Paramagnetic bis(amidinate) iron(II) complexes and their diamagnetic dicarbonyl derivatives

Vendemiati, B.; Prini, G.; Meetsma, A.; Hessen, B.; Teuben, J.H; Traverso, O.

Published in:
European Journal of Inorganic Chemistry

DOI:
10.1002/1099-0682(200103)2001:3<707::AID-EJIC707>3.0.CO;2-Z

Paramagnetic Bis(amidinate) Iron(II) Complexes and their Diamagnetic Dicarbonyl Derivatives[‡]

Beatrice Vendemiati,[a] Giansiro Prini,[b] Auke Meetsma,[a] Bart Hessen,*[a] Jan H. Teuben,[a] and Orazio Traverso[b]

Keywords: Iron / N ligands / Magnetic properties / X-ray diffraction / Carbonyl complexes

Reactions of two equivalents of the lithium amidinate salts Li[*t*BuC(NR)$_2$] (R = *i*Pr, cyclohexyl) with $FeCl_2$ have been found to yield paramagnetic bis(amidinate) iron(II) compounds of the type [*t*BuC(NR)$_2$]$_2$Fe. In the case of R = cyclohexyl, the product has been characterized by single-crystal X-ray diffraction analysis as having a distorted tetrahedral geometry. The derivative with R = *i*Pr is an oil, but its ^{1}H and ^{13}C NMR spectra indicate a similar monomeric structure. Both species have been found to react readily with CO to give the new diamagnetic Fe^{II} dicarbonyls [*t*BuC(NR)$_2$]$_2$Fe(CO)$_2$. The compound with R = *i*Pr has been structurally characterized, which showed it to have a strongly distorted octahedral structure with the carbonyls in a *cis* arrangement.

Introduction

The amidinates [RC(NR′)$_2$]$^-$ (R = H, alkyl, aryl; R′ = alkyl, aryl, $SiMe_3$) constitute a class of versatile monoanionic ancillary ligands for transition metals.[1] They can bind in a chelating *N*,*N*′-η^2 fashion to a single metal center, or form *N*,*N*′-μ bridges between two metals. In the latter case, "lantern" complexes of the type {[μ-RC(NR′)$_2$]$_2$M}$_2$ can be formed that may contain very short M−M bonding contacts.[2,3] Amidinates have also found extensive use as ancillary ligands in catalytically active metal complexes, e.g. in Group 4 metal mono- and bis(amidinate) complexes, which can be activated with methylalumoxane (MAO) to give active olefin polymerization catalysts,[4] in cationic aluminum amidinate alkyls,[5] and in neutral (alkyl)bis(amidinate)vanadium ethene oligomerization catalysts.[6] To date, the chemistry of amidinate complexes of iron has yielded only a few well-defined complexes. For Fe^{II}, one type of dimeric bis(amidinate) complex has been reported, {[RC(NPh)$_2$]$_2$Fe}$_2$ (R = H, Ph), which has a "twisted" A-frame structure with two bridging and two dihapto amidinate ligands.[7] In addition, one example of a monomeric bis(amidinate) Fe^{II} complex is known, which contains amidinate ligands bearing ferrocenyl substituents on their backbone carbons, i.e. {[FcC(NCy)$_2$]$_2$Fe} (Fc = ferrocenyl).[8] As yet, no details of the reactivities of these complexes have been reported.

We are interested in the chemistry of iron(II) amidinates, especially with respect to their Lewis acidic behavior, their redox chemistry, and their potential as catalyst precursors. We describe herein the synthesis and characterization of paramagnetic monomeric iron(II) complexes of the highly substituted amidinate ligands [*t*BuC(NR)$_2$]$^-$ (R = *i*Pr, cyclohexyl).[9] The bis(amidinate) species [*t*BuC(NR)$_2$]$_2$Fe has been structurally characterized for R = Cy. These complexes appear to be quite light-sensitive. They react with CO to give the new distorted octahedral dicarbonyls *cis*-[*t*BuC(NR)$_2$]$_2$Fe(CO)$_2$, of which the derivative with R = *i*Pr has also been structurally characterized.

