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# 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 Fe((2,6-xylyl)NC)$_3$(*i*-PrDAB) (**7**) with para-substituted phenyl isothiocyanates (R″C$_6$H$_4$NCS; R″ = 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**, $C_{51}H_{57}N_7SFe$, are monoclinic, space group $I2/a$, with cell constants $a = 24.041(2)$ Å, $b = 12.095(2)$ Å, $c = 36.161(6)$ Å, $V = 10502(3)$ Å$^3$, $Z = 8$, 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 **11a–d** ⇄ **10a–d** + 2,6-xylyl-NC have been studied by $^1$H NMR. The equilibrium constants at various temperatures (303 K $\leq T \leq$ 368 K) have been determined from which for the first time $\Delta G°$ (**a**, 16.2 ± 2.7; **b**, 22.7 ± 1.6; **c**, 23.2 ± 1.9; **d**, 24.7 ± 1.1 kJ/mol), $\Delta H°$ (**a**, 61.6 ± 6.3; **b**, 74.5 ± 3.3; **c**, 65.5 ± 2.0; **d**, 86.9 ± 2.5 kJ/mol), and $\Delta S°$ (**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** ⇄ **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 M(CO)$_{3-n}$(CNR)$_n$(R′DAB)[2] (M = Fe, Ru; *n* = 0, 1, and 3) complexes with unsaturated substrates (e.g., activated alkynes,[3] alkenes,[4] and heteroallenes[5]) involving C–C and C–N bond formation leading to interesting heterocycles (see Scheme 1).

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 M—N=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 process[4] and the reactivity of two dipolarophiles containing C=S bonds, namely COS and CS$_2$.[5] In the present paper we again employ dipolarophiles with reactive C=S bonds, namely aryl isothiocyanates, R″C$_6$H$_4$NCS, which are also known

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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 R′N=CH—CH=NR′ are abbreviated as R′DAB.

[3] (a) Part 1: Frühauf, H.-W.; Seils, F.; Goddard, R. J.; Romão, M. J. *Angew. Chem.* **1983**, *95*, 1014; *Angew. Chem., Int. Ed. Engl.* **1983**, 1435. (b) Part 2: Frühauf, H.-W.; Seils, F.; Romão, M. J.; Goddard, R. J. *Organometallics* **1985**, *4*, 948. (c) Part 3: Frühauf, H.-W.; Seils, F. *J. Organomet. Chem.* **1986**, *302*, 59. (d) Part 4: Frühauf, H.-W.; Seils, F. *J. Organomet. Chem.* **1987**, *323*, 67. (e) Part 5: Frühauf, H.-W.; Seils, F.; Stam, C. H. *Organometallics* **1989**, *8*, 2338. (f) Part 6: de Lange, P. P. M.; Frühauf, H.-W.; van Wijnkoop, M.; Vrieze, K.; Wang, Y.; Heijdenrijk, D.; Stam, C. H. *Organometallics* **1990**, *9*, 1691. (g) Part 7: van Wijnkoop, M.; de Lange, P. P. M.; Frühauf, H.-W.; Vrieze, K.; Wang, Y.; Goubitz, K.; Stam, C. H. *Organometallics* **1992**, *11*, 3607. (h) Part 8: de Lange, P. P. M.; Frühauf, H.-W.; Kraakman, M. J. A.; van Wijnkoop, M.; Kranenburg, M.; Groot, A. H. J. P.; Vrieze, K.; Fraanje, J.; Wang, Y.; Numan, M. *Organometallics* **1993**, *12*, 417. (i) Part 9: van Wijnkoop, M.; Siebenlist, R.; de Lange, P. P. M.; Frühauf, H.-W.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1993**, *12*, 4172. (j) Part 10: de Lange, P. P. M.; Frühauf, H.-W.; Vrieze, K.; Goubitz, K. *Organometallics* **1993**, *12*, 428.

[4] (a) de Boer, R. P.; de Lange, P. P. M.; Frühauf, H.-W.; Vrieze, K. *J. Chem. Soc., Chem. Commun.* **1992**, 580. (b) Part 11: de Lange, P. P. M.; de Boer, R. P.; van Wijnkoop, M.; Ernsting, J. M.; Frühauf, H.-W.; Vrieze, K.; Smeets, W. J. J.; Spek, A. L.; Goubitz, K. *Organometallics* **1993**, *12*, 440.

