMR Study of the Equilibrium $11 \rightleftharpoons 10 + 2,6\text{-Xylyl-NC}$. Solutions of 11a–d in toluene- d_8 (calculated concentrations: 11a, 0.06094 M; 11b, 0.05490 M; 11c, 0.03019 M; 11d, 0.04112 M) were made up in an NMR tube and allowed to reach equilibrium at a temperature at which signals of 10 could be observed. From the integrals of the imine proton resonances the equilibrium constants could be calculated at a series of temperatures after the equilibrium was established (circa 45 min between each temperature increase). Each series of measurements was concluded by lowering the temperature to the initial, lowest temperature used in the experiment to check whether the same equilibrium constant was reattained. This was in all cases the same, indicating a true dynamic equilibrium behavior.

Crystal Structure of Complex 10a. Crystals were grown from a saturated $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (4/1) solution at -80°C . A crystal with approximate dimensions $0.20 \times 0.25 \times 0.40 \text{ mm}^3$ was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated $\text{Cu K}\alpha$ radiation and an ω – 2θ scan. A total of 5375 unique reflections was measured within the range $-23 \leq h \leq 23$, $-12 \leq k \leq 0$, $0 \leq l \leq 35$. Of these, 2918 were above the significance level of $2.5\sigma(I)$. The maximum value of $(\sin \theta)/\lambda$ was $0.50 \text{ \AA}^{-1}$. Two reference reflections (1,–1,2, –4,0,4) were measured every hour and showed a 5% decrease during the 62-h collecting time, which was corrected for. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with $70 < 2\theta < 72^\circ$. Corrections for Lorentz and polarization effects were applied. The structure was solved by direct methods. The hydrogen atoms were calculated. Full-matrix least-squares refinement on F , anisotropic for the non-hydrogen atoms and isotropic for the hydrogen atoms, restraining the latter in such a way that the distance to their carrier remained

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Table 1. Crystallographic Data and Details of Data Collection and Refinement of 10a

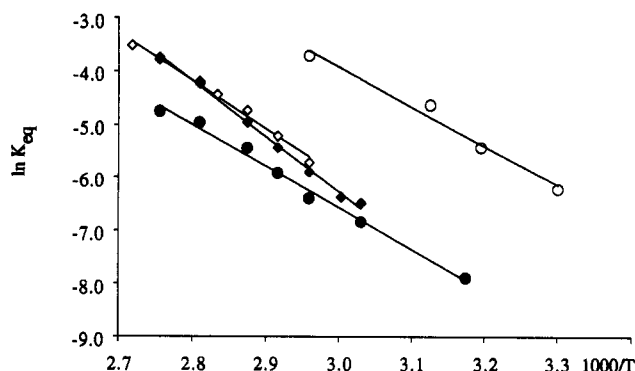
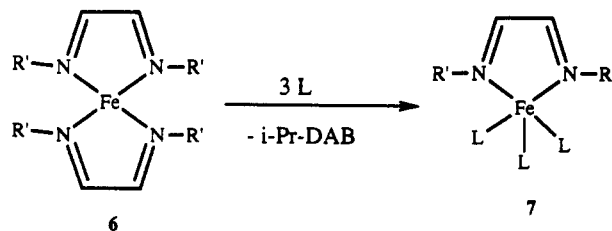
Crystal Data	
formula	C ₅₁ H ₅₇ N ₇ SFe
mol wt	856.0
cryst syst	monoclinic
space group	I2/a
a, b, c (Å)	24.041(2), 12.095(2), 36.161(6)
β (deg)	92.72(1)
V (Å) ³	10502(3)
Z	8
D _{calc} (g cm ⁻³)	1.08
F(000)	1632
μ (cm ⁻¹)	29.44
cryst size (mm ³)	0.20 × 0.25 × 0.40
Data Collection	
temp (K)	248
θ _{min} , θ _{max} (deg)	2.5, 50.4
radiation, λ (Å)	Cu Kα, 1.5418
scan type	ω-2θ
ref reflections	1, -1, 2, -4, 0, 4
total no. of data	5375
total no. of unique data	5375
no. of obs data	2918 [I > 2.5σ(I)]
Refinement	
DIFABS cor range	0.68–1.36
no. of refined params	771
final R, R _w , S	0.109, 0.152, 2.3(4)
(Δ/σ) _{max} in final cycle	0.81
min and max resd dens (e Å ⁻³)	-0.5, 1.3

constant at approximately 1.09 Å, and keeping the temperature factors of the hydrogen atoms fixed at $V = 0.15$ Å², converged to $R = 0.109$, $R_w = 0.152$, $(\Delta/\sigma)_{\max} = 0.81$. A weighting scheme $w = (6.3 + F_o + 0.0141F_o^2)^{-1}$ was used. An empirical absorption correction (DIFABS⁹) was applied, with coefficients in the range 0.68–1.36. The secondary isotropic extinction coefficient¹⁰ refined to $\text{Ext} = 2.3(4)$. A final difference Fourier map revealed a residual electron density between -0.5 and +1.3 e Å⁻³ in the vicinity of the heavy atom. Scattering factors were taken from Cromer and Mann.¹¹ The anomalous scattering of Fe and S was taken into account. All calculations were performed with XTAL¹² unless stated otherwise. Crystal data and numerical details of the structure determination are given in Table 1.

Results and Discussion

The reactions discussed in this paper are schematically shown in Scheme 3.

A solution of $\text{Fe}(\text{2,6-xylyl-NC})_3(\text{i-PrDAB})$ in either THF or hexane was prepared in situ from $\text{Fe}(\text{i-PrDAB})_2$ and 5 equiv of 2,6-xylyl-NC (Scheme 2).^{8,31} The additional 2 equiv of isocyanide is required for the formation of the [3.2.2] bicyclic complexes. As has been reported in the cases of CS₂ and COS, the isothiocyanates R'NCS add their C=S bond over the Fe—N=C unit of 7, followed by the insertion of one or two 2,6-xylyl-NC molecules, leading to [2.2.2] and [3.2.2] bicyclic complexes, respectively. Depending on the kind of R' group a different product distribution of 10 and 11 was observed. In hexane as solvent, only isothiocyanate a (R' = H) undergoes a clean reaction to give the [2.2.2] bicyclic compound 10a. The other isothiocyanates discussed in this paper gave

**Figure 1.** van't Hoff plot for the equilibrium $11 \rightleftharpoons 10 + 2,6\text{-xylyl-NC}$: R' = H (O); Me (◇) OMe (●); NO₂ (◆).**Scheme 2.** Formation of $\text{Fe}(\text{2,6-xylylNC})_3\text{-}i\text{-PrDAB}$ (7)

L = 2,6-xylyl-NC
R' = i-Pr

untractable mixtures of products and decomposition products when hexane was used as solvent. In THF as solvent, the reaction directly leads to the formation of complexes 11a–d; 10a and 10b were formed in a minor amount.

