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1,3-Dipolar Cycloaddition to the Fe–N=C Fragment. 10.[1] Synthesis of Fe(CNR)$_3$(α-diimine) Complexes and Their Reactivity toward Dimethyl Acetylenedicarboxylate

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The series of complexes Fe(CNR)$_3$(*i*-Pr-α-diimine) (**4**: R = 2,6-xylyl (**a**), *t*-Bu (**b**), c-Hex (**c**)) has been prepared by starting from Fe(α-diimine)$_2$ and isocyanides. NMR measurements indicate a dynamic process which scrambles the three isocyanide ligands and interchanges the α-diimine halves. IR revealed that the complex Fe(*t*-BuNC)$_3$(*i*-Pr-α-diimine) (**4b**) exists in two distinct isomeric forms, visible not only at 147 K but also at 293 K. The relative amounts of the two isomers depend on the temperature. Reaction of Fe(CNR)$_3$(*i*-Pr-α-diimine) with dimethyl acetylenedicarboxylate gives two types of products, depending on the type of isocyanide used. For the aromatic isocyanide, a ferra [2.2.2] bicyclic complex (**7a**) is formed via 1,3-dipolar cycloaddition to the Fe—N═C unit, followed by isocyanide insertion. 1,4,3a,6a-Tetrahydropyrrolo[3,2-*b*]pyrrole complexes (**10b,c**) are formed with aliphatic isocyanides, as the result of two successive cycloadditions of alkyne to both Fe—N═C units. The single-crystal X-ray structure of Fe(*t*-BuNC)$_3$(tetrahydropyrrolo[3,2-*b*]pyrrole) (**10b**; FeC$_{35}$H$_{55}$N$_5$O$_8$, triclinic, space group $P\bar{1}$, a = 10.292 (2) Å, b = 10.915 (2) Å, c = 18.833 (3) Å, α = 79.81 (1)°, β = 77.75 (1)°, γ = 80.23 (2)°, Z = 2, R = 0.081, R_w = 0.089) shows that the Fe(*t*-BuNC)$_3$ moiety is η^3-coordinated to one of the pyrrole rings. In the presence of water, the [2.2.2] bicyclic complex **7a** was found to undergo a cyclometalation reaction with one of the ester groups to form the tricyclic complex **8a**. The molecular structure of Fe(2,6-xylylNC)$_3$(tric) (**8a**) consists of three five-membered rings, with the metal incorporated in two of them.

Introduction

Complexes of the type M(CO)$_3$(DAB) (the 1,4-diaza 1,3-dienes of formula R′N═C(H)C(H)═NR′ are abbreviated as R′-DAB) and M$_2$(CO)$_6$(DAB) (M = Mn, Mo, Fe, Ru, Os) have been studied extensively in our laboratory. Reactions with small molecules such as CO, alkynes, phosphines, and allenes resulted in a rewarding chemistry, yielding a variety of new and quite unique complexes.[3] In most of these cases organometallic compounds have been used which, besides the α-diimine, bear only CO ligands. The substitution of CO by a better σ-donating/worse π-accepting[4] isocyanide ligand can strongly influence the reactivity of the complexes. The 1,3-dipolar cycloaddition reaction discussed in this paper gives an example where even the course of the reaction depends on the properties of these ligands.

With the tricarbonyl complexes Fe(CO)$_3$(DAB) (**1**), electron-deficient alkynes undergo an oxidative 1,3-dipolar [3 + 2] cycloaddition to one of the Fe—N═C fragments. Consecutive CO insertion into the Fe—N bond resulted in the formation of [2.2.2] bicyclic structures (**2**) (see Scheme I). When the temperature is raised, these [2.2.2] bicyclic structures may isomerize via reductive elimination, followed by recoordination of the double bond, yielding a 1,5-dihydropyrrol-2-one complex (**3**).[5] The reactivity of complexes **1** has been found to change dramatically when just one CO is substituted by a CNR ligand. With the introduction of a donating isocyanide not only the Fe—N═C fragment in the Fe(CO)$_2$(CNR)(DAB) complex but also the remaining Fe$^{\text{II}}$—N═C fragment in the initially formed [2.2.1] bicyclic intermediate underwent a cycloaddition reaction with dimethyl acetylenedicarboxylate (DMAD), resulting in the formation of a Fe(CO)$_2$(CNR) unit with a η^3-coordinated 1,4,3a,6a-tetrahydropyrrolo-[3,2-*b*]pyrrole (THPP) ligand.[6] Therefore, we were interested in the consequences of substituting all three carbonyls in Fe(CO)$_3$(DAB) for isocyanide ligands.

In this paper we report on the synthesis and properties

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(2) (a) The [2.2.2] bicyclic structure is abbreviated as bic. (b) The tricyclic structure is abbreviated as tric.

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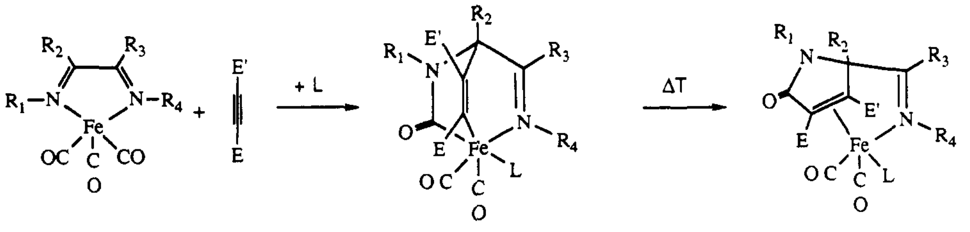
Scheme I. Cycloaddition Reactions of Electron-Deficient Alkynes with $Fe(CO)_3$(α-diimines)



1 2 3

E = E' = CO_2Me; COPh
E = H, E' = CO_2Me
$R_1 = R_4$ = alkyl; $R_2 = R_3$ = H, CH_3
R_1 = alkyl; R_2 = H; R_3, $R_4 = (CH)_4$
L = CO; $P(OMe)_3$

of $Fe(CNR)_3$(*i*-PrDAB) (4). In the reaction of 4 with DMAD two products were formed, the [2.2.2] bicyclic complex 7a and the double-cycloaddition product Fe(*t*-BuNC)$_3$(*i*-Pr-THPP) (10), the X-ray structure of which is described. Also, the cyclometalation of one of the ester groups in 7a, followed by a ring closure leading to the tricyclic structure 8a, has been investigated. The single-crystal X-ray structure of the tricyclic compound 8a is discussed.

Experimental Section

Materials and Apparatus. ^1H and ^{13}C NMR spectra were recorded on Bruker AC 100 and AMX 300 spectrometers. IR spectra were obtained on a Perkin-Elmer 283 spectrophotometer, using matched NaCl cells. The variable-temperature IR measurements were performed on a Nicolet 7199B FT-IR spectrophotometer with a liquid-nitrogen-cooled HgCdTe detector. FD-mass spectra were measured on a Varian Mat 711 double-focusing mass spectrometer, fitted with a 10-μm tungsten-wire FD emitter containing microneedles with an average length of 30 μm, using emitter currents of 0–10 mA. Solvents were dried and distilled before use. All preparations were performed under an atmosphere of purified nitrogen, using Schlenk techniques. Unless stated otherwise, column chromatography was carried out using silica gel 60, silanized (Merck, 70–230 mesh) activated before use as the stationary phase. Use of normal silica gel leads to nearly complete decomposition of the products. Elemental analyses were carried out by the Elemental Analysis section of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands, and by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr, Germany. DMAD (Aldrich), 2,6-xylyl (**a**), *tert*-butyl (**b**), and cyclohexyl (**c**) isocyanides and $Fe^{III}Cl_3$ were obtained commercially (Fluka) and used without purification. *i*-Pr-DAB was prepared according to known procedures.[7]

Synthesis of Fe(*i*-Pr-DAB)$_2$. For the preparation of Fe(*i*-Pr-DAB)$_2$ a procedure from the literature,[8] with small modifications, was followed. A suspension of $Fe^{II}Cl_2$ (1542 mg, 12 mmol; prepared from $Fe^{III}Cl_3$[9]) and *i*-Pr-DAB (3412 mg, 24 mmol) in 40 mL of Et_2O was stirred at room temperature. During the reaction the mixture became purple. After one night, sodium (559 mg, 24 mmol), cut in small pieces, was added. The reduction reaction was complete within a few hours, the color having changed to dark reddish brown. The solvent was removed in vacuo, and the product was obtained (from the tarlike mass) by extraction with pentane. The pentane fractions were filtered over a G3 filter and collected. The red-brown Fe(*i*-Pr-DAB)$_2$ solution was stored at −20 °C. For further reactions small quantities were taken, dried in vacuo, weighed, and redissolved in pentane.

Synthesis of $Fe(CNR)_3$(*i*-Pr-DAB) (4). To a stirred solution of Fe(*i*-Pr-DAB)$_2$ (223 mg, 0.7 mmol) in 20 mL of pentane was added 2.8 mmol of the respective isocyanide. Immediately the reaction mixture turned dark green, promptly followed by deep red. After 30 min the intensely red solution was filtered over a G3 filter and used for further reactions, assuming a quantitative formation of the tris(isocyanide) complex. To obtain an analytically pure compound, the crude product could be purified by subliming the free CNR and *i*-Pr-DAB ligands, with gentle heating, into a Schlenk tube cooled with liquid N_2.

Synthesis of $Fe(CNR)_3$(*i*-Pr-THPP) (10b,c). To a solution of $Fe(CNR)_3$(*i*-Pr-DAB) (**4b,c**; 0.9 mmol) in 20 mL of pentane, prepared in situ, was added at −78 °C a solution of DMAD (250 mg, 1.8 mmol) in 5 mL of Et_2O and 15 mL of pentane, over a period of 45 min. The resulting precipitate was washed three times with 20 mL of cold pentane and dried in vacuo. The crude product was purified by column chromatography. Elution with Et_2O yielded a yellow fraction containing $Fe(CNR)_3$(*i*-Pr-THPP) (**10**), yield 60–80%.

Synthesis of Fe(2,6-xylylNC)$_3$(bic)[2a] (7a). To a solution of Fe(2,6-xylylNC)$_3$(*i*-Pr-DAB) (**4a**; 389 mg, 0.7 mmol) in 20 mL of pentane, prepared in situ, was added at −25 °C a solution of DMAD (93.8 mg, 0.7 mmol), in 5 mL of Et_2O and 15 mL of pentane, over a period of 1 h. The precipitate was washed three times with 20 mL of cold pentane and dried in vacuo, yielding 512 mg (90%). The crude yellow product may be purified by column chromatography. Elution with Et_2O resulted in a yellow fraction. Evaporation of the solvent yielded Fe(2,6-xylyl)$_3$(bic) (**7a**).