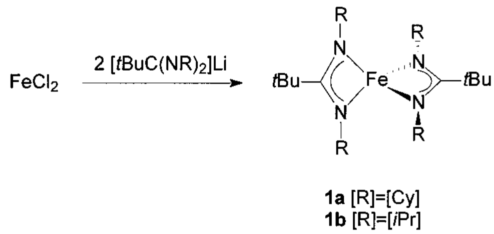
Results and Discussion

The lithium amidinates Li[*t*BuC(NR)$_2$] (R = *i*Pr, Cy) used in this study were readily available from the reaction of the corresponding carbodiimides with *t*BuLi.[9] Reaction of two equivalents of Li[*t*BuC(NCy)$_2$] with $FeCl_2$ in THF solution produced a brown-yellow colored solution, which gradually turned red-brown on exposure to ambient light. When the reaction mixture was worked-up under these conditions, a significant amount of a red-brown oil was recovered, which hampered isolation of the desired product. However, when the reaction and subsequent workup were performed with the exclusion of light, extraction with and crystallization from pentane yielded the bis(amidinate) Fe^{II} complex [*t*BuC(NCy)$_2$]$_2$Fe (**1a**) as yellow crystals in 54% isolated yield (Scheme 1). An analogous procedure with Li[*t*BuC(N*i*Pr)$_2$] resulted in a relatively low yield of a deep-brown/yellow oil that resisted all attempts to crystallize it. NMR spectroscopy (vide infra) indicated that this oil consisted mainly of [*t*BuC(N*i*Pr)$_2$]$_2$Fe (**1b**), although some impurities were present.

[‡] Netherlands Institute for Catalysis Research (NIOK) publication RUG-00-4-3.

[a] Center for Catalytic Olefin Polymerization, Stratingh Institute for Chemistry and Chemical Engineering, University of Groningen,
Nijenborgh 4, 9747 AG Groningen, The Netherlands
E-mail: hessen@chem.rug.nl
[b] Dipartimento di Chimica, Centro di Studio su Fotoreattivitá e Catalisi, Universitá di Ferrara,
Via Borsari 46, 44100 Ferrara, Italy

  1434−1948/01/0303−0707 $ 17.50+.50/0



Scheme 1. Formation of the bis(amidinate) iron(II) complexes

A crystal structure determination of **1a** was performed (Figure 1; selected interatomic distances and angles are listed in Table 1). It showed the compound to be monomeric, with two dihapto amidinate ligands and the iron in a distorted tetrahedral environment. The geometry of the two Fe−N−C−N four-membered rings is essentially planar [largest deviation seen in the Fe−N(3)−C(30)−N(4) dihedral angle of 10.3(2)°, Fe−N(1)−C(13)−N(2) = −4.9(2)°]. The angle between these two least-squares planes is 86.4(1)°. The structure is similar to that of the only other known monomeric bis(amidinate) Fe^{II} complex, $\{[FcC(NCy)_2]_2Fe\}$,[8] although in the latter the average Fe−N distance is longer (2.037 Å vs. 2.020 Å in **1a**) and the dihapto amidinates are less symmetrically bound (the largest difference between the Fe−N distances for one amidinate ligand is 0.025 Å vs. 0.011 Å in **1a**).

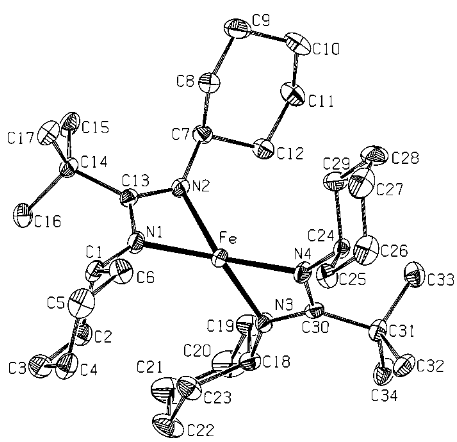


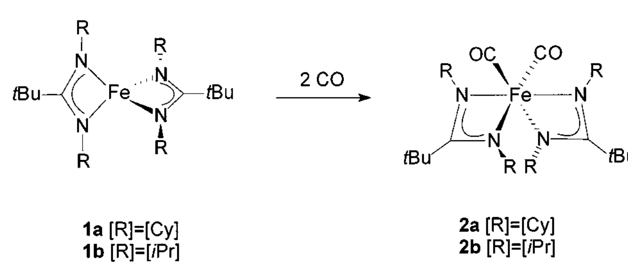
Figure 1. Molecular structure of **1a**; hydrogen atoms are omitted for clarity