When complexes 11a–d are slightly warmed in either benzene-*d*₆ or toluene-*d*₈, they undergo an isocyanide deinsertion leading to the [2.2.2] bicyclic compounds 10a–d, respectively. On further heating to reflux temperature in deuterated toluene in a NMR tube, an immediate color change from yellow to red was observed. This indicates the back-formation of complex 7, which was also proven by ¹H NMR. On cooling again, the red color disappeared. So, the whole reaction sequence shown in Scheme 3 is reversible.

The first step in this reversible process, the deinsertion of an isocyanide, going from 11 to 10, was monitored by ¹H NMR in deuterated toluene at different temperatures. At every temperature, which was chosen in a suitable temperature range, an equilibrium constant (K_{eq}) could be calculated from the start concentration of 11 and the relative amounts of 10 and 11 at a certain temperature, determined from the integrals of the imine proton resonances in the ¹H NMR spectra. The measured data points give straight lines when plotting the reciprocal temperature ($1/T$) values against the natural logarithm ($\ln K_{\text{eq}}$) values (Figure 1). Using the assumption that ΔH° and ΔS° are constant over the employed temperature range, the thermodynamic standard parameters ΔH° , ΔG° , and ΔS° for the isocyanide deinsertion reaction $11 \rightleftharpoons 10$ have been calculated¹³ and are collected in Table 2. We also tried to determine the thermodynamic values for the reverse reaction $10 \rightleftharpoons 7$, but this, just as in the case of dimethyl maleate as dipolarophile,⁴ was impeded by the

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(13) ΔH° is obtained from the slope $-\Delta H/R$; $\Delta G^\circ = R \cdot 298 \text{ K} \cdot \ln K_{\text{eq}}(298 \text{ K})$; $\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/298 \text{ K}$.

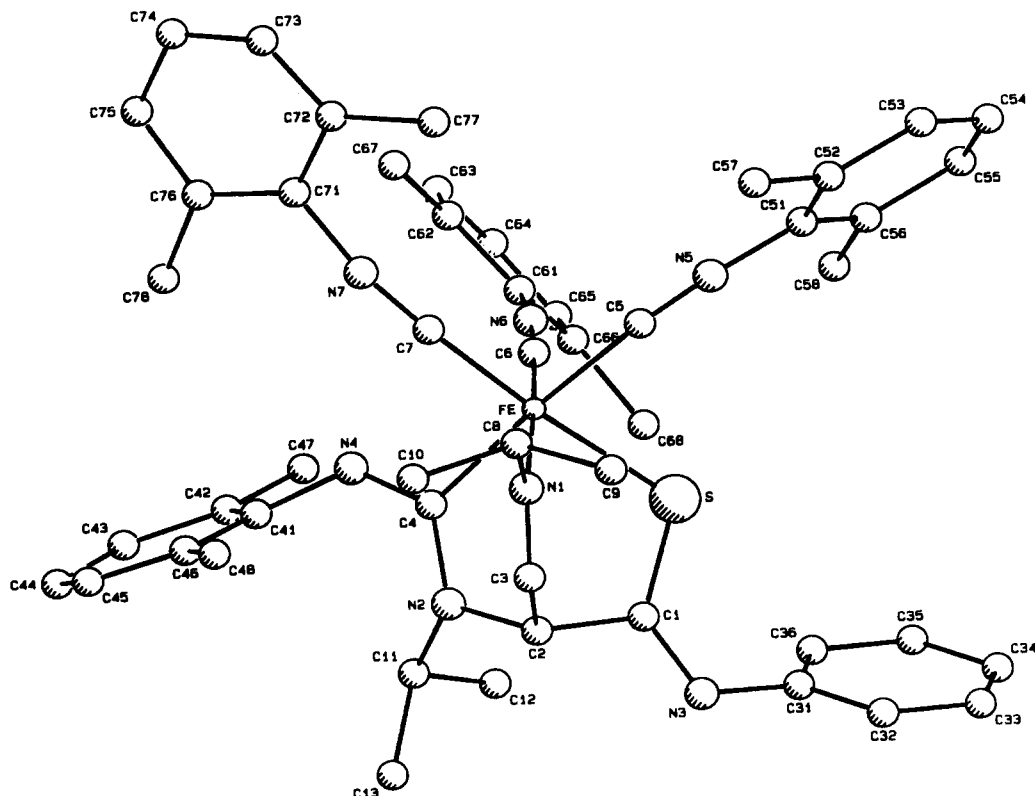
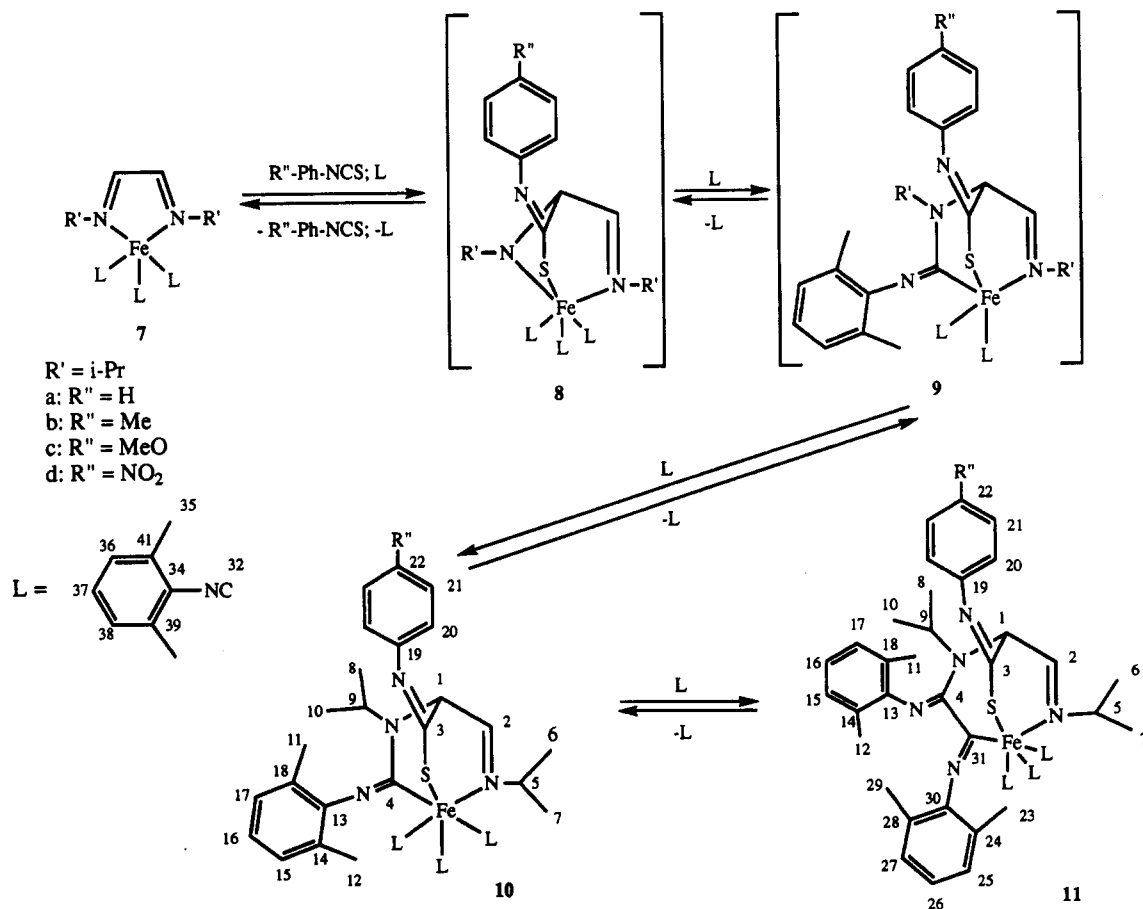