[5] Part 12: de Lange, P. P. M.; Alberts, E.; van Wijnkoop, M.; Frühauf, H.-W.; Vrieze, K.; Kooijman, H.; Spek, A. L. *J. Organomet. Chem.* **1994**, *465*, 241.

[6] (a) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193. (b) Carmona, E.; Galindo, E.; Matin, J. M. *Polyhedron* **1988**, *7*, 1831. (c) Yamamoto, Y.; Yamazaki, H. *Coord. Chem. Rev.* **1972**, *8*, 225. (d) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209.

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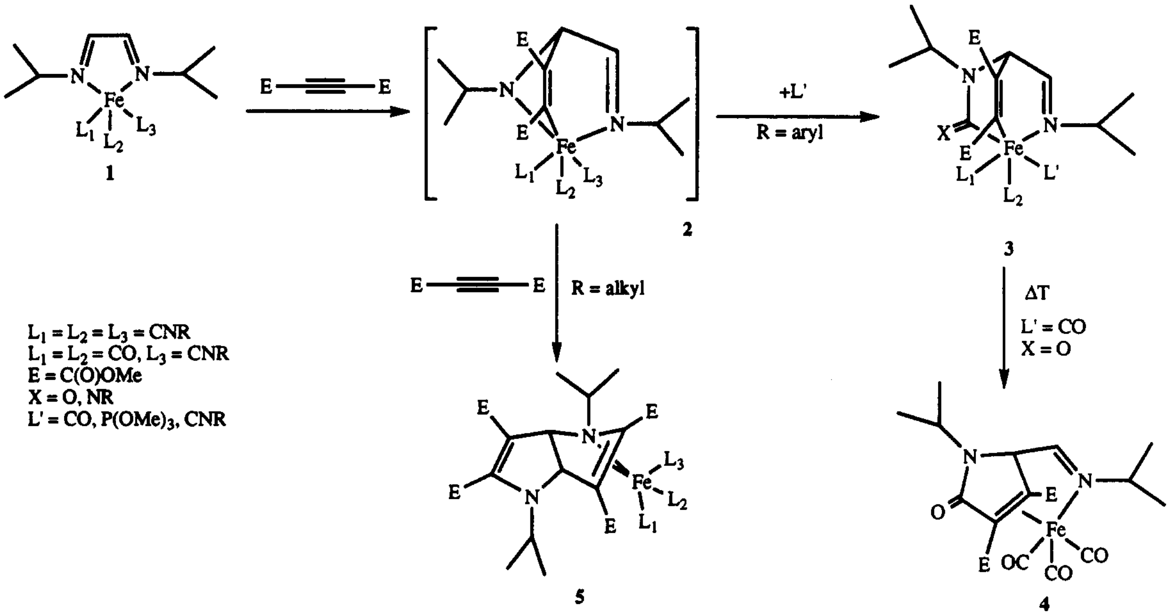
**Scheme 1. Reaction Steps in the Cycloaddition of DMAD to the Fe—N=C Fragment in Complexes $Fe(CO)_{3-n}(CNR)_n(DAB)$ ($n$ = 0, 1, 3)**



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 commerically and used without purification. Fe(2,6-xylyl isocyanide)$_3$(*i*-PrDAB) (**7**) was prepared in situ from Fe(*i*-PrDAB)$_2$ (**6**) and 2,6-xylyl isocyanide according to published procedures.[3i,8]

**Synthesis of Fe((2,6-xylyl)NC)$_3$([2.2.2]bic) (10a).** A solution of Fe(*i*-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 Fe((2,6-xylyl)NC)$_3$([2.2.2]-bic) (**10a**) is 90–95%. The product can be crystallized from a concentrated $Et_2O/CH_2Cl_2$ (5/1) solution at −20 °C.