Synthesis of Fe(2,6-xylylNC)$_3$(tric)[2b] (8a). A solution of Fe(2,6-xylylNC)$_3$(bis) (**7a**; 274 mg, 0.32 mmol) in 10 mL of THF with 18 μL H_2O (0.96 mmol) was stirred for 2 days at room temperature. The solution was dried in vacuo and separated by column chromatography ("normal" Kieselgel 60, 70–230 mesh, Merck, dried and activated before use). Elution with Et_2O afforded a yellow band containing a small amount of the starting complex **7a**. Further elution with THF gave another yellow band. Evaporation of the solvent yielded Fe(2,6-xylylNC)$_3$(tric) (**8a**) as a yellow powder in a total yield of 50%.

Crystal Structure Determination of Fe(*t*-BuNC)$_3$(*i*-Pr-THPP) (10b). Crystals were grown from a saturated Et_2O solution at −30 °C. A crystal with approximate dimensions 0.13 × 0.13 × 0.30 mm^3 was used for data collection on an Enraf-Nonius Cad-4 diffractometer with graphite-monochromated Cu Kα radiation and with an θ–2θ scan. A total of 4118 unique reflections was measured within the range $-9 \le h \le 10$, $0 \le k \le 10$, $-17 \le l \le 18$. Of these, 2118 were above the significance level of $2.5\sigma(I)$. The maximum value of $(\sin\theta)/\lambda$ was 0.50 Å^{-1}. Unit-

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Table I. Crystal Data and Details of the Structure Determination of Fe(*t*-BuNC)$_3$(*i*-Pr-THPP) (10b)

Crystal Data	
formula	$FeC_{35}H_{55}N_5O_8$
mol wt	729.7
cryst syst	triclinic
space group	$P\bar{1}$
a, b, c (Å)	10.292 (2), 10.915 (2), 18.833 (3)
a, β, γ (deg)	79.81 (1), 77.75 (1), 80.23 (2)
V (Å^3)	2015.6 (9)
Z	2
D_{calc} (g cm^{-3})	1.2
$F(000)$	780
μ(Cu Kα) (cm^{-1})	34.1
cryst size (mm)	0.13 × 0.13 × 0.30
Data Collection	
temp (K)	295
θ_{min}, θ_{max} (deg)	2.5, 65
radiation	Cu Kα (1.5418 Å)
scan type	θ–2θ
$\Delta\omega$	$1.2 + 0.15 \tan\theta$
ref rflns	−1,2,1; 114
data set	h, −9 to +10; k, 0–10; l, −17 to +18
total no. of data	4208
total no. of unique data	4118
no. of obs data	2118 ($I > 2.5\sigma(I)$)
DIFABS cor range	0.63–1.34
Refinement	
no. of refined params	663
weighting scheme	$w = 1.0/[14.2 + F_o + 0.011F_o^2]$
final R, R_w	0.081, 0.089
$(\Delta/\sigma)_{max}$ in final cycle	0.65
min and max resd dens (e Å^{-3})	−3.8, 5.2

cell parameters were refined by a least-squares fitting procedure using 23 reflections with $50 < 2\theta < 65°$. Corrections for Lorentz and polarization effects were applied. The Fe position was found by direct methods using the program Multan80.[10] The remainder of the non-H atoms was found by the program AUTOFOUR.[11] The hydrogen atoms were calculated. Block-diagonal least-squares refinement on F, anisotropic for the non-hydrogen atoms with the hydrogen atoms fixed on their calculated positions with $U = 0.09$ Å^2, converged to $R = 0.081$, $R_w = 0.089$, and $(\Delta/\sigma)_{max} = 0.65$. The weighting scheme $w = (14.2 + F_o + 0.011F_o^2)^{-1}$ was used. An empirical absorption correction (DIFABS[12]) was applied, with coefficients in the range of 0.63–1.34. A final difference Fourier map revealed a residual electron density between −3.8 and +5.2 e Å^{-3}. The anisotropicity of some atoms belonging to the *t*-Bu groups is very large (C28, C29, C30, C34, and C35). Scattering factors were taken from Cromer and Mann.[13] The anomalous scattering of Fe was taken into account. Calculations were performed with XTAL3.0,[14] unless stated otherwise. Crystal data and numerical details of the structure determination are given in Table I. Final atomic coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms are given in Table II.

Results

The ligands and complexes discussed in this article are shown in Scheme II. The type of complex is identified by arabic numbers. The three different isocyanides are indicated by the letters **a**–**c**.

Table II. Fractional Coordinates of the Non-Hydrogen Atoms and Equivalent Isotropic Thermal Parameters for Fe(*t*-BuNC)$_3$(*i*-Pr-THPP) (10b)

atom	x	y	z	U_{eq} (Å^2)^a
Fe	0.9857 (2)	0.1441 (2)	0.2054 (1)	0.034 (1)
C1	0.668 (1)	0.238 (1)	0.3351 (6)	0.027 (8)
C2	0.704 (1)	0.354 (1)	0.3203 (6)	0.030 (8)
C3	0.719 (1)	0.299 (1)	0.2046 (6)	0.031 (8)
C4	0.684 (1)	0.189 (1)	0.2639 (7)	0.041 (9)
C5	0.843 (1)	0.114 (1)	0.1635 (7)	0.032 (8)
C6	0.840 (1)	0.248 (1)	0.1515 (6)	0.026 (8)
C7	0.588 (1)	0.187 (1)	0.4017 (7)	0.05 (1)
C8	0.513 (2)	0.199 (1)	0.5278 (7)	0.06 (1)
C9	0.684 (1)	0.448 (1)	0.3746 (8)	0.046 (9)
C10	0.746 (2)	0.496 (2)	0.476 (1)	0.11 (2)
C11	0.793 (1)	0.515 (1)	0.2094 (7)	0.042 (9)
C12	0.880 (2)	0.564 (1)	0.250 (1)	0.07 (1)
C13	0.677 (2)	0.607 (1)	0.1920 (8)	0.06 (1)
C14	0.832 (1)	0.024 (1)	0.1141 (7)	0.037 (9)
C15	0.819 (2)	0.009 (1)	−0.0075 (8)	0.06 (1)
C16	0.860 (1)	0.315 (1)	0.0778 (7)	0.037 (9)
C17	0.991 (2)	0.336 (1)	−0.0424 (7)	0.06 (1)
C18	0.792 (1)	−0.046 (1)	0.2816 (7)	0.036 (9)
C19	0.0826 (1)	−0.065 (1)	0.3574 (7)	0.046 (9)
C20	0.655 (2)	−0.083 (1)	0.2831 (8)	0.05 (1)
C21	1.130 (1)	0.195 (1)	0.1444 (7)	0.039 (9)
C22	1.365 (1)	0.267 (1)	0.0827 (8)	0.05 (1)
C23	1.462 (2)	0.0175 (2)	0.116 (1)	0.10 (2)
C24	1.360 (2)	0.396 (2)	0.107 (1)	0.11 (2)
C25	1.390 (2)	0.290 (2)	0.000 (1)	0.1 (2)
C26	1.086 (1)	−0.010 (1)	0.2251 (7)	0.044 (9)
C27	1.242 (2)	−0.215 (2)	0.249 (1)	0.08 (1)
C28	1.344 (2)	−0.202 (2)	0.283 (2)	0.20 (3)
C29	1.163 (3)	−0.292 (3)	0.318 (2)	0.23 (4)
C30	1.268 (4)	−0.295 (3)	0.197 (2)	0.28 (4)
C31	1.024 (2)	0.213 (2)	0.2810 (8)	0.06 (1)
C32	1.132 (2)	0.215 (2)	0.388 (1)	0.11 (2)
C33	1.211 (2)	0.096 (2)	0.391 (1)	0.13 (2)
C34	1.202 (5)	0.322 (3)	0.382 (2)	0.35 (6)
C35	1.040 (4)	0.216 (4)	0.456 (2)	0.32 (5)
N1	0.746 (1)	0.3933 (9)	0.2486 (6)	0.035 (7)
N2	0.803 (1)	0.0854 (9)	0.2445 (5)	0.031 (6)
N3	1.233 (1)	0.227 (1)	0.1080 (6)	0.056 (9)
N4	1.153 (1)	−0.104 (1)	0.2359 (7)	0.07 (1)
N5	1.055 (1)	0.245 (1)	0.3299 (7)	0.07 (1)
O1	0.529 (1)	0.0952 (9)	0.4099 (5)	0.062 (7)
O2	0.582 (1)	0.2479 (8)	0.4590 (5)	0.060 (7)
O3	0.589 (1)	0.5274 (9)	0.3780 (5)	0.061 (7)
O4	0.774 (1)	0.4212 (9)	0.4162 (5)	0.058 (7)
O5	0.841 (1)	−0.0883 (9)	0.1282 (5)	0.073 (8)
O6	0.813 (1)	0.0848 (8)	0.0492 (5)	0.050 (6)
O7	0.785 (1)	0.4112 (9)	0.0571 (5)	0.067 (7)
O8	0.09717 (9)	0.2769 (8)	0.0319 (5)	0.046 (6)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

For the preparation of Fe(CNR)$_3$(*i*-Pr-DAB) (4) the route described earlier by tom Dieck et al.[8] was followed:

$$FeCl_2 + DAB \rightarrow FeCl_2(DAB) + DAB \xrightarrow{Na} Fe(DAB)_2 + 3CNR \rightarrow \underset{4}{Fe(CNR)_3(DAB)} \quad (1)$$

The extremely labile complexes 4 were formed very rapidly, as indicated by the almost instant color change of the reaction mixture from red-brown to deep dark red. Due to their lability, isolation of the pure compounds was rather difficult and the pentane solution obtained was directly used for the further reactions, assuming a quantitative formation of Fe(CNR)$_3$(*i*-Pr-DAB). The complexes were formed equally well with either aliphatic or aromatic isocyanides. Fe(c-HexNC)$_3$(*i*-Pr-DAB) (4c) proved to be the least stable, which made it impossible to obtain a ^{13}C NMR spectrum.