Figure 2. PLUTO drawing of complex 10a.

Scheme 3. Reversible Cycloaddition of $\text{Fe}((2,6\text{-xylyl})\text{NC})_3(i\text{-PrDAB})$ to $\text{R}''\text{PhNCS}$ 

fact that no stable equilibria could be obtained at the required temperatures, because compound 7 starts to decompose above 373 K.

The present clean reactions are only observed with aryl isocyanides in 7 and aryl isothiocyanates as dipolarophiles. Attempts to use alkyl isothiocyanates as dipolarophiles

Table 2. Thermodynamic Values for the Reactions $11 \rightleftharpoons 10 + \text{RNC}$ (RNC = 2,6-Xylyl-NC)

R'' group	K_{eq} (298 K) (mol/L)	ΔG° (298 K) (kJ/mol)	ΔH° (298 K) (kJ/mol)	ΔS° (298 K) [J/(mol K)]
H	1.43×10^{-3}	16.2 ± 2.7	61.6 ± 6.3	152 ± 29
Me	1.06×10^{-4}	22.7 ± 1.6	74.5 ± 3.3	174 ± 14
OMe	8.50×10^{-5}	23.2 ± 1.9	65.5 ± 2.0	142 ± 12
NO ₂	4.59×10^{-5}	24.7 ± 1.1	86.9 ± 2.5	208 ± 11

Table 3. Fractional Coordinates of the Non-Hydrogen Atoms, and Equivalent Isotropic Thermal Parameters of Complex 10a (Esd's in Parentheses)

	x	y	z	U_{eq} (Å ²)
Fe	0.51339(9)	0.2550(2)	0.65551(6)	0.047(1)
S	0.5773(2)	0.3935(3)	0.6714(1)	0.056(3)
C(1)	0.6274(6)	0.326(1)	0.6985(4)	0.05(1)
C(2)	0.6201(6)	0.203(1)	0.7021(5)	0.06(1)
C(3)	0.5653(7)	0.176(1)	0.7218(4)	0.05(1)
C(4)	0.5749(6)	0.150(1)	0.6429(4)	0.05(1)
C(5)	0.4603(6)	0.363(2)	0.6664(4)	0.05(1)
C(6)	0.5182(6)	0.306(1)	0.6089(5)	0.05(1)
C(7)	0.4620(7)	0.157(1)	0.6383(4)	0.05(1)
C(8)	0.4697(7)	0.159(1)	0.7265(4)	0.06(1)
C(9)	0.4672(8)	0.226(2)	0.7625(6)	0.09(1)
C(10)	0.4728(9)	0.034(2)	0.7338(7)	0.10(2)
C(11)	0.6767(6)	0.116(1)	0.6530(5)	0.06(1)
C(12)	0.7062(8)	0.221(2)	0.6399(6)	0.08(1)
C(13)	0.7150(9)	0.058(2)	0.6827(7)	0.11(2)
C(31)	0.6801(7)	0.484(1)	0.7136(5)	0.06(1)
C(32)	0.6810(7)	0.544(2)	0.7456(6)	0.07(1)
C(33)	0.6889(9)	0.656(2)	0.7442(8)	0.10(2)
C(34)	0.6968(8)	0.710(2)	0.712(1)	0.10(2)
C(35)	0.6974(9)	0.650(2)	0.6783(8)	0.10(2)
C(36)	0.6884(8)	0.534(2)	0.6807(6)	0.09(2)
C(41)	0.5957(6)	-0.002(1)	0.6011(4)	0.05(1)
C(42)	0.6196(7)	0.001(1)	0.5673(5)	0.06(1)
C(43)	0.6432(8)	-0.100(2)	0.5519(6)	0.09(2)
C(44)	0.643(1)	-0.195(2)	0.5708(7)	0.10(2)
C(45)	0.6145(9)	-0.197(2)	0.6052(7)	0.09(2)
C(46)	0.5930(7)	-0.103(2)	0.6203(5)	0.06(1)
C(47)	0.623(1)	0.111(2)	0.5455(6)	0.10(2)
C(48)	0.5664(8)	-0.109(2)	0.6564(6)	0.08(1)
C(51)	0.4049(6)	0.538(1)	0.6762(4)	0.05(1)
C(52)	0.3587(8)	0.546(1)	0.6975(5)	0.07(1)
C(53)	0.3324(9)	0.648(2)	0.6997(6)	0.08(1)
C(54)	0.353(1)	0.739(2)	0.6842(7)	0.09(2)
C(55)	0.398(1)	0.729(2)	0.6624(7)	0.09(2)
C(56)	0.4260(8)	0.630(2)	0.6586(5)	0.07(1)
C(57)	0.3361(8)	0.443(2)	0.7163(6)	0.09(2)
C(58)	0.475(1)	0.615(2)	0.6363(6)	0.10(2)
C(61)	0.5354(8)	0.362(1)	0.5415(4)	0.06(1)
C(62)	0.501(1)	0.314(2)	0.5138(6)	0.09(2)
C(63)	0.516(2)	0.340(3)	0.4770(8)	0.14(3)
C(64)	0.564(2)	0.408(4)	0.471(1)	0.19(4)
C(65)	0.596(2)	0.448(2)	0.4994(8)	0.14(3)
C(66)	0.581(1)	0.428(2)	0.5354(7)	0.09(2)
C(67)	0.452(2)	0.246(3)	0.522(1)	0.15(3)
C(68)	0.618(1)	0.470(3)	0.5678(9)	0.13(2)
C(71)	0.3812(8)	0.045(1)	0.6058(5)	0.06(1)
C(72)	0.3283(7)	0.079(2)	0.6133(5)	0.07(1)
C(73)	0.286(1)	0.024(3)	0.5943(7)	0.11(2)
C(74)	0.293(1)	-0.049(3)	0.5678(7)	0.11(2)
C(75)	0.346(1)	-0.083(2)	0.5613(6)	0.11(2)
C(76)	0.3940(8)	-0.036(2)	0.5790(5)	0.07(1)
C(77)	0.319(1)	0.162(2)	0.6435(9)	0.12(2)
C(78)	0.452(1)	-0.070(2)	0.5729(7)	0.10(2)
N(1)	0.5189(6)	0.190(1)	0.7066(3)	0.050(8)
N(2)	0.6219(5)	0.142(1)	0.6670(3)	0.052(8)
N(3)	0.6695(6)	0.370(1)	0.7175(3)	0.057(9)
N(4)	0.5680(5)	0.094(1)	0.6122(3)	0.052(8)
N(5)	0.4316(6)	0.437(1)	0.6730(4)	0.056(9)
N(6)	0.5230(6)	0.335(1)	0.5790(4)	0.06(1)
N(7)	0.4272(5)	0.097(1)	0.6243(4)	0.059(9)