Table 1. Selected interatomic distances (Å) and bond angles (°) in **1a**

Fe−N(1)	2.014(2)	N(1)−C(13)	1.336(3)
Fe−N(2)	2.025(2)	N(2)−C(13)	1.340(3)
Fe−N(3)	2.026(2)	N(3)−C(30)	1.328(3)
Fe−N(4)	2.015(2)	N(4)−C(30)	1.347(3)
N(1)−Fe−N(2)	65.38(8)	N(1)−Fe−N(4)	143.41(8)
N(3)−Fe−N(4)	65.15(8)	N(2)−Fe−N(3)	124.71(8)
N(1)−Fe−N(3)	137.38(8)	N(2)−Fe−N(4)	132.90(8)
N(1)−C(13)−N(2)	109.2(2)	N(3)−C(30)−N(4)	108.9(2)
Fe−N(1)−C(1)	135.8(2)	Fe−N(2)−C(7)	133.8(2)
Fe−N(3)−C(18)	133.8(2)	Fe−N(4)−C(24)	137.3(2)

The bis(amidinate) Fe^{II} compounds **1** are paramagnetic. Magnetic susceptibility measurements on solid **1a** showed Curie−Weiss behavior over the temperature range 5−300 K with μ_{eff} = 4.82 and θ = −1.36 K, consistent with a magnetically dilute solid with tetrahedral d^6 ions (S = 2). ^{1}H NMR spectra of the compounds **1** in C_6D_6 (25 °C) consequently show broad resonances, but nevertheless allow assignments to be made. For **1b**, three resonances are observed at δ = 190.4, 8.8, and −2.2 (in a 2:9:12 ratio) which can be attributed to the *i*Pr CH, *t*Bu CH_3, and *i*Pr CH_3 groups, respectively. For **1a**, the first two resonances are also present (at δ = 188.6 and 9.0), but these are accompanied by additional resonances (at δ = 11.9 and 10.7, as well as a group of less-well-resolved resonances in the δ = 4−0 region of the spectrum) that can be attributed to the cyclohexyl methylene protons. NMR spectroscopy thus suggests that complexes **1a** and **1b** have a similar structure in solution. The ^{13}C NMR spectrum of **1b** (C_6D_6, 25 °C) consists of two broad resonances at δ = 336 and 310, most probably attributable to the *t*Bu and *i*Pr methyl groups, respectively, and a third broad feature at δ = 661. The assignment of the latter resonance is ambiguous, as it could feasibly be attributed to the *i*Pr CH group or the *t*Bu quaternary carbon. The ^{13}C NMR spectrum of **1a** shows similar resonances (at δ = 628, 335, and 304), with two additional narrower resonances at δ = 27.9 and 20.1, associated with the δ- and γ-CH_2 groups, respectively, of the cyclohexyl moiety.

Both 14-electron bis(amidinate) Fe^{II} complexes **1** react with CO in hexane solution in the absence of light to give the diamagnetic carbonyl derivatives $[tBuC(NR)_2]_2Fe(CO)_2$ (R = Cy, **2a**; *i*Pr, **2b**), which were obtained in the form of orange crystals (Scheme 2). The IR spectra of these compounds show two carbonyl vibrations [**2a**: ν(CO) = 1999 and 1929 cm^{-1}], indicative of a *cis*-dicarbonyl structure. The ^{1}H and ^{13}C NMR spectra of the derivative with R = *i*Pr (**2b**) show the resonances of one *t*Bu group and two nonequivalent *i*Pr groups, each with two diastereotopic methyl groups. This, together with the IR data, suggests a C_2-symmetric octahedral *cis*-bis(η^2-amidinate)$Fe(CO)_2$ structure for **2b** that is nonfluxional on the NMR time scale at ambient temperature. The ^{1}H NMR spectrum of **2a** is less-well-resolved, but is consistent with the same structure type. For both complexes, the carbonyl ^{13}C NMR resonance is found at δ = 219.