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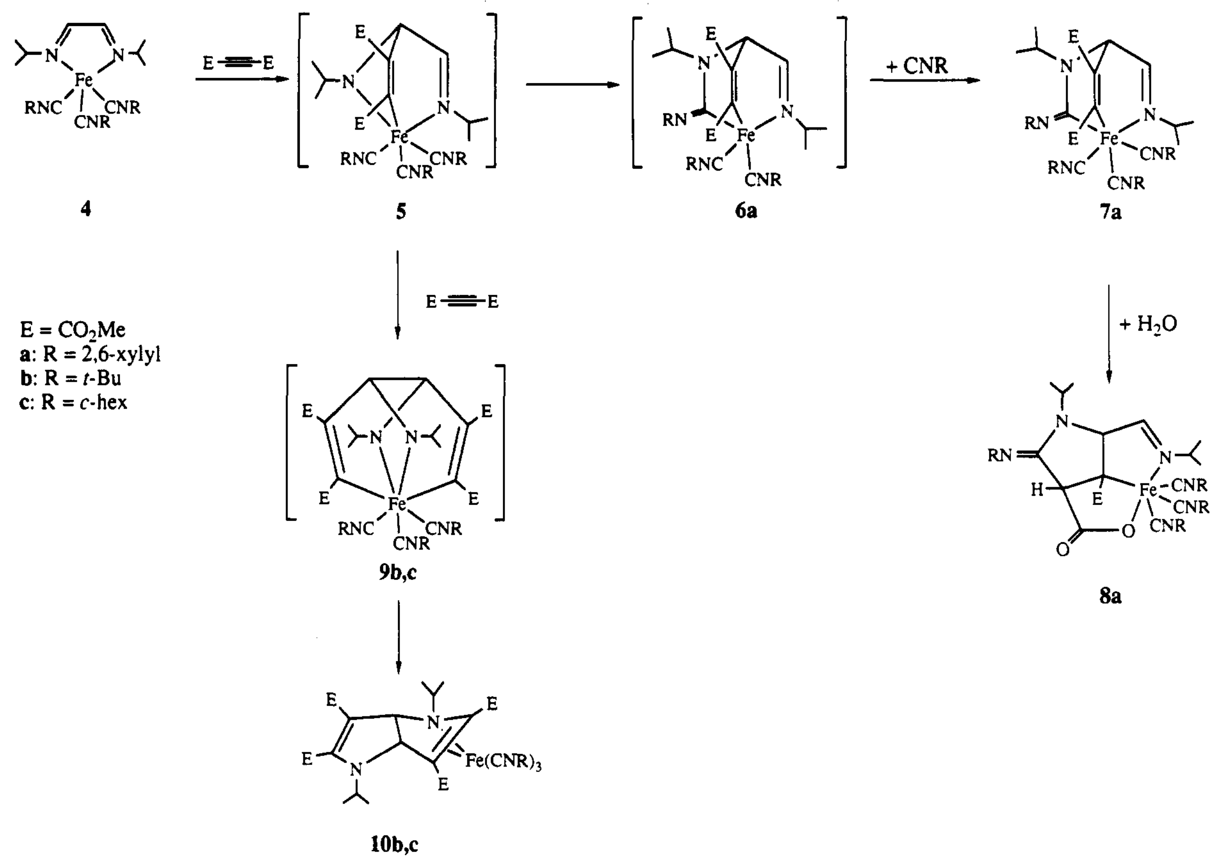
Scheme II. Reaction of $Fe(CNR)_3$(*i*-Pr-DAB) (4) with Dimethyl Acetylenedicarboxylate



The reaction of $Fe(CNR)_3$(*i*-Pr-DAB) (4) with DMAD resulted in the formation of two types of products, which were determined by the substituents on the isocyanides, just as has been described for the reactions of $Fe(CO)_2$(CNR)(DAB).[6] With the aromatic 2,6-xylyl isocyanide (**a**) a bicyclic compound (**7a**) was formed via a 1,3-dipolar cycloaddition of the alkyne to one of the Fe—N=C fragments. For the aliphatic *t*-Bu (**b**) and c-Hex (**c**) isocyanides a heterocyclic complex (**10b,c**), resulting from two successive cycloaddition reactions of two alkynes to both of the Fe—N=C fragments, was observed. The $Fe(CNR)_3$(*i*-Pr-THPP) complexes **10b,c** were very labile in solution, making ^{13}C NMR experiments very hard to perform. The ready dissociative loss of THPP from $Fe(CNR)_3$(*i*-Pr-THPP) gives the option of substituting THPP in complex **10** by DAB ligands and thereby regenerating the starting complex. This interesting feature is presently being investigated. The molecular structure of **10b** has been determined by a single-crystal X-ray structure analysis and will be discussed below.

The bicyclic complex **7a** showed an interesting reaction behavior. When it was treated with water, the unique tricyclic complex **8a** was formed, in which one of the ester groups is σ-bound to the metal. The molecular structure will be discussed below.

Molecular Structure of Fe(*t*-BuNC)$_3$(*i*-Pr-THPP) (10b). The bond distances and angles are given in Tables III and IV. The molecular structure together with the atomic numbering is shown in Figures 1 and 2.

The solid-state structure of Fe(*t*-BuNC)$_3$(*i*-Pr-THPP) (**10b**) consists of an Fe(*t*-BuNC)$_3$ unit η^3-bonded to a nitrogen atom and to the C–C double bond within the same pyrrole ring of the THPP ligand. The planar uncoordinated pyrrole ring makes an angle of 147.8° with the plane formed by the atoms C3–C4–C6–N2 of the coordinated ring. This last plane C3–C4–C6–N2 in turn makes an angle of 131° with the η^3-coordinated atoms C5–C6–N2. In the molecular structure of an uncoordinated pyrrolo[3,2-*b*]pyrrole the two planar pyrrole rings make a much more acute angle of 66.9°.[15] The coordination to the iron therefore forces the two rings to open up and folds the C5–C6–N2 unit away. The delocalization of the nitrogen (N1) lone pair and the double bond (C1–C2) of the uncoordinated pyrrole ring is interesting. This is reflected in the average sp^2 bond angles of 120° around N1 and in the slight shortening of the C2–N1 bond (1.34 (1) Å). As a consequence of the coordination to the metal the average bond angles around C5, C6, and N2 (106, 107, and 107°, respectively) and the bond distances of C5–N2

Table III. Bond Lengths (Å) for the Non-Hydrogen Atoms of Fe(*t*-BuNC)$_3$(*i*-Pr-THPP) (10b) (Esd's in Parentheses)

Fe–C5	1.90 (1)	Fe–C6	2.06 (1)	Fe–C21	1.78 (1)
Fe–C26	1.84 (1)	Fe–C31	1.86 (2)	Fe–N2	2.04 (1)
C1–C2	1.35 (2)	C1–C4	1.50 (2)	C1–C7	1.43 (2)
C2–C9	1.53 (2)	C2–N1	1.34 (1)	C3–C4	1.53 (2)
C3–C6	1.51 (2)	C3–N1	1.52 (2)	C4–N2	1.54 (2)
C5–C6	1.44 (2)	C5–C14	1.50 (2)	C5–N2	1.49 (2)
C6–C16	1.44 (2)	C7–O1	1.23 (2)	C7–O2	1.35 (2)
C8–O2	1.40 (2)	C9–O3	1.19 (2)	C9–O4	1.30 (2)
C10–O4	1.47 (2)	C11–C12	1.50 (3)	C11–C13	1.48 (2)
C11–N1	1.51 (2)	C14–O5	1.20 (2)	C14–O6	1.32 (2)
C15–O6	1.45 (2)	C16–O7	1.24 (2)	C16–O8	1.33 (1)
C17–O8	1.42 (2)	C18–C19	1.51 (2)	C18–C20	1.53 (2)
C18–N2	1.49 (1)	C21–N3	1.20 (2)	C22–C23	1.45 (2)
C22–C24	1.55 (3)	C22–C25	1.50 (2)	C22–N3	1.45 (2)
C26–N4	1.15 (2)	C27–C28	1.38 (4)	C27–C29	1.56 (4)
C27–C30	1.38 (4)	C27–N4	1.41 (2)	C31–N5	1.17 (2)
C32–C33	1.41 (3)	C32–C34	1.45 (5)	C32–C35	1.41 (4)
C32–N5	1.44 (3)				

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Table IV. Bond Angles (deg) for the Non-Hydrogen Atoms of Fe(*t*-BuNC)$_3$(*i*-Pr-THPP) (10b) (Esd's in Parentheses)

C5–Fe–C6	42.3 (5)	C5–Fe–C21	117.8 (6)	C5–Fe–C26	106.0 (6)
C5–Fe–C31	143.7 (6)	C5–Fe–N2	44.1 (5)	C6–Fe–C21	98.9 (5)
C6–Fe–C26	146.9 (6)	C6–Fe–C31	116.1 (6)	C6–Fe–N2	67.8 (4)
C21–Fe–C26	88.5 (6)	C21–Fe–C31	91.0 (7)	C21–Fe–N2	161.9 (6)
C26–Fe–C31	95.7 (7)	C26–Fe–N2	96.3 (5)	C31–Fe–N2	105.8 (5)
C2–C1–C4	108 (1)	C2–C1–C7	126 (1)	C4–C1–C7	123 (1)
C1–C2–C9	126 (1)	C1–C2–N1	114 (1)	C9–C2–N1	119 (1)
C4–C3–C6	106.1 (9)	C4–C3–N1	103 (1)	C6–C3–N1	115 (1)
C1–C4–C3	105 (1)	C1–C4–N2	119 (1)	C3–C4–N2	102.4 (9)
Fe–C5–C6	74.6 (8)	Fe–C5–C14	133.7 (8)	Fe–C5–N2	72.8 (7)
C6–C5–C14	132 (1)	C6–C5–N2	103 (1)	C14–C5–N2	121 (1)
Fe–C6–C3	111.7 (8)	Fe–C6–C5	63.1 (7)	Fe–C6–C16	126.7 (9)
C3–C6–C5	106.1 (9)	C3–C6–C16	116.5 (9)	C5–C6–C16	120 (1)
C1–C7–O1	126 (1)	C1–C7–O2	114 (1)	O1–C7–O2	120 (1)
C2–C9–O3	120 (1)	C2–C9–O4	112 (1)	O3–C9–O4	128 (1)
C12–C11–C13	114 (1)	C12–C11–N1	113 (1)	C13–C11–N1	110 (1)
C5–C14–O5	127 (1)	C5–C14–O6	111 (1)	O5–C14–O6	122 (1)
C6–C16–O7	123 (1)	C6–C16–O8	117 (1)	O7–C16–O8	119 (1)
C19–C18–C20	112 (1)	C19–C18–N2	111 (1)	C20–C18–N2	111 (1)
Fe–C21–N3	175 (1)	C23–C22–C24	110 (2)	C23–C22–C25	116 (1)
C23–C22–N3	109 (1)	C24–C22–C25	106 (1)	C24–C22–N3	108 (1)
C25–C22–N3	108 (1)	Fe–C26–N4	177 (1)	C28–C27–C29	95 (2)
C28–C27–C30	119 (2)	C28–C27–N4	115 (2)	C29–C27–C30	103 (2)
C29–C27–N4	104 (1)	C30–C27–N4	116 (2)	Fe–C31–N5	174 (1)
C33–C32–C34	116 (3)	C33–C32–C35	107 (2)	C33–C32–N5	115 (2)
C34–C32–C35	105 (3)	C34–C32–N5	105 (2)	C35–C32–N5	108 (2)
C2–N1–C3	109 (1)	C2–N1–C11	131 (1)	C3–N1–C11	120 (1)
Fe–N2–C4	116.1 (8)	Fe–N2–C5	63.1 (6)	Fe–N2–C18	120.4 (7)
C4–N2–C5	104.0 (8)	C4–N2–C18	118.6 (9)	C5–N2–C18	121 (1)
C21–N3–C22	165 (1)	C26–N4–C27	176 (2)	C31–N5–C32	148 (2)
C7–O2–C8	117 (1)	C9–O4–C10	113 (1)	C14–O6–C15	117 (1)
C16–O8–C17	118 (1)				