**Synthesis of 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).** To a solution of Fe(*i*-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 ⇄ 10 + 2,6-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 $Et_2O/CH_2Cl_2$ (4/1) solution at −80 °C. A crystal with approximate dimensions 0.20 × 0.25 × 0.40 mm$^3$ was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu Kα radiation and an $\omega$–$2\theta$ scan. A total of 5375 unique reflections was measured within the range $-23 \le h \le 23, -12 \le k \le 0, 0 \le l \le 35$. Of these, 2918 were above the significance level of $2.5\sigma(I)$. The maximum value of $(\sin \sigma)/\lambda$ was 0.50 Å$^{-1}$. 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 $70 < 2\theta < 72°$. 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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[7] (a) Caramella, P.; Grünanger, P. In *1,3-dipolar cycloaddition chemistry*; Padwa, A., Ed.; John Wiley and Sons Inc.: New York, 1984; Chapter 3. (b) Lown, J. W.; Dallas, G.; Maloney, T. W. *Can. J. Chem.* **1969**, *47*, 3557.

[8] tom Dieck, H.; Diercks, R.; Stamp, L.; Schuld, T. *Chem. Ber.* **1987**, *120*, 1943.

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

| | |
|---|---|
| **Crystal Data** | |
| formula | $C_{51}H_{57}N_7SFe$ |
| mol wt | 856.0 |
| cryst syst | monoclinic |
| space group | $I2/a$ |
| $a, b, c$ (Å) | 24.041(2), 12.095(2), 36.161(6) |
| $\beta$ (deg) | 92.72(1) |
| $V$(Å)$^3$ | 10502(3) |
| $Z$ | 8 |
| $D_{calc}$ (g cm$^{-3}$) | 1.08 |
| $F$(000) | 1632 |
| $\mu$ (cm$^{-1}$) | 29.44 |
| cryst size (mm$^3$) | 0.20 × 0.25 × 0.40 |
| **Data Collection** | |
| temp (K) | 248 |
| $\theta_{min}$, $\theta_{max}$ (deg) | 2.5, 50.4 |
| radiation, λ (Å) | Cu K$\alpha$, 1.5418 |
| scan type | $\omega$–2$\sigma$ |
| ref reflections | 1, –1,2, –4,0,4 |
| total no. of data | 5375 |
| total no. of unique data | 5375 |
| no. of obs data | 2918 [$I > 2.5\sigma(I)$] |
| **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) |
| $(\Delta/\sigma)_{max}$ 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 $V = 0.15$ Å$^2$, 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 (DIFABS[9]) was applied, with coefficients in the range 0.68–1.36. The secondary isotropic extinction coefficient[10] refined to 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 XTAL[12] 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 Fe(2,6-xylyl—NC)$_3$($i$-PrDAB) in either THF or hexane was prepared in situ from Fe($i$-PrDAB)$_2$ and 5 equiv of 2,6-xylyl-NC (Scheme 2).[8,3i] 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 CS$_2$ 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 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.

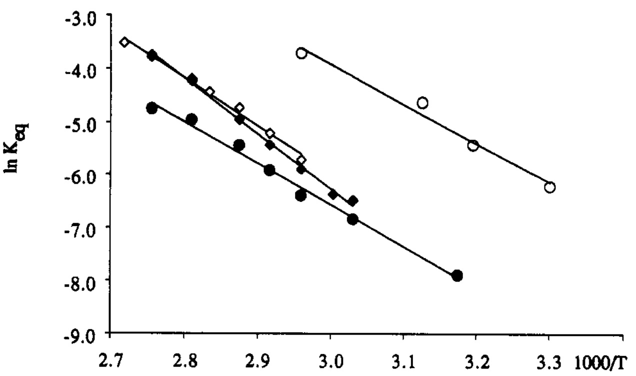
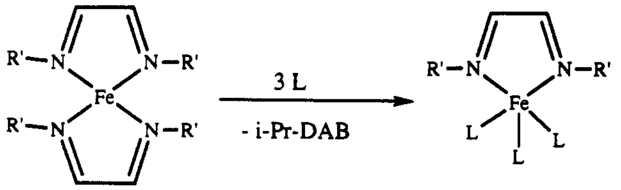


**Figure 1.** van't Hoff plot for the equilibrium **11** ⇄ **10** + 2,6-xylyl-NC: R″ = H (○); Me (◇) OMe (●); NO$_2$ (◆).