Scheme 2. Formation of the bis(amidinate) iron(II) dicarbonyl complexes

An X-ray crystal structure determination of **2b** corroborated the conclusions drawn from the spectroscopic studies.

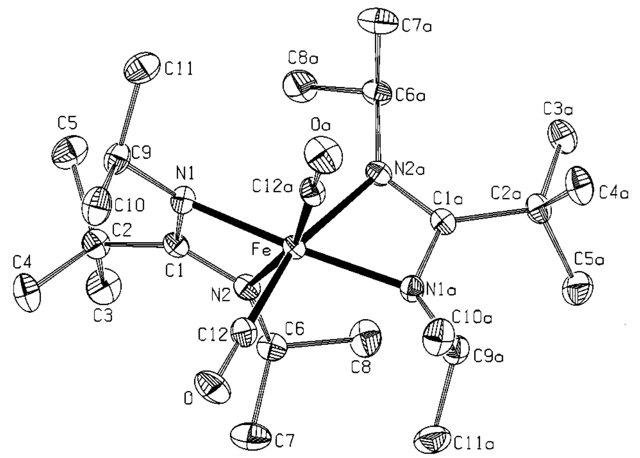


Figure 2. Molecular structure of **2b**; hydrogen atoms are omitted for clarity

Table 2. Selected interatomic distances (Å) and bond angles (°) in **2b**

Fe−N(1)	1.986(1)	N(1)−C(1)	1.342(2)
Fe−N(2)	2.031(1)	N(2)−C(1)	1.324(2)
Fe−C(12)	1.771(2)	O−C(12)	1.143(2)
N(1)−Fe−N(2)s	62.53(5)	N(1)−Fe−N(2a)	104.21(5)
N(1)−Fe−C(12)	90.48(6)	N(2)−Fe−C(12)	90.65(6)
N(1)−Fe−C(12a)	99.85(6)	N(2)−Fe−C(12a)	163.99(6)
N(1)−Fe−N(1a)	165.01(5)	N(2)−Fe−N(2a)	90.01(5)
C(12)−Fe−C(12a)	93.09(7)	Fe−C(12)−O	179.1(1)

The structure is shown in Figure 2, while pertinent interatomic distances and angles are listed in Table 2. The compound crystallizes in the space group C_2/c, with a C_2 symmetry axis passing through the Fe atom. The amidinate ligands are again bound in a dihapto fashion with the FeNCN ring having a planar geometry [the dihedral angle Fe−N(1)−C(1)−N(2) is −4.6(1)°]. The two Fe-amidinate planes, related by C_2 symmetry, are essentially orthogonal [87.49(8)°]. The Fe−N(2) distance is 0.045 Å longer than the Fe−N(1) distance, as a consequence of the *trans*-position of N(2) in relation to the CO ligand. Compared to the two known Fe^{II} *cis*-dicarbonyl complexes with bidentate monoanionic ligands — the phosphanyl-enolate and phosphanyl-carboxylate derivatives $[Ph_2PCHC(Ph)O]_2Fe(CO)_2$ [10] and $[Ph_2PCH_2C(O)O]_2Fe(CO)_2$[11] — complex **2b** has a much more strongly distorted octahedral geometry. This is due to the very small "bite angle" of the dihapto amidinate ligand, i.e. N(1)−Fe−N(2) is just 64.53(5)°, as compared to O−Fe−P angles of 82−86° in the other two complexes. In all three complexes, the C−Fe−C angle is about 93°, and hence this feature would appear to be quite insensitive to changes in the ligand. In the IR spectra, the carbonyl vibrations for **2** are found at noticeably lower wavenumbers than for the phosphanyl-carboxylate and -enolate complexes (2048, 1998 cm^{-1} and 2023, 1969 cm^{-1}, respectively), indicating that the amidinate ligands are better donors.

In conclusion, we have prepared two paramagnetic 14-electron bis(amidinate) iron(II) complexes and their diamagnetic 18-electron dicarbonyl derivatives. ^1H and ^{13}C NMR spectroscopy of the paramagnetic complexes proved helpful in establishing their structural relationship, which was especially useful as **1b** could not be crystallized. We are presently studying the Lewis acidities, electrochemistry, and photochemistry of the new complexes. Preliminary results suggest that the binding of the two CO molecules to the (amidinate)$_2$Fe moiety can be readily reversed upon irradiation.