were not successful. Reactions of Fe((alkyl)NC)₃(i-PrDAB) with some of the para-substituted aromatic isothiocyanates have also been carried out. The products are also [2.2.2] bicyclic compounds, but in these com-

Table 4. Bond Lengths (Å) for the Non-Hydrogen Atoms of Complex 10a (Esd's in Parentheses)

Fe—S	2.326(5)	C(42)—C(43)	1.46(3)
Fe—C(4)	2.01(2)	C(42)—C(47)	1.55(3)
Fe—C(5)	1.88(2)	C(43)—C(44)	1.35(3)
Fe—C(6)	1.80(2)	C(44)—C(45)	1.45(4)
Fe—C(7)	1.80(2)	C(45)—C(46)	1.37(3)
Fe—N(1)	2.01(1)	C(46)—C(48)	1.48(3)
S—C(1)	1.72(2)	C(51)—C(52)	1.39(2)
C(1)—C(2)	1.50(2)	C(51)—C(56)	1.38(3)
C(1)—N(3)	1.31(2)	C(51)—N(5)	1.39(2)
C(2)—C(3)	1.56(2)	C(52)—C(53)	1.39(3)
C(2)—N(2)	1.47(2)	C(52)—C(57)	1.53(3)
C(3)—N(1)	1.23(2)	C(53)—C(54)	1.34(3)
C(4)—N(2)	1.40(2)	C(54)—C(55)	1.37(4)
C(4)—N(4)	1.31(2)	C(55)—C(56)	1.40(3)
C(5)—N(5)	1.16(2)	C(56)—C(58)	1.47(3)
C(6)—N(6)	1.15(2)	C(61)—C(62)	1.40(3)
C(7)—N(7)	1.20(2)	C(61)—C(66)	1.39(3)
C(8)—C(9)	1.54(3)	C(61)—N(6)	1.44(2)
C(8)—C(10)	1.53(3)	C(62)—C(63)	1.43(4)
C(8)—N(1)	1.46(2)	C(62)—C(67)	1.47(5)
C(11)—C(12)	1.54(3)	C(63)—C(64)	1.44(7)
C(11)—C(13)	1.55(3)	C(64)—C(65)	1.35(5)
C(11)—N(2)	1.47(2)	C(65)—C(66)	1.39(4)
C(31)—C(32)	1.37(3)	C(66)—C(68)	1.52(4)
C(31)—C(36)	1.36(3)	C(71)—C(72)	1.38(3)
C(31)—N(3)	1.41(2)	C(71)—C(76)	1.42(3)
C(32)—C(33)	1.36(3)	C(71)—N(7)	1.42(2)
C(33)—C(34)	1.37(4)	C(72)—C(73)	1.37(3)
C(34)—C(35)	1.41(4)	C(72)—C(77)	1.51(4)
C(35)—C(36)	1.42(4)	C(73)—C(74)	1.32(4)
C(41)—C(42)	1.38(2)	C(74)—C(75)	1.37(4)
C(41)—C(46)	1.41(2)	C(75)—C(76)	1.41(3)
C(41)—N(4)	1.41(2)	C(76)—C(78)	1.47(3)

pounds there are two molecules of isothiocyanate involved. We do not observe double cycloaddition products analogous to 5. The structure and properties of these products are still under investigation.

Molecular Structure of Complex 10a. The molecular structure of complex 10a together with the atomic numbering is shown in Figure 2. In Tables 3–5 the atomic coordinates and bond lengths and angles are given.

The molecular structure of complex 10a has a familiar [2.2.2] bicyclic skeleton that has been found earlier for the CS₂ case⁵ and is therefore comparable with the latter. This structure clearly shows that the isothiocyanate has been cycloadded over the C(1)=S bond. The geometry around the metal atom is slightly distorted octahedral. The Fe—S bond length in complex 10a (2.326(5) Å) is comparable with the value found for the CS₂ compound (2.311(3) Å). In complex 10a the bond distance of C(1)—S is 1.72(2) Å; in the CS₂ structure this distance is 1.662(12) Å. The angle S—C(1)—N(3) in 10a is greater than the corresponding S—C=S angle. This is attributed to a decreased delocalization in the S—C(1)—N(3) unit. Also the greater electronegativity of the N(3) atom as compared to that of an S atom may play a role.