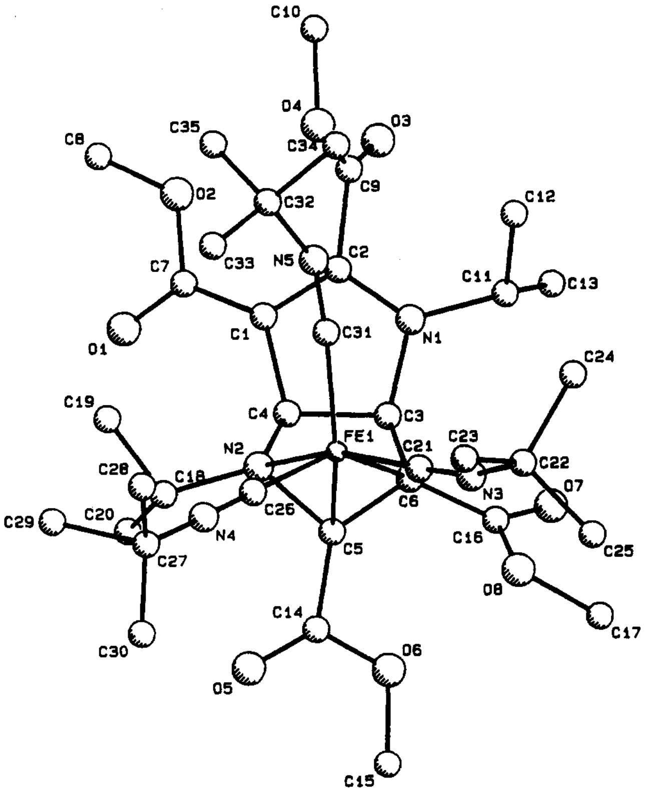

Figure 1. PLUTO drawing of Fe(*t*-BuNC)$_3$(THPP) (**10b**). Hydrogen atoms are omitted for clarity.

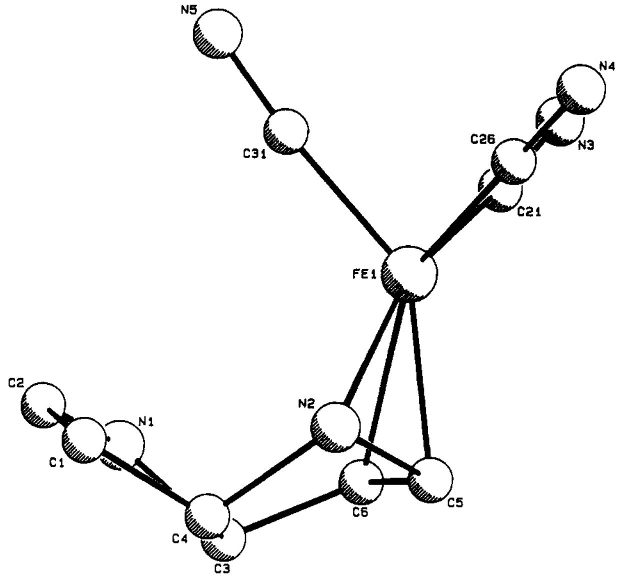

Figure 2. Side view of Fe(*t*-BuNC)$_3$(THPP) (**10b**). The *t*-Bu groups and the heterocycle substituents are omitted for clarity.

(1.49 (2) Å) and C5–C6 (1.44 (2) Å) are increased with respect to those in the uncoordinated pyrrole ring. These angles indicate sp^3 hybridization of C5, C6, and N2. The molecular structure of the coordinated THPP ligand is similar to that of the same ligand in the analogous Fe(CO)$_2$(*t*-BuNC)(*i*-Pr-THPP) complex, which we have described earlier.[6] To our knowledge these are the first examples of a single-crystal X-ray determination of an η^3-coordinated *N*,*N*-dialkyl enamine.

The C≡N and the N—C bond lengths of the three terminal isocyanide groups are 1.17 Å (mean) and 1.43 Å (mean), respectively, which is in accordance with a triple and a single bond. The bond angles around the isocyanide nitrogen atoms N3 and N4 are close to linear (165 (2) and 176 (2)°, respectively). These bond lengths and bond angles have also been found in many other isocyanide complexes.[4c,16] The rather small bond angle of 148 (2)°

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Table V. Bond Distances (Å) for the Non-Hydrogen Atoms of Fe(2,6-xylylNC)$_3$(tric) (8a) (Esd's in Parentheses)

Fe–C1	2.07 (1)	Fe–C23	1.82 (1)	Fe–C32	1.86 (1)
Fe–C41	1.80 (1)	Fe–N2	2.025 (8)	Fe–O1	1.95 (1)
C1–C2	1.49 (1)	C1–C5	1.52 (2)	C1–C7	1.46 (2)
C2–C3	1.49 (2)	C2–N1	1.46 (1)	C3–N2	1.26 (1)
C4–C5	1.54 (2)	C4–N1	1.36 (1)	C4–N3	1.30 (1)
C5–C6	1.53 (2)	C6–O1	1.25 (1)	C6–O2	1.26 (2)
C7–O3	1.36 (2)	C7–O4	1.22 (1)	C8–O3	1.47 (2)
C9–C10	1.52 (2)	C9–C11	1.52 (2)	C9–N1	1.46 (2)
C12–C13	1.50 (2)	C12–C14	1.53 (2)	C12–N2	1.50 (1)
C15–C16	1.38 (2)	C15–C20	1.38 (2)	C15–N3	1.42 (1)
C16–C17	1.36 (2)	C16–C21	1.50 (2)	C17–C18	1.38 (2)
C18–C19	1.38 (3)	C19–C20	1.44 (2)	C20–C22	1.52 (2)
C23–N4	1.17 (1)	C24–C25	1.38 (2)	C24–C29	1.36 (2)
C24–N4	1.43 (1)	C25–C26	1.40 (2)	C25–C30	1.48 (2)
C26–C27	1.38 (2)	C27–C28	1.38 (2)	C28–C29	1.40 (2)
C29–C31	1.50 (2)	C32–N5	1.18 (2)	C33–C34	1.35 (2)
C33–C38	1.36 (2)	C33–N5	1.42 (1)	C34–C35	1.39 (2)
C34–C39	1.48 (2)	C35–C36	1.37 (2)	C36–C37	1.37 (2)
C37–C38	1.39 (2)	C38–C40	1.49 (2)	C41–N6	1.16 (2)
C42–C43	1.37 (2)	C42–C47	1.37 (2)	C42–N6	1.41 (2)
C43–C44	1.40 (2)	C43–C48	1.49 (2)	C44–C45	1.39 (2)
C45–C46	1.37 (2)	C46–C47	1.37 (2)	C47–C49	1.51 (2)

at N5 is remarkable. This bending of a terminal isocyanide atom, which has been encountered before,[17] has been attributed either to extensive π back-donation, resulting in an increase of the sp^2 character at the nitrogen atom, or to steric factors. Within the accuracy of the present data, however, the bond lengths of the C31–N5–C32 unit clearly indicate a triple and a single bond. The wavenumbers for $\nu_{C\equiv N}$ in the IR spectrum (2177, 2123, 2043 cm^{-1}; vide infra) also clearly indicate a triple bond. Therefore, the bending of the isocyanide ligand underneath the organic heterocycle is probably of steric origin.

Molecular Structure of Fe(2,6-xylylNC)$_3$(tric) (8a). The single-crystal X-ray structure of the tricyclic complex **8a** has been determined. The experimental details of the data collection, determination, and refinement of the structure have been reported elsewhere.[18] The bond distances and bond lengths are given in Tables V and VI. Figure 3 shows the molecular structure together with the atomic numbering.

The structure consists of three five-membered rings, interconnected by one of the former alkyne carbon atoms (C1). The metal atom is incorporated in two of the rings. According to the classification of Altona et al.[19] the conformation of the three rings is as follows. The ring consisting of C1–C2–C3–N2–Fe can be described as a half-chair (Δ = 0.23), the ring of C1–C2–C4–C5–N1 resembles a pseudo-half-chair (Δ = 6.8), and the last ring, C1–C5–C6–O1–Fe, is classified as a distorted envelope (Δ = 19.9). The C4–N3 bond length of the inserted isocyanide is elongated to 1.30 (1) Å. Also, the bond angle around N1 has changed from linear to 122°, clearly indicating sp^2 hybridization. The bond distances of 1.25 (1) and 1.26 Å for O1–C6 and C6–O2 respectively indicate a large degree of delocalization, which is commonly encountered for ester functions.[20] The Fe–O1 σ bond has a length of 1.95 (1) Å. This value is close to the mean value of 2.02 Å found for Fe–O–C(O) units, after a search in the Cambridge Structural Data Base system.[20]

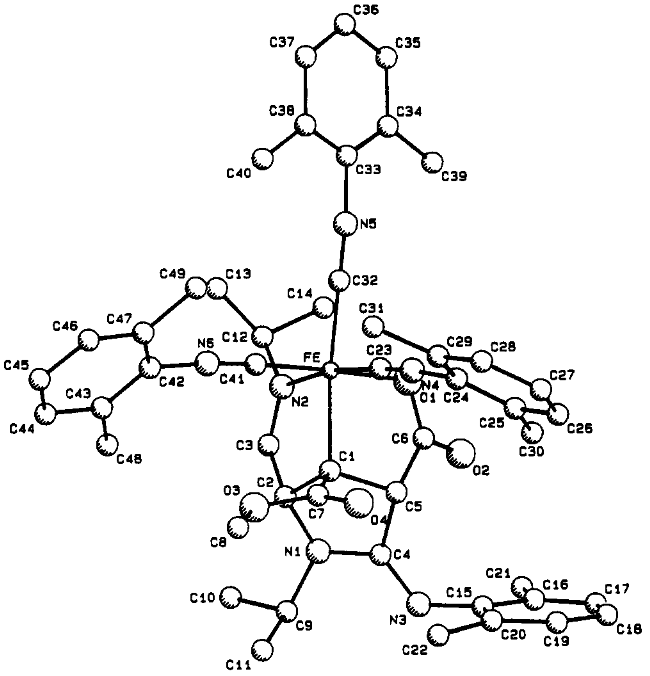

Figure 3. PLUTO drawing of Fe(2,6-xylylNC)$_3$(tric) (**8a**). Hydrogen atoms are omitted for clarity.

The C≡N bond lengths in the three terminal 2,6-xylyl isocyanides are 1.17 Å (mean). The bond distances between the nitrogen atoms and the phenyl rings amount to 1.42 Å (mean). The bond angles at the isocyanide nitrogen atoms are 174° (mean). These bond lengths and bond angles are commonly found for terminal isocyanides[4c,16] and agree with a bonding situation as described by resonance structure A in Figure 4.

NMR Spectroscopy. The ^{1}H and ^{13}C NMR data for Fe(CNR)$_3$(*i*-Pr-DAB) (**4**), Fe(CNR)$_3$(*i*-Pr-THPP) (**10b**,**c**), Fe(2,6-xylylNC)(bic) (**7a**), and Fe(2,6-xylylNC)(tric) (**8a**) are listed in Tables VII and VIII.