Experimental Section

General: All experiments were performed under a nitrogen atmosphere using standard Schlenk, glove-box, and vacuum line techniques. All manipulations involving compounds **1** were performed in the absence of light, the samples being protected by enveloping glassware in a black plastic bag whenever possible. Solvents (pentane, hexane, THF) were distilled from Na/K alloy prior to use. Deuterated benzene was dried over Na/K alloy and vacuum transferred before use. The Li salts Li[*t*BuC(NR)$_2$] (R = Cy, *i*Pr)[9] and anhydrous $FeCl_2$ [12] were prepared according to literature procedures. − NMR spectra were recorded on Varian VXR-300 or Unity 500 spectrometers. The ^1H NMR spectra were referenced to the resonances of residual protons in the deuterated solvent. Chemical shifts (δ) are given relative to tetramethylsilane (downfield shifts are positive). − IR spectra were recorded on a Mattson 4020 Galaxy FT-IR spectrophotometer. − Elemental analyses were performed at the Microanalytical Department of the University of Groningen; all data are the average of at least two independent determinations. − Magnetic susceptibility measurements on solid **1a** were performed on an MPMS-7 Quantum Design instrument under zero-field cooled conditions (1000 T field, 5−300 K temperature range). The EMU and temperature data are the average of three independent determinations; μ_{eff} was calculated from the total spin quantum number $S = 1.96$ obtained from the Curie−Weiss law ($C = 2.90$, $\theta = -1.35$ K).

Preparation of [*t*BuC(NCy)$_2$]$_2$Fe (1a): All manipulations were performed under the exclusion of light (vide supra). To a stirred suspension of $FeCl_2$ (0.653 g, 5.51 mmol) in THF (40 mL), solid Li[*t*-BuC(NCy)$_2$] (2.843 g, 10.5 mmol) was added at ambient temperature. After stirring for 2 h, the solvent was removed in vacuo, and then any residual THF was removed by stirring the mixture with pentane (20 mL) and subsequently pumping off the volatiles. Extraction of the residue with pentane (30 mL), concentration of the extract, and cooling it to −25 °C afforded 1.640 g (2.81 mmol, 54%) of **1a** as analytically pure yellow crystals. − ^1H NMR ([D$_6$]benzene, 25 °C): δ = 188 ($\Delta\nu_{1/2}$ = 280 Hz, 4 H, *i*Pr CH), 11.9 ($\Delta\nu_{1/2}$ = 40 Hz, 8 H, Cy CH$_2$), 10.7 ($\Delta\nu_{1/2}$ = 60 Hz, 8 H, Cy CH$_2$), 9.0 ($\Delta\nu_{1/2}$ = 60 Hz, 18 H, *t*Bu Me), 2.7 ($\Delta\nu_{1/2}$ = 470 Hz, 8 H, Cy CH$_2$), 1.5 ($\Delta\nu_{1/2}$ = 73 Hz, 4 H, Cy CH$_2$), 1.1 ($\Delta\nu_{1/2}$ = 33 Hz, 4 H, Cy CH$_2$), 0.5 ($\Delta\nu_{1/2}$ = 785 Hz, 8 H, Cy CH$_2$). − $^{13}C\{^1H\}$ NMR ([D$_6$]benzene, 25 °C): δ = 628 (assignment uncertain), 335 (*t*Bu Me), 304 (Cy β-CH$_2$), 27.9 (Cy δ-CH$_2$), 20.1 (Cy γ-CH$_2$). − $C_{34}H_{62}N_4Fe$ (582.7): calcd. C 70.08, H 10.72, N 9.61, Fe 9.58; found C 69.74, H 10.79, N 9.39, Fe 9.75.