**Scheme 2. Formation of Fe((2,6-xylyl)NC)$_{3-n}$($i$-PrDAB) (7)**



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7

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

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 $^1$H NMR. On cooling again, the red color dissappeared. 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 $^1$H 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 $^1$H NMR spectra. The measured data points give straight lines when plotting the reciprocal temperature ($1/T$) values against the natural logarithm ($\ln K_{eq}$) values (Figure 1). Using the assumption that $\Delta H$ and $\Delta S$ are constant over the employed temperature range, the thermodynamic standard parameters $\Delta H°$, $\Delta G°$, and $\Delta S°$ for the isocyanide deinsertion reaction **11** ⇄ **10** have been calculated[13] and are collected in Table 2. We also tried to determine the thermodynamic values for the reverse reaction **10** ⇄ **7**, but this, just as in the case of dimethyl maleate as dipolarophile,[4] was impeded by the

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[9] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

[10] (a) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *A23*, 558. (b) Larson, A. C. The Inclusion of Secondary Extinction in Least-Squares Refinement of Crystal Structures. In *Crystallographic Computing*; Ahmed, F. R.; Hall, S. R., Huber, C. P., Eds.; Munksgaard: Copenhagen, Denmark, 1969; p 291.

[11] (a) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321. (b) Cromer, D. T.; Mann, J. B. In *International Tables for X-ray Crystallography*; Kynoch Press: Birminghem, U.K., 1974; Vol. IV, p 55.

[12] Hall, S. R.; Flack, H. D.; Stewart, J. M. *XTAL3.2 Reference Manual*; Universities of Western Australian, Geneva, and Maryland, 1992.