^{1}H NMR. The imine protons of Fe(CNR)$_3$(*i*-Pr-DAB) (**4**) appear as a singlet at 7.6 ppm, which is within the 7–9 ppm range commonly observed for $\sigma(N),\sigma(N')$-coordinated DAB ligands.[21,22] The three isocyanides give rise to only one (broad) signal, suggesting a scrambling of the isocyanides. The dynamic process will be discussed in the ^{13}C NMR section (vide infra).

The [2.2.2] bicyclic complex **7a** shows two characteristic doublets of the former imine proton and the remaining imine proton. The proton of the intact imine unit resonates at 8.53 ppm. The proton attached to the C–C-coupled former imine carbon gives rise to a signal at 5.75 ppm. This upfield shift is a logical consequence of the cycloaddition reaction, resulting in a rehybridization from sp^2 to

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Table VI. Bond Angles (deg) for the Non-Hydrogen Atoms of Fe(2,6-xylylNC)$_3$(tric) (8a) (Esd's in Parentheses)

C1–Fe–C23	90.4 (5)	C1–Fe–C32	173.5 (6)	C1–Fe–C41	93.2 (5)
C1–Fe–N2	81.1 (4)	C1–Fe–O1	84.4 (4)	C23–Fe–C32	89.2 (5)
C23–Fe–C41	93.7 (6)	C23–Fe–N2	170.3 (4)	C23–Fe–O1	89.3 (5)
C32–Fe–C41	93.3 (6)	C32–Fe–N2	98.7 (4)	C32–Fe–O1	89.1 (5)
C41–Fe–N2	91.4 (5)	C41–Fe–O1	176.2 (4)	N2–Fe–O1	85.3 (4)
Fe–C1–C2	110.6 (7)	Fe–C1–C5	106.6 (8)	Fe–C1–C7	111.3 (8)
C2–C1–C5	103 (1)	C2–C1–C7	114 (1)	C5–C1–C7	110.6 (9)
C1–C2–C3	110.1 (9)	C1–C2–N1	106.7 (8)	C3–C2–N1	112 (1)
C2–C3–N2	120 (1)	C5–C4–N1	107.9 (9)	C5–C4–N3	127.5 (9)
N1–C4–N3	125 (1)	C1–C5–C4	102.5 (9)	C1–C5–C6	107.9 (9)
C4–C5–C6	114 (1)	C5–C6–O1	118 (1)	C5–C6–O2	119 (1)
O1–C6–O2	123 (1)	C1–C7–O3	114.5 (9)	C1–C7–O4	125 (1)
O3–C7–O4	120 (1)	C10–C9–C11	109 (1)	C10–C9–N1	111 (1)
C11–C9–N1	112 (1)	C13–C12–C14	115 (1)	C13–C12–N2	110 (1)
C14–C12–N2	109.4 (9)	C16–C15–C20	121 (1)	C16–C15–N3	120 (1)
C20–C15–N3	118 (1)	C15–C16–C17	121 (1)	C15–C16–C21	120 (1)
C17–C16–C21	120 (1)	C16–C17–C18	119 (1)	C17–C18–C19	121 (1)
C18–C19–C20	119 (1)	C15–C20–C19	118 (1)	C15–C20–C22	125 (1)
C19–C20–C22	117 (1)	Fe–C23–N4	177 (1)	C25–C24–C29	126 (1)
C25–C24–N4	118 (1)	C29–C24–N4	116 (1)	C24–C25–C26	116 (1)
C24–C25–C30	123 (1)	C26–C25–C30	121 (1)	C25–C26–C27	120 (1)
C26–C27–C28	123 (1)	C27–C28–C29	118 (1)	C24–C29–C28	117 (1)
C24–C29–C31	124 (1)	C28–C29–C31	118 (1)	Fe–C32–N5	175 (1)
C34–C33–C38	125 (1)	C34–C33–N5	119 (1)	C38–C33–N5	116 (1)
C33–C34–C35	118 (1)	C33–C34–C39	122 (1)	C35–C34–C39	120 (1)
C34–C35–C36	118 (1)	C35–C36–C37	123 (1)	C36–C37–C38	119 (1)
C33–C38–C37	117 (1)	C33–C38–C40	124 (1)	C37–C38–C40	119 (1)
Fe–C41–N6	177 (1)	C43–C42–C47	121 (1)	C43–C42–N6	118 (1)
C47–C42–N6	121 (1)	C42–C43–C44	120 (1)	C42–C43–C48	122 (1)
C44–C43–C48	118 (1)	C43–C44–C45	119 (1)	C44–C45–C46	121 (2)
C45–C46–C47	120 (1)	C42–C47–C46	120 (1)	C42–C47–C49	121 (1)
C46–C47–C49	119 (1)	C2–N1–C4	110.7 (9)	C2–N1–C9	125 (1)
C4–N1–C9	117.5 (9)	Fe–N2–C3	116.4 (7)	Fe–N2–C12	126.5 (7)
C3–N2–C12	117.0 (9)	C4–N3–C15	122 (1)	C23–N4–C24	172 (1)
C32–N5–C33	174 (1)	C41–N6–C42	175 (1)	Fe–O1–C6	115.3 (9)
C7–O3–C8	117.0 (9)				

Table VII. ^{1}H NMR Data[a] for Fe(CNR)$_3$(DAB) (4),[b] Fe(2,6-xylylNC)$_3$([2.2.2]bic) (7a), Fe(2,6-xylylNC)$_3$(tric) (8a), and Fe(CNR)$_3$(*i*-Pr-THPP) (10b,c)

compd	^{1}H NMR data[c]
4a	7.66 (2H, s, *H*C=N), 6.76 (9H, m, aryl *H*), 5.38 (2H, sept, 7 Hz, $\mathrm{C}H(\mathrm{CH_3})_2$), 2.35 (6H, s, aryl $\mathrm{C}H_3$), 1.67 (12H, d, 7 Hz, $\mathrm{CH(C}H_3)_2$)
4b	7.58 (2H, s, *H*C=N), 5.21 (2H, sept, 7 Hz, $\mathrm{C}H(\mathrm{CH_3})_2$), 1.71 (27H, s, $\mathrm{C{\equiv}NC(C}H_3)_3$), 1.24 (12H, d, 7 Hz, $\mathrm{CH(C}H_3)_2$)
4c	7.66 (2H, s, *H*C=N), 5.33 (2H, sept, 7 Hz, $\mathrm{C}H(\mathrm{CH_3})_2$), 3.45 (3H, m, c-Hex C*H*), 1.78–0.91 (42H, m, $\mathrm{CH(C}H_3)_2$, c-Hex$\mathrm{C}H_2$)
7a	8.53 (1H, d, 7 Hz, *H*C=N), 7.80–6.90 (9H, m, aryl *H*), 6.78, 6.71 (2 × 1H, 2 × d, 7 Hz, *m* aryl *H*), 6.44 (1 H, dd, 7 Hz, 7 Hz, *p* aryl *H*), 5.75 (1H, d, 4 Hz, N=CC*H*), 4.43 (1H, sept, 7 Hz, $\mathrm{C}H(\mathrm{CH_3})_2$), 3.73, 3.57 (2 × 3H, 2 × s, $\mathrm{OC}H_3$; 1H, m, $\mathrm{C}H(\mathrm{CH_3})_2$), 2.50, 2.41, 2.23 (3 × 6H, s, terminal C≡N aryl $\mathrm{C}H_3$), 1.92, 1.81 (2 × 3H, s, ring C=N aryl $\mathrm{C}H_3$), 1.40, 1.24, 0.83, 0.82 (12H, 4 × d, 7Hz, $\mathrm{CH(C}H_3)_2$)
8a	7.93 (1H, s, b, *H*C=N), 7.15–6.95 (10H, m, aryl *H*), 6.89 (1H, d, 6 Hz, m aryl *H*), 6.75 (1H, dd, 6 Hz, 6 Hz, *p* aryl *H*), 5.50 (1 H, s, b, N=CC*H*), 4.67, 4.32 (2 × 1H, 2 × sept, 7 Hz, $\mathrm{C}H(\mathrm{CH_3})_2$), 4.11 (1 H, s, C(O)C*HC*=N aryl), 3.35 (3H, s, $\mathrm{OC}H_3$), 2.44, 2.41, 2.22 (3 × 6H, s, terminal C≡N aryl $\mathrm{C}H_3$), 2.37, 2.01 (2 × 3H, s, ring C=N aryl $\mathrm{C}H_3$), 1.42, 1.35, 1.29 (12 H, 3 × d, 7 Hz, $\mathrm{CH(C}H_3)_2$)
10b	4.91, 4.17 (2 × 1H, d, 9 Hz, bridgehead *H*), 3.83, 3.69, 3.55, 3.53 (4 × 3H, 4 × s, $\mathrm{OC}H_3$; 2H, m ($\mathrm{C}H(\mathrm{CH_3})_2$), 1.39 (27H, s, b, $\mathrm{C{\equiv}NC(C}H_3)_3$), 1.19, 1.10, 0.83 (12H, 3 × d, 8 Hz, $\mathrm{CH(C}H_3)_2$)
10c	4.96, 4.23 (2 × 1H, d, 9Hz, bridgehead *H*), 3.85, 3.72. 3.56, 3.55 (4 × 3 H, 4 × s, $\mathrm{OC}H_3$; 2H, m, $\mathrm{C}H(\mathrm{CH_3})_2$; 3H, m, c–Hex C*H*), 1.83–1.03 (42H, m, $\mathrm{CH(C}H_3)_2$, c-Hex($\mathrm{C}H_2$)

[a] The chemical shift values, in ppm relative to Me$_4$Si, measured in CDCl$_3$ at 293 K and 300.15 MHz. [b] Measured in C$_6$D$_6$. [c] Abbreviations: s= singlet, d = doublet, m = multiplet, b = braod.