The mean angles around C(1) (120°) indicate the change from sp to sp² hybridization, due to the cycloaddition reaction. Correspondingly, the hybridization around N(3) has also changed.

Due to the insertion the C(4)—N(4) bond is reduced from a triple to a double bond, which is reflected in a greater bond distance compared with that found in the terminally coordinated isocyanides. Also the angle round N(4) indicates sp² hybridization.

The distances and angles found in the C≡N—C_{aryl} units are characteristic for terminally coordinated isocyanides.⁶

Table 5. Bond Angles (deg) for the Non-Hydrogen Atoms of Complex 10a (Esd's in Parentheses)

S-Fe-C(4)	91.4(5)	C(44)-C(45)-C(46)	122(2)
S-Fe-C(5)	83.9(5)	C(41)-C(46)-C(45)	120(2)
S-Fe-C(6)	85.1(5)	C(41)-C(46)-C(48)	120(2)
S-Fe-C(7)	173.3(5)	C(45)-C(46)-C(48)	120(2)
S-Fe-N(1)	92.2(4)	C(52)-C(51)-C(56)	121(2)
C(4)-Fe-C(5)	174.8(7)	C(52)-C(51)-N(5)	119(1)
C(4)-Fe-C(6)	85.6(7)	C(56)-C(51)-N(5)	119(1)
C(4)-Fe-C(7)	90.4(7)	C(51)-C(52)-C(53)	118(2)
C(4)-Fe-N(1)	87.0(6)	C(51)-C(52)-C(57)	120(2)
C(5)-Fe-C(6)	91.7(7)	C(53)-C(52)-C(57)	122(2)
C(5)-Fe-C(7)	94.0(7)	C(52)-C(53)-C(54)	122(2)
C(5)-Fe-N(1)	95.4(6)	C(53)-C(54)-C(55)	119(2)
C(6)-Fe-C(7)	88.7(7)	C(54)-C(55)-C(56)	122(2)
C(6)-Fe-N(1)	172.0(6)	C(51)-C(56)-C(55)	117(2)
C(7)-Fe-N(1)	94.3(6)	C(51)-C(56)-C(58)	119(2)
Fe-S-C(1)	103.7(5)	C(55)-C(56)-C(58)	124(2)
S-C(1)-C(2)	116(1)	C(62)-C(61)-C(66)	125(2)
S-C(1)-N(3)	128(1)	C(62)-C(61)-N(6)	116(2)
C(2)-C(1)-N(3)	116(1)	C(66)-C(61)-N(6)	119(2)
C(1)-C(2)-C(3)	111(1)	C(61)-C(62)-C(63)	114(2)
C(1)-C(2)-N(2)	114(1)	C(61)-C(62)-C(67)	123(2)
C(3)-C(2)-N(2)	110(1)	C(63)-C(62)-C(67)	123(3)
C(2)-C(3)-N(1)	122(1)	C(62)-C(63)-C(64)	120(3)
Fe-C(4)-N(2)	119(1)	C(63)-C(64)-C(65)	122(3)
Fe-C(4)-N(4)	117(1)	C(64)-C(65)-C(66)	119(3)
N(2)-C(4)-N(4)	124(1)	C(61)-C(66)-C(65)	119(2)
Fe-C(5)-N(5)	174(1)	C(61)-C(66)-C(68)	121(2)
Fe-C(6)-N(6)	177(1)	C(65)-C(66)-C(68)	120(2)
Fe-C(7)-N(7)	175(1)	C(72)-C(71)-C(76)	125(2)
C(9)-C(8)-C(10)	112(2)	C(72)-C(71)-N(7)	119(2)
C(9)-C(8)-N(1)	110(1)	C(76)-C(71)-N(7)	116(2)
C(10)-C(8)-N(1)	108(1)	C(71)-C(72)-C(73)	115(2)
C(12)-C(11)-C(13)	109(2)	C(71)-C(72)-C(77)	121(2)
C(12)-C(11)-N(2)	111(1)	C(73)-C(72)-C(77)	123(2)
C(13)-C(11)-N(2)	112(1)	C(72)-C(73)-C(74)	124(2)
C(32)-C(31)-C(36)	120(2)	C(73)-C(74)-C(75)	119(2)
C(32)-C(31)-N(3)	116(2)	C(74)-C(75)-C(76)	123(2)
C(36)-C(31)-N(3)	124(2)	C(71)-C(76)-C(75)	113(2)
C(31)-C(32)-C(33)	119(2)	C(71)-C(76)-C(78)	122(2)
C(32)-C(33)-C(34)	122(3)	C(75)-C(76)-C(78)	125(2)
C(33)-C(34)-C(35)	119(2)	Fe-N(1)-C(3)	119(1)
C(34)-C(35)-C(36)	117(2)	Fe-N(1)-C(8)	122(1)
C(31)-C(36)-C(35)	122(2)	C(3)-N(1)-C(8)	119(1)
C(42)-C(41)-C(46)	119(2)	C(2)-N(2)-C(4)	117(1)
C(42)-C(41)-N(4)	117(1)	C(2)-N(2)-C(11)	118(1)
C(46)-C(41)-N(4)	123(1)	C(4)-N(2)-C(11)	121(1)
C(41)-C(42)-C(43)	120(2)	C(1)-N(3)-C(31)	119(1)
C(41)-C(42)-C(47)	120(2)	C(4)-N(4)-C(41)	129(1)
C(43)-C(42)-C(47)	119(2)	C(5)-N(5)-C(51)	167(2)
C(42)-C(43)-C(44)	121(2)	C(6)-N(6)-C(61)	173(2)
C(43)-C(44)-C(45)	117(2)	C(7)-N(7)-C(71)	170(2)

NMR Spectroscopy. ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR data of the $\text{Fe}((2,6\text{-xylyl})\text{NC})_3[2.2.2]\text{bic}$ (10a,b) and $\text{Fe}((2,6\text{-xylyl})\text{NC})_3[3.2.2]\text{bic}$ (11a-d) are listed in Tables 6 and 7, respectively; the atomic numbering is given in Scheme 3.