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

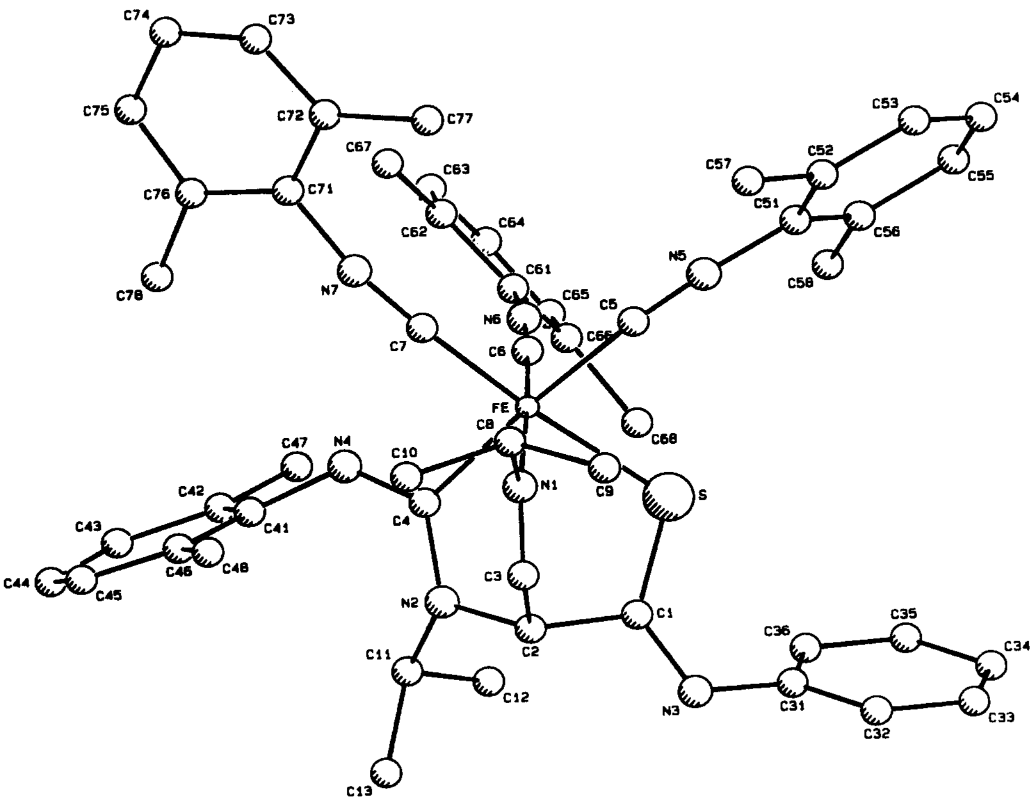
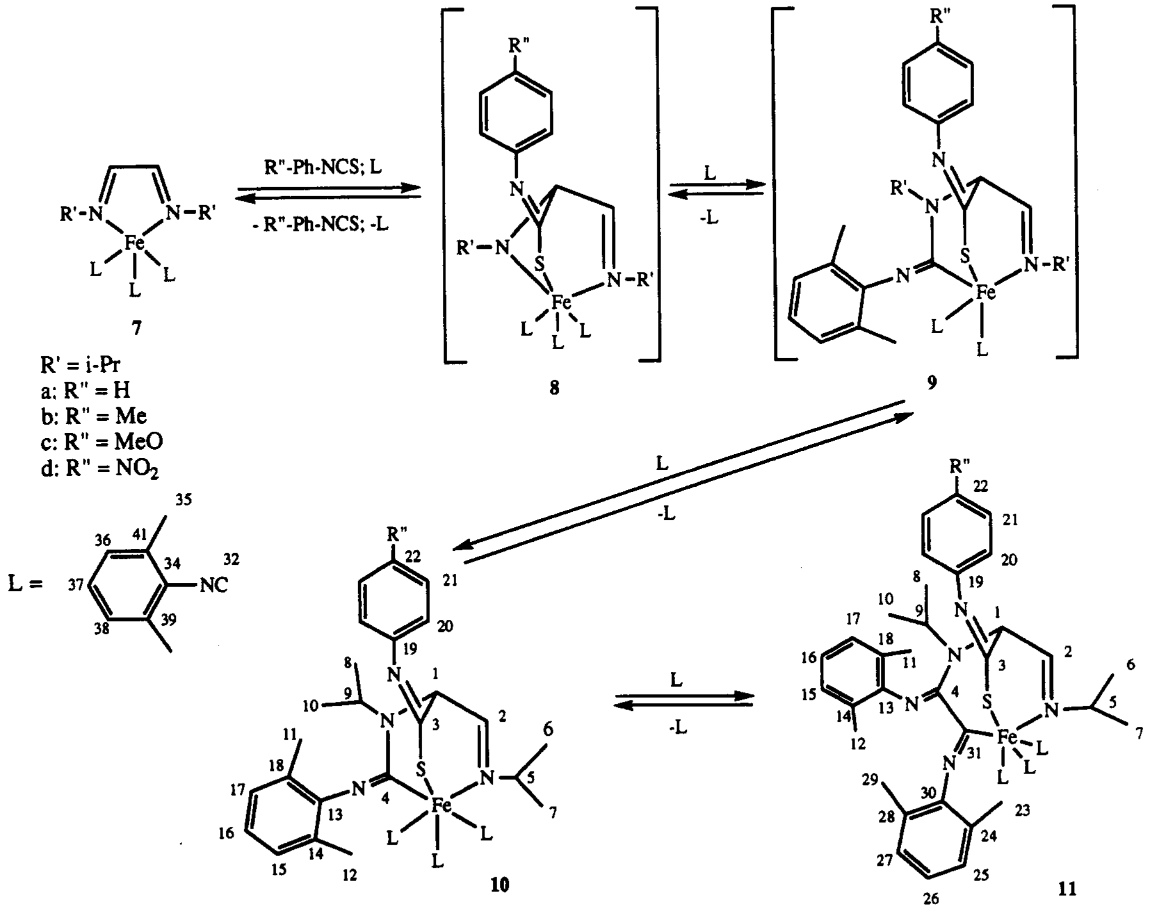


**Figure 2.** PLUTO drawing of complex **10a**.

**Scheme 3. Reversible Cycloaddition of Fe((2,6-xylyl)NC)$_3$(*i*-PrDAB) to R″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 ⇄ 10 + RNC (RNC = 2,6-Xylyl-NC)**

| R″ group | $K_{eq}$(298 K) (mol/L) | $\Delta G°$(298 K) (kJ/mol) | $\Delta H°$(298 K) (kJ/mol) | $\Delta S°$(298 K) [J/(mol K)] |
|---|---|---|---|---|
| H | $1.43 \times 10^{-3}$ | 16.2 ± 2.7 | 61.6 ± 6.3 | 152 ± 29 |
| Me | $1.06 \times 10^{-4}$ | 22.7 ± 1.6 | 74.5 ± 3.3 | 174 ± 14 |
| OMe | $8.50 \times 10^{-5}$ | 23.2 ± 1.9 | 65.5 ± 2.0 | 142 ± 12 |
| $NO_2$ | $4.59 \times 10^{-5}$ | 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) |

**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) |

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 compounds 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 familar [2.2.2] bicyclic skeleton that has been found earlier for the $CS_2$ case[5] 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 $CS_2$ compound (2.311(3) Å). In complex **10a** the bond distance of C(1)—S is 1.72(2) Å; in the $CS_2$ 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 sp$^2$ 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 sp$^2$ 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.** $^1$H NMR and $^{13}$C{$^1$H} NMR data of the 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**) are listed in Tables 6 and 7, respectively; the atomic numbering is given in Scheme 3.