Table VIII. ^{13}C NMR Data[a] for Fe(CNR)$_3$(DAB) (4),[b] Fe(2,6-xylylNC)$_3$([2.2.2]bic) (7a), Fe(2,6-xylylNC)$_3$(tric) (8a), and Fe(CNR)$_3$(*i*-Pr-THPP) (10b,c)

compd	^{13}C NMR data
4a	191.8 (*C*≡N aryl), 133.4 (*C*=N), 132.1, 130.2, 126.8, 124.5 (aryl *C*), 59.6 ($C\mathrm{H(CH_3)_2}$), 24.5 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 17.5 (C≡N aryl $C\mathrm{H_3}$)
4b	190.8 (*C*≡N-*t*-Bu), 130.8 (*C*=N), 58.5 ($C\mathrm{H(CH_3)_2}$), 55.1 ($\mathrm{C{\equiv}N}C\mathrm{(CH_3)_3}$), 30.25 ($\mathrm{C{\equiv}NC(}C\mathrm{H_3)_3}$), 24.3 ($\mathrm{CH(}C\mathrm{H_3)_2}$)
7a	213.4, 125.8 (Fe—*C*=*C*), 195.4 (ring *C*=N aryl), 181.4, 180.4, 178.0 (*C*≡N), 168.1 (imine *C*=N), 160.8, 153.8 (ester *C*O), 134.6, 134.5, 134.3, 129.2, 129.1, 128.8, 127.7, 127.6, 127.3, 127.0, 126.6, 126.1, 126.0, 125.9, 125.8, 125.2, 116.3 (aryl *C*), 63.1, 47.1 ($C\mathrm{H(CH_3)_2}$), 55.7, 50.7 (ester $\mathrm{O}C\mathrm{H_3}$), 51.9 (N=C*C*), 24.1, 23.7, 19.8, 19.6 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 19.2, 15.3 (ring C=N aryl $C\mathrm{H_3}$), 19.1, 18.9, 18.3 (terminal C≡N aryl $C\mathrm{H_3}$)
8a[c]	182.4, 182.2 (C$_6$, C$_7$), 179.7, 177.6, 176.0 (C$_{23}$, C$_{32}$, C$_{41}$), 174.2 (C$_3$), 149.9 (C$_4$), 135.7, 135.1, 134.6 (C$_{25}$, C$_{29}$, C$_{34}$, C$_{38}$, C$_{43}$, C$_{47}$), 129.8, 129.3, 129.0 (C$_{24}$, C$_{33}$, C$_{42}$), 128.9, 128.7, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.2 (C$_{26}$, C$_{27}$, C$_{28}$, C$_{35}$, C$_{36}$, C$_{37}$, C$_{44}$, C$_{45}$, C$_{46}$, C$_{15}$, C$_{16}$, C$_{17}$, C$_{18}$, C$_{19}$, C$_{20}$), 121.5 (C$_5$), 71.7 (C$_2$), 62.5 (C$_{12}$), 52.0 (C$_1$), 51.1 (C$_8$), 44.8 (C$_9$), 24.4, 23.3, 23.1 (C$_{10}$, C$_{11}$, C$_{13}$, C$_{14}$), 19.6, 19.8 (C$_{22}$, C$_{21}$), 20.1, 19.4, 19.1 (C$_{30}$, C$_{31}$, C$_{39}$, C$_{40}$, C$_{48}$, C$_{49}$)
10b[d]	178.7, 175.2, 165.2 (C$_7$, C$_9$, C$_{14}$, C$_{16}$), 154.1 (C$_2$), 95.1 (C$_1$), 82.0 (C$_5$), 72.3, 69.4 (C$_3$, C$_4$), 58.5 (C$_6$), 56.0, 55.8, 55.7 (C$_{21}$, C$_{26}$, C$_{31}$), 56.5, 54.4, 53.3, 51.8, 51.3, 50.6 (C$_8$, C$_{10}$, C$_{11}$, C$_{15}$, C$_{17}$, C$_{18}$), 31.5, 31.2, 30.4 (C$_{22}$, C$_{27}$, C$_{32}$), 21.5, 20.0, 19.6 (C$_{23}$, C$_{24}$, C$_{25}$, C$_{28}$, C$_{29}$, C$_{30}$, C$_{33}$, C$_{34}$, C$_{35}$)

[a] The chemical shift values, in ppm relative to Me$_4$Si, measured in CDCl$_3$ at 243 K and 75.47 MHz. [b] Measured in acetone-d_6. [c] See Figure 1 for atomic numbering. [d] See Figure 3 for atomic numbering. Not all signals could be observed.

sp^3. The inserted 2,6-xylyl isocyanide displays interesting features. As a result of the insertion, the 2,6-xylyl isocyanide has lost a rotational degree of freedom. This results in an asymmetric xylyl group, with two inequivalent methyl groups resonating at 1.92 and 1.81 ppm. From the aromatic protons, which are shifted upfield compared to those of the terminal isocyanides, the two meta protons give two doublets (J = 7 Hz) at 6.78 and 6.71 ppm. The para proton is split into a double doublet at 6.43 ppm. As a result of the identical coupling constants (J = 7 Hz) the signal appears as a triplet. The two inequivalent ester methyl groups resonate at 3.7 and 3.57 ppm.

The asymmetric character of the $\mathrm{Fe(CNR)_3}$(*i*-Pr-THPP) complexes **10b,c**, resulting from the η^3 coordination of one pyrrole ring to the $\mathrm{Fe(CNR)_3}$ unit, is clearly visible in the ^{1}H NMR spectrum. As a consequence of the double cycloaddition the hybridization of both of the former imine carbon atoms (C3, C4) has changed to sp^3 resulting in an upfield shift of the attached protons of ca. 3 ppm. Their signals appear as two doublets as a consequence of the inequivalency of the two pyrrole rings. The four inequivalent methoxy groups give rise to a set of four singlets.

In the complex Fe(2,6-xylylNC)(tric) (**8a**), the imine proton (H–C3) and the former imine proton (H–C2) resonate at 7.93 and 5.50 ppm, respectively. Instead of the expected two doublets two slightly broadened singlets are found. The Newman projection along the C2–C3 axis (cf. Figure 3) shows a torsion angle between the two protons of 75°, which according to the Karplus relation will result in minimal coupling. The newly introduced proton on the former alkyne carbon atom (C5) gives rise to a singlet at 4.11 ppm. When the tricyclic structure is synthesized with $\mathrm{D_2O}$ instead of $\mathrm{H_2O}$, this signal is absent in the ^{1}H NMR spectrum. Instead it is found in the ^{2}H NMR spectrum at 4.1 ppm. This proves that the proton is delivered by water. The remaining ester methyl group resonates at 3.35 ppm. As in the bicyclic structure **7a**, the inserted 2,6-xylyl isocyanide has become asymmetric. This is reflected in the appearance of the aromatic protons as a double doublet at 6.75 ppm for the para position and a doublet at 6.89 ppm for one of the meta protons (the other doublet is hidden under the bulk of the other aromatic signals). The two isocyanide methyl groups resonate at 2.37 and 2.01 ppm. The methyl groups of the three terminal isocyanides give rise to three singlets, as was also observed for the bicyclic complex **7a**; i.e., the terminal isocyanide ligands do not interchange on the NMR time scale, and their aryl substituents can rotate freely.

^{13}C NMR.[23] The imine carbon nuclei of $\mathrm{Fe(CNR)_3}$(*i*-Pr-DAB) (**4**) resonate near 130 ppm. In comparison to signals of the imine carbon nuclei of free *i*-Pr-DAB (158.5 ppm), $\mathrm{Fe(CO)_3}$(*i*-Pr-DAB) (144 ppm), and $\mathrm{Fe(CO)_2(CNR)}$(*i*-Pr-DAB) (138 ppm)[22] an increased paramagnetic shielding is observed. Coordination of an *i*-Pr-DAB ligand to a $\mathrm{Fe(CNR)_3}$ moiety leads to an upfield coordination shift of 28 ppm for the imine carbon. The shift difference between the tris-CO and the tris-CNR complexes for the imine carbon nucleus amounts to 14 ppm. This is rationalized by the better σ-donating/worse π-accepting capacities of CNR compared to CO,[4] enhancing the electron density on the complex.

The three terminal carbon nuclei of the CNR ligands give a single resonance near 190 ppm. It is interesting that both the aromatic 2,6-xylyl isocyanide (**a**) and the aliphatic *tert*-butyl isocyanide (**b**) give a signal at comparably low frequency. In any other examples, e.g., for uncoordinated isocyanides[24] as in the $\mathrm{Fe(CO)_2(CNR)}$(DAB)[22a] complexes, the terminal carbon atom of the aromatic isocyanide resonates at a higher frequency than in the aliphatic analogues. This behavior may be explained by considering the three resonance structures for the metal isocyanide fragment in Figure 4. Resonance structure A, where the σ donation of the isocyanides dominates, is most important for aliphatic isocyanides. Resonance structure B is valid for both aliphatic and aromatic isocyanides; there is a substantial amount of π back-donation into the isocyanide ligand. Structure C, which enhances the electron-withdrawing properties, plays a role for the aromatic isocyanides.[4a,c,d,24b,25] For the complexes $\mathrm{Fe(CNR)_3}$(*i*-Pr-DAB) (**4**), the following reasoning has to be used. Due to the presence of three terminal isocyanide ligands, the metal has to redistribute the electron density via strongly enhanced π back-donation to the ligands. Therefore, for the tris(*tert*-butyl isocyanide) complex **4b** mainly resonance structure B is valid; for the tris(2,6-xylyl isocyanide) complex **4a** either resonance structure B or C applies. For both structures B and C the electronic situation at the terminal isocyanide carbon nucleus is comparable, resulting in comparable chemical shifts for both the tris *t*-Bu and the tris xylyl complexes. Interestingly, the three terminal CNR ligands are identical on the NMR time scale down to 243 K. A similar observation for terminal CO ligands has been reported by us for $\mathrm{Fe(CO)_2(CNR)}$(DAB)[22a] and by Leibfritz et al. for $\mathrm{Fe(CO)_3}$(DAB).[22b] Furthermore, the two N-*i*-Pr groups give rise to only one set of signals in both ^{1}H and ^{13}C NMR. The diastereotopic methyl groups would be expected to appear as a set of two signals. All of this may be explained by Berry pseudorotations,[26] which scramble the three terminal ligands and interchange the two faces of the chelating DAB ligand.

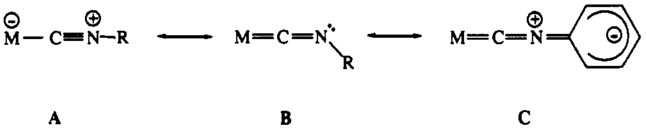

Figure 4. Resonance structures of the metal–isocyanide unit.

The typical features of the [2.2.2] bicyclic structure **7a** are clearly refected in the ^{13}C NMR spectrum (see Table VIII). The imine carbon nucleus resonates at 168.1 ppm. The C–C-coupled former imine carbon nucleus gives a signal at 55.7 ppm, reflecting its change of hybridization from sp^2 to sp^3. As a consequence of the cycloaddition reaction the two former alkyne carbon atoms have become inequivalent. The alkyne carbon nucleus which is bound to the former imine carbon atom resonates at 125.8 ppm. The other former alkyne carbon atom which is σ-bonded to the metal is shifted downfield to 213.4 ppm. The carbon nucleus of the inserted isocyanide, which is incorporated in one of the rings, resonates at 195.4 ppm. These values

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(23) This discussion concerns only the complexes with the *tert*-butyl and 2,6-xylyl isocyanides, since it proved to be impossible to record ^{13}C NMR spectra of the cyclohexyl complexes, due to their extreme lability.