^1H NMR. The ^1H NMR data for complexes 10a,b are in agreement with those of the isostructural complexes 3.^{1,3i-5} The spectra show the familiar pattern for this kind of [2.2.2] bicyclic complexes. Not surprisingly, the spectra of the [3.2.2] complexes 11 show a pattern similar to that of their bicyclo[2.2.2] precursors 10, except for the appearance of in total four methyl signals in the region 2.21–2.70 ppm. The imine proton atoms resonate in the region 8.38–8.41 ppm as doublets with a coupling constant of 5.8–5.9 Hz. This is 0.11–0.15 ppm shifted upfield whereas the coupling constant is not significantly different from that for complexes 10.

^{13}C NMR. The effect of rehybridization of the former imine carbon atom from sp^2 to sp^3 is also observed in the ^{13}C NMR spectra of complexes 10 and 11. The intact imine carbon nucleus (C(2)) resonates at 169.0 ppm for 10

and around 162.5 ppm for 11, whereas the bridgehead, the former imine carbon nucleus (C(5)), resonates at 64.5–64.6 ppm for 10 and 61.6–61.8 ppm for 11. The terminal isocyanide carbon nuclei (C(32)) give three signals for complexes 10 and 11. This indicates that the three terminal isocyanide ligands do not interchange positions on the NMR time scale. The signals found for 11 are shifted downfield compared with the chemical shifts of the signals of 10. This means a greater deshielding effect for the carbon nuclei which can be explained by a greater π -back-donation from metal to ligand. The aryl rings of the terminal isocyanide ligands can rotate freely, which is evident from the equivalency of the methyl groups which give three signals for the six methyl groups. The carbon atoms (C(3)) of the isothiocyanate unit of 10 and 11 are found at circa 213.5 ppm. In the free isothiocyanates these carbon atoms resonate in the region 135–141 ppm, which means a marked downfield shift of circa 75 ppm as a consequence of the cycloaddition reaction. A comparable downfield shift has also been observed for the CS_2 carbon atom in the [2.2.2] bicyclic compound⁵ formed from 7 and CS_2 . Again, this has to be ascribed to rehybridization during the cycloaddition, in this case from sp to sp^2 .

IR Spectroscopy. The IR data for complexes 10 and 11 together with the elemental analyses and the FAB mass spectral data are listed in Table 8.

The $\text{C}\equiv\text{N}$ stretching vibration values are a measure of the amount of π -back-donation from the metal into the orthogonal, $\text{C}\equiv\text{N}$ antibonding π^* -orbitals of the terminal isocyanide ligands. For this reason it is interesting to compare the $\text{C}\equiv\text{N}$ stretching frequencies in 10 and 11 with those in cycloaddition products of 7 and other dipolarophiles.

Compared with the earlier described cycloaddition products formed from 7 and dipolarophiles containing $\text{C}=\text{S}$ bonds⁵ (COS and CS_2), complexes 10 show more π -back-donation from the iron(II) ion to the isocyanide ligands. The $\text{C}\equiv\text{N}$ stretching bonds of complexes 10 are found at slightly higher wavenumbers than those of the [2.2.2] bicyclic compound^{3i,4} formed from 7 and DMAD or DMM. The $\text{C}\equiv\text{N}$ stretching frequencies of 11 are lower than those of 10, i.e., less π -back-donation to the terminal isocyanide ligands of the latter.

If the aryl groups of the isocyanide ligands are less electron withdrawing, this will increase the $\text{C}-\text{N}$ bond order and consequently the $\text{C}\equiv\text{N}$ stretching frequency. So, for a given isocyanide, the order for π -back-donation from metal to ligand is



Dependent on the type of bicyclic compound and on the dipolarophile used for the cycloaddition reaction, different degrees of π -back-donation character can be observed. This trend is also observed in the ^{13}C NMR spectra of 10 and 11 (vide supra).

Compared with the $\text{C}\equiv\text{N}$ stretching frequencies of the $\text{Fe}(0)$ starting complex 7³ⁱ (2070 (strong) and 1970 (broad) cm^{-1}), the terminal isocyanides of all complexes show more σ -donation and less π -back-donation after the cycloaddition reaction. This is a logical consequence of the fact that the central iron atom after the reaction is in the formal oxidation state (+2).

Complex Formation. The first step in the reaction of $\text{Fe}(\text{CO})_{3-n}(\text{RNC})_n(i\text{-PrDAB})$ complexes with alkynes ($n = 0, 1, 3$), alkenes ($n = 3$), and heteroallenic $\text{C}=\text{S}$ bonds

Table 6. ^1H NMR Data^a for Complexes 10 and 11 (Atomic Numbering as in Scheme 3)