**$^1$H NMR.** The $^1$H 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 $\pi$-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 compound[5] 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 C≡N stretching vibration values are a measure of the amount of $\pi$-back-donation from the metal into the orthogonal, C≡N antibonding $\pi^*$-orbitals of the terminal isocyanide ligands. For this reason it is interesting to compare the C≡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 C=S bonds[5] (COS and CS$_2$), complexes **10** show more $\pi$-back-donation from the iron(II) ion to the isocyanide ligands. The C≡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 C≡N stretching frequencies of **11** are lower than those of **10**, i.e., less $\pi$-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 C—N bond order and consequently the C≡N stretching frequency. So, for a given isocyanide, the order for $\pi$-back-donation from metal to ligand is

$$\mathrm{CS_2} < \mathbf{10} < \mathrm{DMAD} < \mathbf{11} \approx \mathrm{DMM}$$

Dependent on the type of bicyclic compound and on the dipolarophile used for the cycloaddition reaction, different degrees of $\pi$-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 C≡N stretching frequencies of the Fe(0) starting complex **7**[3i] (2070 (strong) and 1970 (broad) cm$^{-1}$), the terminal isocyanides of all complexes show more $\sigma$-donation and less $\pi$-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 Fe(CO)$_{3-n}$(RNC)$_n$(*i*-PrDAB) complexes with alkynes ($n$ = 0, 1, 3), alkenes ($n$ = 3), and heteroallenic C=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<br>2.67, sept, 1H, 6.8 Hz | 4.58, sept, 1H, 6.6 Hz<br>4.51, sept, 1H, 6.7 Hz | 4.20, sept, 1H, 6.6 Hz<br>2.66, sept, 1H, 6.2 Hz | 4.19, sept, 2H, 6.6 Hz | 4.22, sept, 1H, 6.7 Hz<br>3.13, sept, 1H, 6.8 Hz |
| H(6)–H(8), H(10) | 1.43, d, 3H, 6.7 Hz<br>1.39, d, 3H, 6.6 Hz<br>1.11, d, 3H, 6.8 Hz<br>0.99, d, 3H, 6.6 Hz | 1.31, d, 3H, 6.6 Hz<br>0.93, d, 3H, 6.3 Hz<br>0.87, d, 3H, 6.3 Hz<br>0.87, d, 3H, 6.2 Hz | 1.42, d, 3H, 6.7 Hz<br>1.39, d, 3H, 6.6 Hz<br>1.10, d, 3H, 6.7 Hz<br>0.98, d, 3H, 6.6 Hz | 1.31, d, 3H, 6.5 Hz<br>0.92, d, 3H, 6.4 Hz<br>0.87, d, 3H, 6.6 Hz<br>0.86, d, 3H, 6.2 Hz | 1.30, d, 3H, 6.5 Hz<br>0.93, d, 3H, 6.3 Hz<br>0.87, d, 6H, 6.4 Hz | 1.30, d, 3H, 6.5 Hz<br>1.23, d, 3H, 6.3 Hz<br>0.94, d, 3H, 6.4 Hz<br>0.87, d, 3H, 6.4 Hz |
| H(11)–H(12), H(23), H(29) | 2.03, s, 3H<br>1.95, s, 3H | 2.69, s, 3H<br>2.64, s, 3H<br>2.29, s, 3H<br>2.23, s, 3H | 2.02, s, 3H<br>1.95, s, 3H | 2.69, s, 3H<br>2.63, s, 3H<br>2.29, s, 3H<br>2.22, s, 3H | 2.70, s, 3H<br>2.64, s, 3H<br>2.31, s, 3H<br>2.23, s, 3H | 2.67, s, 3H<br>2.63, s, 3H<br>2.27, s, 3H<br>2.21, s, 3H |
| H(15)–H(17), H(25)–H(27) | 6.69, d,1H, 6.8 Hz<br>6.57, d, 1H,7.0 Hz<br>6.40, dd,1H, 7.2/7.3 Hz | 6.53, d, 1H, 7.0 Hz<br>6.47, d, 1H, 7.0 Hz<br>6.38, d, 1H, 7.1 Hz<br>5.86, dd, 1H, 7.4/7.4 Hz<br>7.21–6.76, m, 1H[b] | 6.72, d, 1H, 7.1 Hz<br>6.57, d, 1H, 7.2 Hz<br>6.39, dd, 1H, 7.3/7.4 Hz | 6.45, d, 1H, 8.0 Hz<br>6.37, d, 1H, 7.3 Hz<br>5.84, dd, 1H, 7.4/7.4 Hz<br>7.18–6.70, m, 3H | 6.60–6.47, m, 4H<br>6.37, d, 1H, 7.1 Hz<br>5.82, dd, 1H, 7.4/7.4 Hz | 6.89, dd, 1H 8.0/7.1 Hz<br>6.49, d, 1H, 7.4 Hz<br>6.39, d, 1H, 7.4 Hz<br>5.88, dd,1H, 7.4/7.4 Hz |
| 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 | 6.5–7.8, m, 13H |
| H(35), H(40) | 2.35, s, 6H<br>2.33, s, 6H<br>2.27, s, 6H | 2.57, s, 6H<br>2.39, s, 6H<br>2.00, s, 6H | 2.34, s, 12H<br>2.28, s, 6H | 2.56, s, 6H<br>2.38, s, 6H<br>2.00, s, 6H | 2.57, s, 6H<br>2.41, s, 6H<br>2.01, s, 6H | 2.55, s, 6H<br>2.39, s, 6H<br>2.00, s, 6H |
| R″ | 7.4–6.9, s, 1H | 7.21–6.76, m, 1H | 2.31, s, 3H | 2.20, s, 3H | 3.73, s, 3H | |