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Table IX. IR Data and Elemental Analyses for Fe(CNR)$_3$(DAB) (4), Fe(2,6-xylylNC)$_3$([2.2.2]bic) (7a), Fe(2,6-xylylNC)$_3$(tric) (8a), and Fe(CNR)$_3$(*i*-Pr-THPP) (10b,c) and FD Mass Data^d for Fe(CNR)$_3$(DAB) (4)

compd	$\nu_{C\equiv N}$^{a} (cm^{-1})	M^d	elemental anal. (%)^b C	H	N
4a	2070 (s), 1970 (b)^c	590 (590)			
4b	2095 (b), 2058 (b), 1972 (b), 1931 (b)^c	445 (446)			
4c	2085, 2050, 1978, 1920^{c,e}	523 (524)			
7a	2129 (s), 2065 (b)		69.46 (69.59)	6.85 (6.78)	9.64 (9.74)
8a	2140 (s), 2075 (b)		67.96 (69.33)	6.71 (6.65)	9.65 (9.90)
10b	2177 (w), 2123 (s), 2043 (s)		57.60 (57.61)	7.72 (7.60)	9.53 (9.60)
10c	2175 (w), 2120 (s), 2045 (s)		58.28 (60.96)	7.31 (7.62)	8.32 (8.67)

^{a} Measured in CHCl$_3$. ^{b} Observed (calculated). ^{c} Measured in C$_5$H$_{12}$, at room temperature. ^{d} Observed (calculated) masses of the molecular ion (*m/e*); the M values are based upon the ^{56}Fe isotope. ^{e} The bands are superimposed on a broad line.

are comparable to those in the analogous (bicyclo[2.2.2])-Fe(CO)$_3$ compounds.[5] The asymmetry of the aryl substituent of the inserted isocyanide is also visible in the ^{13}C NMR spectrum. The two inequivalent methyl carbons resonate at 19.2 and 15.3 ppm. The aromatic carbon resonances are obscured by the bulk of the aromatic signals of the terminal ligands. The three carbon nuclei of the terminally coordinated isocyanides resonate at 178.0, 180.4, and 181.4 ppm. The six *o*-methyl carbon groups give three signals at 18.3, 18.9, and 19.1 ppm. This shows that the three terminal isocyanides to not interchange positions on the NMR time scale but that they can freely rotate around the bond to the metal.

The ^{13}C NMR spectra of Fe(CNR)$_3$(*i*-Pr-THPP) (**10b,c**) are of insufficient quality (due to decomplexation to give free THPP) to discuss the spectroscopic properties thoroughly. However, features comparable to those observed for Fe(CO)$_2$(CNR)(*i*-Pr-THPP)[6b] should most likely be encountered for the present complexes **10b,c**.

The effects of the cyclometalation reaction of one of the ester groups is reflected in the ^{13}C NMR spectrum (see Table VIII) of the tricyclic complex **8a**. As a consequence of the ring-closure reaction, the former alkyne carbon atoms have become sp^3 hybridized and have shifted upfield. The carbon nucleus (C1) σ-bonded to the metal resonates at 52.0 ppm. The other former alkyne carbon atom (C5), to which the newly introduced proton is attached, gives a signal at 121.5 ppm. The carboxy atom (C6) of the metal-bound ester group gives a signal at 182.2 ppm, close to the one (C7) of the remaining ester group (182.4 ppm). As has been discussed for the bicyclic complex **7a**, the restricted rotation of the aryl ring of the inserted isocyanide results in two signals for the two *o*-methyl groups (C21, C22) at 19.8 and 19.6 ppm. The three terminal carbon nuclei of the terminal isocyanides (C23, C32, C41) give rise to a set of three separate signals around 178 ppm. This again indicates that the three terminal isocyanide ligands do not interchange on the NMR time scale in the octahedral coordination geometry.

IR Spectroscopy. The IR data, together with the FD mass data of the Fe(CNR)$_3$(*i*-Pr-DAB) (4) complexes, are listed in Table IX.

Due to their low intensity and to overlap with other bands the C=N stretching vibrations of the α-diimine ligands of complexes 4 and the imine functions of complexes 7, 8, and 10 could not be assigned. The C=O absorptions of the esters of complexes 7, 8, and 10 are visible as a broad band around 1700 cm^{-1} and are therefore not suitable for subtracting additional information about the geometry of the complexes.

The IR spectrum of Fe(2,6-xylylNC)$_3$(*i*-Pr-DAB) (**4a**) shows two intense $\nu_{C\equiv N}$ absorptions at 1970 (very broad) and 2070 cm^{-1}. The broad band at 1970 cm^{-1} may indicate the presence of a degenerate (E) vibration for a complex having C_{3v} local symmetry. The asymmetry of this band, however, points to a somewhat lower symmetry. Comparable observations have been made for the CO vibrations in Fe(CO)$_3$(DAB) and Ru(CO)$_3$(DAB) complexes.[21b,27]

The IR spectrum of Fe(*t*-BuNC)$_3$(*i*-Pr-DAB) (**4b**) shows an interesting temperature dependence. At room temperature four rather broad bands at 1931, 1972, 2058 and 2095 cm^{-1} are observable. When the temperature is lowered to 147 K, the bands become remarkably better resolved, and at the same time the bands at 1972 and 2095 cm^{-1} increase in relative intensity. These bands remain more broadened than the other two. The four bands clearly point to the presence of two isomeric forms of Fe(*t*-BuNC)$_3$-(*i*-Pr-DAB) (**4b**). These may be geometrical isomers or isomers with different coordination of the DAB ligand (vide infra). The geometrical isomers would be of square-pyramidal (sqp) C_s and most likely a trigonal-bipyramidal (tbp) C_{3v} structure. Two isomeric tbp structures are not possible, since the bite angle of the DAB ligand never exceeds 80 ± 1°.[21b,27a,28] Consequently, in the tbp coordination geometry one of the nitrogen atoms is always equatorial and the other is axially oriented. At least in principle, two isomeric sqp structures are possible: one in which both nitrogen atoms occupy basal positions and another with one nitrogen atom in a basal and the other one in an apical position. However, it has been found that in all analogous Fe(CO)$_3$(DAB) complexes of sqp geometry the two nitrogen atoms of the DAB ligand are found in basal positions.[28] At low temperature the less symmetric geometry is more favored, reflected by the increase of the more broadened bands. The interconversion of the two isomers can be visualized by pseudorotations.[26] As has been stated earlier, the two geometrical isomers interconvert rapidly on the NMR time scale (10^4 s^{-1}) and cannot be observed separately. On the IR time scale (10^{12} s^{-1}), however, they can be distinguished and their relative quantities can be monitored as a function of the temperature. This has been encountered before in the case of Fe(CO)$_3$(η^4-diene) complexes.[29] In those complexes the three CO ligands gave only one signal in ^{13}C NMR spectroscopy, as a result of fast scrambling. With IR

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spectroscopy a splitting of bands was observed on cooling. At room temperature only one isomer (or one set of bands belonging to one isomer with the bands of the other isomer superimposed on it) was observed.

Besides an interconversion between two geometries around the central iron atom, the appearance of a double set of bands might also be ascribed to a change of coordination mode of the DAB ligand from σ(N),σ(N′) to η^4(CN,CN′), Teuben et al. have described the single-crystal X-ray structure of $[(\eta^5\text{-}C_5Me_5)Hf(i\text{-Pr-DAB})(\mu_2\text{-}H)]_2$, in which the DAB ligand was π,π coordinated.[30] The change of coordination mode to a π,π coordination has been observed for $Fe(CO)_3$(DAB) on photolysis in an Ar matrix at 10 K and in pentane solution at 150 K.[27b,31] This was accompanied by a shift of the CO vibrations of ca. 40 cm^{-1} to higher frequencies and disappearance of the intense MLCT transitions in the visible region. The difference of ca. 40 wavenumbers between the two sets of $\nu_{C\equiv N}$ bands in the present case are at least suggestive and could eventually point to a η^4(CN,CN′) coordination of the DAB ligand in complex **4b**. However, visually we cannot observe any changes in the intense color of the complex when the temperature and therefore the isomer ratio is changed. Quantitative UV measurements were unfortunately not reproducible due to the extreme air sensitivity. The shift of the CO vibrations to higher frequencies on π,π coordination of the DAB ligands indicates better π-accepting properties of the π,π-coordinated DAB. It cannot be excluded that the high electron density at the metal in **4b**, due to the better donor properties of CNR,[4] favors the better π-accepting π,π coordination mode of the DAB ligand.

The IR spectrum of $Fe(c\text{-}HexNC)_3(i\text{-Pr-DAB})$ (**4c**) displays a broad band with a pattern superimposed on it comparable to that of $Fe(t\text{-}BuNC)_3(i\text{-Pr-DAB})$ (**4b**), indicating that the situation may be as has been described for **4b**. However, one has to be careful with conclusions; due to the extreme lability of complex **4c** it was not possible to perform VTIR experiments or even to obtain a well-resolved IR spectrum.

While in **4b**, and probably also in the very labile **4c**, two isomers are present at room temperature, there is only one isomer visible of **4a** with the aromatic isocyanide. This may indicate that in this case one of the isomers is thermodynamically much more stable than the other. Neither steric nor electronic reasoning offers a straightforward explanation for this phenomenon.

Compared to those for the starting complexes **4**, the $\nu_{C\equiv N}$ vibrations of complexes **7**, **8**, and **10** have shifted to higher frequencies. For complexes **10b**,**c** this clearly indicates that the DAB ligand is a worse π-acceptor than the THPP ligand. For complexes **7a** and **8a** the change of the formal oxidation state of the central metal atom from 0 to 2 accounts for the shift to higher frequencies.

FD Mass Spectroscopy. In this study, FD mass spectroscopy has proven an excellent tool for the identification of the mononuclear species $Fe(CNR)_3(i\text{-Pr-DAB})$ (**4**), for which elemental analyses were precluded due to their high lability. Good care was taken to avoid decomposition of the extremely air-sensitive compounds during the sampling period. The molecular ion masses, which are shown in Table IX, confirm the calculated values.

Discussion

Formation of $Fe(CNR)_3(i\text{-Pr-THPP})$ (10b,c). For the complexes $Fe(CO)_3(DAB)$[5e] and $Fe(CO)_2(CNR)(DAB)$,[6b] the reaction with alkynes has been described as an oxidative 1,3-dipolar [3 + 2] cycloaddition, regarding the Fe—N=C fragment as an isolobal analogue of an azomethyne ylide ($R_2C{=}N^+C^-R_2$). The first step in the reaction of $Fe(CNR)_3$(DAB) (**4**) with DMAD (see Scheme II) can likewise be described as a [3 + 2] cycloaddition leading to the formation of a ferrabicyclo[2.2.1] intermediate (**5**) which in the present case, however, cannot be observed. The existence of this intermediate has been established by single-crystal X-ray structure determinations of analogous compounds.[5e,32] Intermediate **5** can either give an intramolecular insertion reaction leading to a [2.2.2] bicyclic structure or undergo an *intermolecular* reaction with another alkyne. This second reaction of intermediate **5** with DMAD is again decribed as a [3 + 2] cycloaddition to the Fe^{II}—N=C fragment, leading to the formation of transient **9**. Whether this unobserved transient with a seven-coordinated iron(IV) center has a definite lifetime is still an open question. In any event, it should give two rapid successive reductive eliminations, forming the $Fe(CNR)_3(i\text{-Pr-THPP})$ complex **10**.