	10a	11a	10b	11b	11c	11d
nucleus						
H(1)	5.26, d, 1H, 5.6 Hz	5.07, d, 1H, 5.9 Hz	5.25, d, 1H, 5.5 Hz	5.06, d, 1H, 5.9 Hz	5.06, d, 1H, 5.9 Hz	5.08, d, 1H, 6.0 Hz
H(2)	8.53, d, 1H, 5.6 Hz	8.41, d, 1H, 5.9 Hz	8.52, d, 1H, 5.6 Hz	8.39, d, 1H, 5.9 Hz	8.40, d, 1H, 5.8 Hz	8.38, d, 1H, 5.9 Hz
H(5), H(9)	4.57, sept, 2H, 6.8 Hz	4.21, sept, 1H, 6.7 Hz 2.67, sept, 1H, 6.8 Hz	4.58, sept, 1H, 6.6 Hz 4.51, sept, 1H, 6.7 Hz	4.20, sept, 1H, 6.6 Hz 2.66, sept, 1H, 6.2 Hz	4.19, sept, 2H, 6.6 Hz	4.22, sept, 1H, 6.7 Hz 3.13, sept, 1H, 6.8 Hz
H(6)–H(8), H(10)	1.43, d, 3H, 6.7 Hz 1.39, d, 3H, 6.6 Hz 1.11, d, 3H, 6.8 Hz 0.99, d, 3H, 6.6 Hz	1.31, d, 3H, 6.6 Hz 0.93, d, 3H, 6.3 Hz 0.87, d, 3H, 6.3 Hz 0.87, d, 3H, 6.2 Hz	1.42, d, 3H, 6.7 Hz 1.39, d, 3H, 6.6 Hz 1.10, d, 3H, 6.7 Hz 0.98, d, 3H, 6.6 Hz	1.31, d, 3H, 6.5 Hz 0.92, d, 3H, 6.4 Hz 0.87, d, 3H, 6.6 Hz 0.86, d, 3H, 6.2 Hz	1.30, d, 3H, 6.5 Hz 0.93, d, 3H, 6.3 Hz 0.87, d, 6H, 6.4 Hz	1.30, d, 3H, 6.5 Hz 1.23, d, 3H, 6.3 Hz 0.94, d, 3H, 6.4 Hz 0.87, d, 3H, 6.4 Hz
H(11)–H(12), H(23), H(29)	2.03, s, 3H 1.95, s, 3H	2.69, s, 3H 2.64, s, 3H 2.29, s, 3H 2.23, s, 3H	2.02, s, 3H 1.95, s, 3H	2.69, s, 3H 2.63, s, 3H 2.29, s, 3H 2.22, s, 3H	2.70, s, 3H 2.64, s, 3H 2.31, s, 3H 2.23, s, 3H	2.67, s, 3H 2.63, s, 3H 2.27, s, 3H 2.21, s, 3H
H(15)–H(17), H(25)–H(27)	6.69, d, 1H, 6.8 Hz 6.57, d, 1H, 7.0 Hz 6.40, dd, 1H, 7.2/7.3 Hz	6.53, d, 1H, 7.0 Hz 6.47, d, 1H, 7.0 Hz 6.38, d, 1H, 7.1 Hz 5.86, dd, 1H, 7.4/7.4 Hz 7.21–6.76, m, 1H ^b	6.72, d, 1H, 7.1 Hz 6.57, d, 1H, 7.2 Hz 6.39, dd, 1H, 7.3/7.4 Hz	6.45, d, 1H, 8.0 Hz 6.37, d, 1H, 7.3 Hz 5.84, dd, 1H, 7.4/7.4 Hz 7.18–6.70, m, 3H	6.60–6.47, m, 4H 6.37, d, 1H, 7.1 Hz 5.82, dd, 1H, 7.4/7.4 Hz	6.89, dd, 1H 8.0/7.1 Hz 6.49, d, 1H, 7.4 Hz 6.39, d, 1H, 7.4 Hz 5.88, dd, 1H, 7.4/7.4 Hz 6.5–7.8, m, 13H
H(20)–H(22), H(36)–H(38)	7.4–6.9, m, 13H	7.21–6.76, m, 13H	7.30–6.90, m, 13H	7.18–6.70, m, 13H	7.3–6.7, m, 13H	
H(35), H(40)	2.35, s, 6H 2.33, s, 6H 2.27, s, 6H	2.57, s, 6H 2.39, s, 6H 2.00, s, 6H	2.34, s, 12H 2.28, s, 6H	2.56, s, 6H 2.38, s, 6H 2.00, s, 6H 2.20, s, 3H	2.57, s, 6H 2.41, s, 6H 2.01, s, 6H 3.73, s, 3H	2.55, s, 6H 2.39, s, 6H 2.00, s, 6H
R''	7.4–6.9, s, 1H	7.21–6.76, m, 1H	2.31, s, 3H			

^a Chemical shifts are in ppm relative to Me₄Si; measured in CDCl₃ at 293 K and 300.13 MHz. ^b Hidden under signals of H(20), etc.Table 7. Relevant ^{13}C NMR Data^a for Complexes 10 and 11 (Atomic Numbering as in Scheme 3)

compd	^{13}C NMR data
10a	213.4 [C(3)]; 191.3 [C(4)]; 180.7, 180.3, 176.6 [C(32)]; 169.0 [C(2)]; 154.5, 154.8 [C(13, 19)]; 135.3, 134.8 [C(39, 41)]; 130.1, 129.9, 129.1, 127.7, 127.6 [C(14, 18, 34)]; 68.6 [C(1)]; 64.5 [C(5)]; 48.2 [C(9)]
10b	214.0 [C(3)]; 191.4 [C(4)]; 181.3, 180.0, 179.2 [C(32)]; 169.0 [C(2)]; 153.8, 151.9 [C(13, 19)]; 135.3, 135.2, 134.8 [C(39, 41)]; 132.0, 130.2, 130.0, 129.1, 127.0 [C(14, 18, 34)]; 69.1 [C(1)]; 64.6 [C(5)]; 48.3 [C(9)]
11a	213.7 [C(3)]; 188.6, 182.8, 178.4 [C(32)]; 181.7, 177.0 [C(4, 31)]; 162.7 [C(2)]; 153.3 [C(19)]; 149.5, 140.4 [C(13, 30)]; 136.2, 135.6, 130.0, 129.7, 129.1, 128.1, 128.0 [C(14, 18, 24, 28, 34)]; 72.1 [C(1)]; 61.6 [C(5)]; 53.3 [C(9)]
11b	213.7 [C(3)]; 188.6, 182.8, 178.5 [C(32)]; 181.9, 176.6 [C(4, 31)]; 162.7 [C(2)]; 150.8 [C(19)]; 149.5, 140.4 [C(13, 30)]; 136.2, 135.5, 130.0, 129.7, 129.0, 128.4, 128.1 [C(14, 18, 24, 28, 34)]; 135.7, 135.6 [C(39, 41)]; 131.7 [C(22)]; 72.1 [C(1)]; 61.6 [C(5)]; 53.3 [C(9)]
11c	213.5 [C(3)]; 188.6, 182.9, 178.5 [C(32)]; 181.7, 176.6 [C(4, 31)]; 162.7 [C(2)]; 155.2 [C(19)]; 149.5, 146.5 [C(13, 30)]; 140.35, 136.2, 130.0, 129.7, 129.0, 128.3, 128.0 [C(14, 18, 24, 28, 34)]; 135.7, 133.9 [C(39, 41)]; 72.2 [C(1)]; 61.6 [C(5)]; 55.8 [C(R''=OMe)]; 53.3 [C(9)]
11d	213.5 [C(3)]; 187.6, 182.4, 177.2 [C(32)]; 180.5, 179.5 [C(4, 31)]; 162.3 [C(2)]; 159.9 [C(19)]; 149.1, 142.9 [C(13, 30)]; 140.1 [C(22)]; 136.1, 135.4, 133.9, 129.7, 129.4, 128.4, 127.8 [C(14, 18, 24, 28, 34)]; 135.5, 135.4 [C(39, 41)]; 71.8 [C(1)]; 61.8 [C(5)]; 53.4 [C(9)]