[a] Chemical shifts are in ppm relative to $Me_4Si$; measured in $CDCl_3$ 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 $Me_4Si$, measured in $CDCl_3$ 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)**

| | | | elemental anal. (%) | | |
|---|---|---|---|---|---|
| compd | $\nu_{C\equiv N}$ (cm$^{-1}$)[a] | M[b] | $C_{obs}$ ($C_{calc}$) | $H_{obs}$ ($H_{calc}$) | $N_{obs}$ ($N_{calc}$) |
| **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 $CDCl_3$. [b] Observed (calculated) masses of the molecular ion (*m*/*e*); the M values are based upon the $^{56}Fe$ 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 isolobally[14] 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 classification[16] 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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[14] Hoffmann, R. *Angew. Chem.* **1982**, *94*, 725.

[15] (a) Huisgen, R. *Angew. Chem.* **1963**, *75*, 725. (b) Huisgen, R. *Angew. Chem.* **1963**, *75*, 742.

[16] (a) Sustmann, R. *Tetrahedron Lett.* **1971**, 2721. (b) Sustmann, R.; Trill, H. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 838. (c) Sustmann, R. *Pure Appl. Chem.* **1974**, *40*, 569. (d) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57. (e) Herndon, W. C. *Chem. Rev.* **1972**, *72*, 157. (f) Bastide, J.; El Ghandour, N.; Henri-Rousseau, O. *Tetrahedron Lett.* **1972**, *41*, 4225. (g) Houk, K. N.; Yamaguchi, K. In 1,3-dipolar cycloaddition chemistry; Padwa, A., Ed.; John Wiley and Sons Inc.: New York, 1984; Chapter 13.

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 $\Delta G$ was found for the deinsertion reaction **11** → **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 $\Delta G°$ energy levels of **10b–d** are too high compared with the $\Delta G°$ energy levels of **11b–d**. This is reflected in Table 3: the $\Delta G°$ 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 insertions[17] 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.

OM940107T

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(17) (a) Otsuka, S.; Nakamura, N.; Yoshida, T. *J. Am. Chem. Soc.* **1969**, *91*, 7196. (b) Otsuka, S.; Nakamura, N.; Ito, K. *Chem. Lett.* **1972**, 939. (c) Otsuka, S.; Nakamura, N.; T. Yoshida, T.; Naruto, K. *J. Am. Chem. Soc.* **1973**, *95*, 3180.