For the cycloaddition reactions of the analogous $Fe(CO)_3(DAB)$[5] only alkynes with electron-withdrawing substituents were found to be reactive. This indicates that the 1,3-dipolar Fe—N=C unit can be described as a nucleophilic or, according to the Sustmann classification,[33] a HOMO-controlled system. This is supported by two facts. First, the isolobal azomethyne ylides are characterized as electron-rich species with relatively high HOMO and LUMO energy levels.[34] Second, preliminary CAS-SCF calculations on the metal-DAB systems indeed reveal high frontier molecular orbital energy levels.[35] These HOMO (dipole) controlled cycloaddition reactions are characterized by a dominant interaction of the HOMO of the dipole with the LUMO of the dipolarophile. The reactivity is enhanced by the introduction of electron-donating substituents on the 1,3-dipole. The introduction of the three better σ-donating/worse π-accepting CNR ligands[4] results in an enhanced electron density at the iron center, which is clearly illustrated in the ^{13}C NMR spectra by the upfield shift of the imine carbon nuclei in going from the tricarbonyl complex **1** to the tris(isocyanide)

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complexes 4 (144 and 130 ppm, respectively). Consequently, the electron-donating isocyanides activate the $Fe^{II}—N=C$ fragment in intermediate 5 sufficiently to undergo a second cycloaddition reaction with DMAD, while for the tricarbonyl complexes no double-cycloaddition products are observed.

In comparison to the reaction of $Fe(CO)_2(CNR)(DAB)$ with an alkyne, the reactivity is enhanced as a result of the introduction of three, instead of only one, isocyanide. This is expressed in two ways. First, the reaction is faster, and second, the product distribution between the THPP and the bicyclic complexes is influenced (vide infra). The enhanced reactivity also results in cycloaddition reactions with less activated dipolarophiles such as alkenes, which is described in the following paper in this issue.

Formation of $Fe(2,6\text{-xylylNC})_3(bic)$ (7a). As mentioned before, the [2.2.1] bicyclic intermediate 5 can either react with another alkyne or undergo an intramolecular insertion reaction. The latter proceeds via nucleophilic attack at the terminal isocyanide carbon atom by the amido nitrogen lone pair and relieves the stress in the one-atom nitrogen bridge. The insertion leads to the formation of the electronically and coordinatively unsaturated [2.2.2] bicyclic intermediate 6, which readily accepts an additional isocyanide to give the stable $Fe(2,6\text{-xylylNC})_3([2.2.2]\text{-bicyclo})$ complex **7a**. Efforts to isomerize the [2.2.2] bicyclic compound **7a** via a reductive elimination in order to obtain a compound comparable with the 1,5-dihydropyrrol-2-one complex 3 formed in the reactions of $Fe(CO)_3(DAB)$ were unsuccessful, resulting only in decomposition. This reluctance to isomerization has been encountered before in the [2.2.2] bicyclic complexes which contain, besides two CO ligands, an electron-donating phosphine[5] or isocyanide ligand.[6b] The reluctance toward reductive elimination in the presence of ancillary donor ligands is rationalized by a stabilization of the Fe(II) oxidation state and the Fe–C σ bond.

Influence of the Isocyanide Ligands on the Course of the Reaction. With *tert*-butyl (**b**) and cyclohexyl (**c**) isocyanide, only the THPP complexes 10 are formed as products, whereas with 2,6-xylyl isocyanide (**a**) the bicyclo[2.2.2] product 7 is found exclusively. The following discussion will show that this product distribution is due to the electronic rather than the steric properties of the respective isocyanide ligands. To discuss possible steric and electronic influences, we have to look at intermediate 5, because at this point the reaction coordinate splits into the two pathways forming 7 and 10. Considering steric effects, one could argue that bulky isocyanides could either hinder the approach of the second alkyne, i.e., disfavor the intermolecular reaction leading to $Fe(CNR)_3(i\text{-Pr-THPP})$ formation, or they could hinder the nucleophilic attack of the nitrogen atom, disfavoring the bicyclo[2.2.2] formation via the intramolecular pathway. From the cone angles of the different isocyanides,[6b] it becomes obvious that steric arguments do not play a role. The nearby cone angles of the three isocyanides are identical: 102°. When we consider the remote cone angles, which only take account of the steric effects of the substituents and neglect the van der Waals radius of the metal-coordinated carbon atom, it again appears that steric arguments are unable to account for the product distribution. The $Fe(CNR)_3(i\text{-Pr-THPP})$ complex 10 is formed both with the smallest cyclohexyl isocyanide (remote cone angle 64°), and with the most bulky *tert*-butyl isocyanide (remote cone angle 76°), while with the isocyanide of intermediate bulkiness, 2,6-xylyl isocyanide (remote cone angle 69°), only the [2.2.2] bicyclic complex 7 is formed. Clearly, steric arguments are unable to account for the product distribution. Only the two stronger electron-donating aliphatic isocyanides activate the $Fe^{II}—N=C$ unit in intermediate 5 sufficiently to make an intermolecular second cycloaddition reaction favorable. The stronger activation for a second cycloaddition reaction of the alkyne by the aliphatic isocyanides is underlined by the fact that exclusively $Fe(CNR)_3(i\text{-Pr-THPP})$ is formed in the present case. In the previously reported reactions of $Fe(CO)_2(CNR)(DAB)$[6b] the THPP complexes were accompanied by varying amounts of bicyclic compounds, depending on the respective aliphatic isocyanides. Now that the $Fe^{II}—N=C$ unit is much more highly activated, no bicyclo[2.2.2] formation is observed at all. In the case of the starting complex with aromatic 2,6-xylyl isocyanide (**4a**) only insertion, leading to the [2.2.2] bicyclic complex **7a**, is observed. In spite of the activation of the $Fe^{II}—N=C$ unit in intermediate 5, no second cycloaddition is found. This underlines another important aspect besides the activation of the iron–imine unit: the reluctance of aliphatic isocyanides to undergo insertion reactions or, rather, the preference of aromatic isocyanides to undergo insertion reactions. In the reactions of $Fe(CO)_2(CNR)(DAB)$[6b] it was found that for the complexes containing aromatic isocyanides only CNR insertion was observed, while for the aliphatic isocyanide containing complexes only CO insertion was encountered. The greater propensity of aromatic isocyanides for insertion reactions, compared to aliphatic isocyanides, has also been reported in other studies.[36] The electron-withdrawing phenyl group enhances the electrophilic character of the terminal isocyanide carbon atom and makes it more susceptible for attacking nucleophiles such as alcohols, amines,[4d,16a,37] and, in the present case, the nitrogen lone pair. The trends found in the study of $Fe(CO)_2(CNR)(DAB)$, i.e., aromatic isocyanides insert, giving mainly bicyclic products, and aliphatic isocyanides give preferentially double-cycloaddition products, is confirmed in the reactions of $Fe(CNR)_3(DAB)$.

Formation of $Fe(2,6\text{-xylylNC})_3(tric)$ (8a). For the formation of the $Fe(2,6\text{-xylylNC})_3$ tricyclic compound **8a** from **7a**, the mechanism given in Scheme III is suggested. As the first step, we suggest hydrolysis of an ester function to the acid, yielding complex **11a**. The hydroxyl group of the acid then oxidatively adds to the electron-rich metal center, forming complex **12a** with a formal Fe(IV) center. Simultaneously, the imine moiety is displaced from the metal. From the high oxidation state, which is most likely stabilized by the donating isocyanides, a reductive elimination regenerates the Fe(II) oxidation state by forming the 1,5-dihydro-2-iminopyrrole complex **13a**, followed by recoordination of the double bond. Via a formal insertion of the ring double bond into the metal–hydrogen bond and recoordination of the imine ligand, the tricyclic complex **8a** is formed. The implication that the new proton originates from water has been confirmed by performing the reaction with D_2O instead of H_2O. The ^2H NMR

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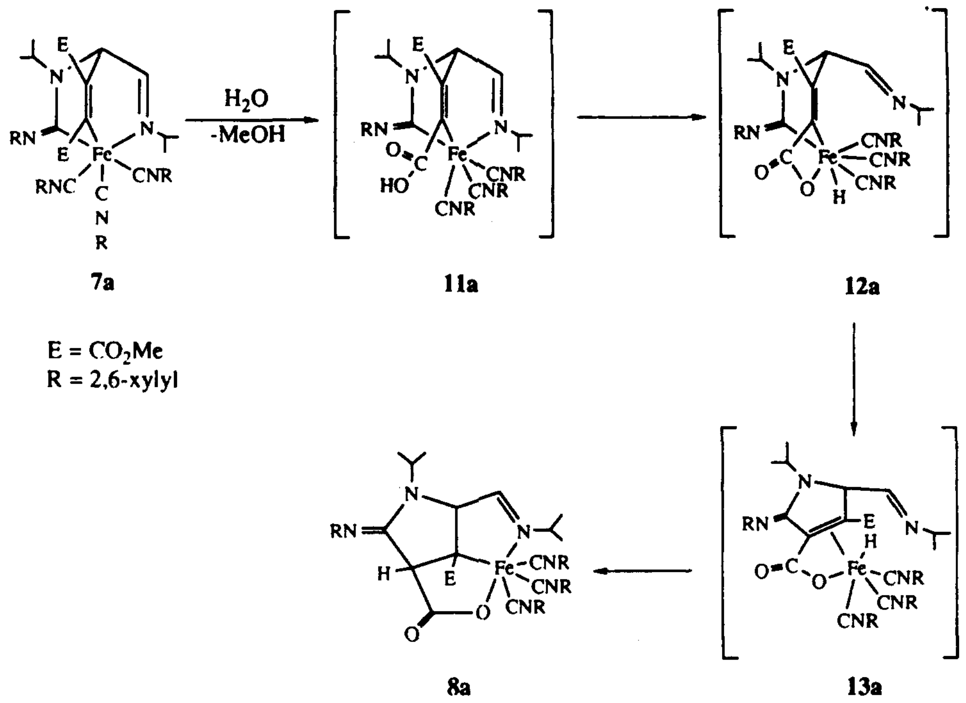
Scheme III. Reaction Mechanism of the Formation of Fe(2,6-xylylNC)$_3$(tric) (8a)



spectrum unequivocally proved the incorporation of deuterium at the former alkyne carbon atom in the complex (vide supra).

An alternative mechanism in which reductive elimination from the [2.2.2] bicyclic complex **7a** and subsequent recoordination of the double bond precedes the following steps, i.e., ester hydrolysis, oxidative addition of O-H to the metal center, insertion of the double bond into the Fe–H bond, and reductive elimination, seems very unlikely. As has been stated above, it has been proven to be impossible to achieve a reductive elimination (during which the oxidation state of the metal changes from Fe(II) to Fe(0)) from a [2.2.2] bicyclic complex containing one or more donating ligands.[5,6b]

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Supplementary Material Available: Tables of anisotropic thermal parameters, all H atom parameters, and bond lengths and bond angles involving H atoms and a thermal motion ellipsoid plot for **10b** (8 pages). Ordering information is given on any current masthead page. Listings of observed and calculated structure factor amplitudes (16 pages) can be obtained from the authors.

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