^a Chemical shifts are in ppm relative to Me₄Si, measured in CDCl₃ at 263 K and 75.47 MHz.Table 8. IR Data, Elemental Analyses, and FAB Mass Data for Fe((2,6-xylyl)NC)₃[(2.2.2)bic] (10a,b) and Fe((2,6-xylyl)NC)₃[(3.2.2)bic] (11a–d)

compd	$\nu_{\text{C=N}}$ (cm ⁻¹) ^a	M ^b	elemental anal. (%)		
			C _{obs} (C _{calc})	H _{obs} (H _{calc})	N _{obs} (N _{calc})
10a	2138, 2075 (s)	856 (856)	71.56 (70.15)	6.72 (7.28)	11.45 (10.28)
10b	2134, 2080 (b)		69.76 (71.79)	7.15 (6.84)	11.14 (11.27)
11a	2118 (w), 2069 (sh), 2051 (s)	987 (987)	73.09 (73.00)	6.69 (6.74)	11.26 (11.35)
11b	2118 (w), 2069 (sh), 2048 (s)	1001 (1001)	72.94 (73.18)	6.79 (6.85)	11.17 (11.19)
11c	2118 (w), 2068 (sh), 2050 (s)	1017 (1017)	72.03 (71.44)	6.74 (7.12)	11.02 (10.76)
11d	2122 (w), 2073 (sh), 2055 (s)	1032 (1032)			

^a Recorded in CDCl₃. ^b Observed (calculated) masses of the molecular ion (*m/e*); the M values are based upon the ⁵⁶Fe isotope.

containing substrates (*n* = 3) has been described as a 1,3-dipolar cycloaddition reaction leading to a [2.2.1] bicyclic intermediate 2. In analogy to isolobally¹⁴ related organic azomethyne ylides^{3e} the Fe—N=C fragment in complexes 1 reacts like a classical 1,3-dipole,¹⁵ i.e. according to the Sustmann classification¹⁶ a HOMO controlled dipole. The reactivity of these dipoles can be increased through the introduction of electron donating substituents. One possibility to increase electron density on the Fe—N=C dipole is to substitute one or more CO ligands in the Fe-(RDAB)(CO)₃ complexes for the more σ -donating/less

π -accepting isocyanides.⁶ As a consequence of this increased reactivity it has been demonstrated^{4,5} that less activated dipolarophiles can be used. The isothiocyanates discussed in this paper add their C=S bonds across the Fe—N=C fragment under formation of a (nonobserved) [2.2.1] bicyclic intermediate 8, analogous to the [2.2.1] bicyclic intermediate 2. This intermediate reacts further by an isocyanide insertion, through nucleophilic attack of

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the lone pair of the amido nitrogen atom on one of the three terminally coordinated isocyanide ligands. The resulting coordinatively and electronically unsaturated [2.2.2] bicyclic intermediate **9** readily adds an additional isocyanide ligand forming the [2.2.2] bicyclic complex **10**. These [2.2.2] bicyclic complexes can again undergo an isocyanide insertion in the Fe—C bond, forming the double isocyanide insertion [3.2.2] bicyclic complexes **11**. The doubly inserted isocyanide complexes **11** are thermodynamically more favorable than the meanwhile well-known [2.2.2] bicyclic complexes. This was shown by warming a solution of **11** in deuterated toluene. At every temperature a stable equilibrium was established. When the equilibrium constant K_{eq} is determined at different temperatures, thermodynamic parameters are accessible via the van't Hoff isochore.¹³ At all temperatures a positive ΔG was found for the deinsertion reaction $11 \rightarrow 10$, indicating that complexes **11** are thermodynamically more stable than complexes **10**. Conversely, the reaction of **10a,b** with 1 equiv 2,6-xylyl—NC in deuterated benzene or toluene in an NMR tube showed the almost immediate formation of **11a,b**.

In hexane, the formation of complex **11** was not observed. Only in the case of phenyl isothiocyanate was the formation of a [2.2.2] bicyclic structure **10** found, whereas the other isothiocyanates gave no products which could be identified. The reason for this could be that complex **10a** precipitates in hexane and the reaction in the solid state is not favorable and fast in these cases. The inhibition of formation of complex **11a** in hexane is thus of kinetic origin. The reason that only isothiocyanate **a** gave an identifiable product in hexane has to be thermodynamic: the ΔG° energy levels of **10b–d** are too high compared with the ΔG° energy levels of **11b–d**. This is reflected in Table 3: the ΔG° for the isocyanide deinsertion reaction is the lowest for complex **11a**. Consequently, the formation of **10** is easiest in the case of phenyl isothiocyanate. This is a nice example of thermodynamics as a tool for understanding reaction pathways, especially in the case of subtle differences in the substrates employed; the differences are subtle indeed, because the R'' groups of the isothiocyanates, which are the only variables, are rather remote from the reacting C=S bonds.

The above described equilibrium between complexes **10** and **11** was also observed in the attempted crystallization of complexes **11**. For example, a saturated solution of **11c** in diethyl ether/dichloromethane (5/1) gave at -80°C crystals of **10c** after several months. So, the dynamic equilibrium between **10** and **11** shifted the product distribution toward **10c**, because this complex was drawn away from the equilibrium by precipitation. In order to get suitable crystals of **11** for an X-ray structure determination we have tried to block the equilibrium between **10** and **11** by coordinating metals to the α -diimine unit of the two inserted isocyanides. But all crystallization attempts have hitherto failed.

Conclusion

Although multiple isocyanide insertions¹⁷ are well documented in the literature, isocyanide deinsertion is still exceptional. The only previous example of a (reversible) isocyanide deinsertion was found in our laboratory by de Lange et al.⁴ They used dimethyl maleate as the dipolarophile. However, they could not establish equilibria at different temperatures. For this reason it is the first time that thermodynamic parameters for the deinsertion reaction of an isocyanide ligand are reported here.

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Supplementary Material Available: Tables of equilibrium data, atomic coordinates, thermal parameters, and bond angles and distances and an ORTEP drawing of **10a** (11 pages). Ordering information is given on any current masthead page.

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