Preparation of [*t*BuC(N*i*Pr)$_2$]$_2$Fe (1b): Following a similar procedure as described above for **1a**, but using Li[*t*BuC(N*i*Pr)$_2$] (0.934 g, 4.91 mmol) and $FeCl_2$ (0.308 g, 2.43 mmol), 0.26 g (0.61 mmol, 25%) of crude **1b** was obtained as a brown-yellow oil upon evaporation of the solvent from the pentane extract. − ^1H NMR ([D$_6$]ben-

Table 1. Data relating to the crystal structure determinations of **1a** and **2b**

	1a	**2b**
Empirical formula	$C_{34}H_{62}FeN_4$	$C_{24}H_{46}FeN_4O_2$
Formula mass	582.74	478.50
Crystal size (mm)	0.25 × 0.30 × 0.38	0.20 × 0.25 × 0.50
Temperature [K]	130	130
Radiation	Mo-K_α	Mo-K_α
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
a [Å]	10.872(2)	17.195(1)
b [Å]	16.962(3)	8.282(1)
c [Å]	18.644(1)	18.779(1)
β [°]	93.69(1)	103.099(7)
Volume [Å^3]	3431.0(9)	2604.7(4)
Z, calcd. density [Mgm^{-3}]	4, 1.128	4, 1.220
μ [mm^{-1}]	0.466	0.605
Scan	ω/2θ	ω/2θ
F(000)	1280	1040
θ range [°]	1.10 to 26.0	1.11 to 27.0
Index ranges	$-13 \leq h \leq 13$	$-21 \leq h \leq 21$
	$0 \leq k \leq 20$	$-10 \leq k \leq 0$
	$-22 \leq l \leq 0$	$-23 \leq l \leq 23$
Refl. collected/unique	7232/6702	6057/2841
Refl. observed [$I > 4.0\sigma(I)$]	4892	2647
Parameters refined	600	222
$wR(F^2)$[a] (for $F_o^2 > 0$)	0.1004	0.0913
Weighting scheme: a, b	0.0441, 1.234	0.0595, 2.3807
$R(F)$[b] [for $F_o > 4.0\ \sigma(F_o)$]	0.0443	0.0347
Diff. peak and hole (e/Å^3)	−0.30, 0.26(6)	−0.40, 1.90(7)

[a] $wR(F^2) = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$ and $P = [\max(F_o{}^2,0) + 2F_c{}^2]/3$. – [b] $R(F) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.

zene, 25 °C): δ = 190 ($\Delta\nu_{1/2}$ = 240 Hz, 4 H, *i*Pr CH), 8.8 ($\Delta\nu_{1/2}$ = 55 Hz, 18 H, *t*Bu Me), −2.2 ($\Delta\nu_{1/2}$ = 305 Hz, 24 H, *i*Pr Me). Resonances attributable to a diamagnetic impurity (probably derived from the ligand) are visible in the NMR spectrum at around δ = 3−4 and 0.6−1.6. − ^{13}C{^{1}H} NMR ([D$_6$]benzene, 25 °C): δ = 661 (assignment uncertain), 336 (*t*Bu Me), 310 (*i*Pr Me).

Preparation of [*t*BuC(NCy)$_2$]$_2$Fe(CO)$_2$ (2a): A 50 mL flask was charged with **1a** (0.323 g, 0.55 mmol) and hexane (10 mL). The flask was attached to a vacuum line, the solution was degassed by several freeze-pump-thaw cycles, and then CO (140 Torr, 1.2 mmol) was admitted. The mixture was allowed to stand (protected from light) for two days at ambient temperature. It was then concentrated and cooled to −25 °C, whereupon orange bar-shaped crystals were deposited. Yield: 0.244 g (0.38 mmol, 69%) of analytically pure **2a**. − ^{1}H NMR ([D$_6$]benzene, 25 °C): δ = 4.19 (m, 2 H, Cy CH), 3.53 (m, 2 H, Cy CH), 2.2−1.5 (m, 32 H, Cy CH$_2$), 1.26 (s, 18 H, *t*Bu Me), 1.20 (m, 8 H, Cy CH$_2$). − ^{13}C (APT) NMR ([D$_6$]benzene, 25 °C): δ = 219.4 (CO), 176.6 (NCN), 57.4 and 58.0 (NCH), 40.9 [*C*(CH$_3$)], 38.6, 36.3, 35.1, and 32.3 (CH$_2$), 30.5 [C(*C*H$_3$)$_3$], 26.5 (2×), 26.2, 26.1, 25.9, and 25.8 (CH$_2$). − IR (Nujol, KBr): $\tilde{\nu}$ = 1999, 1929 cm^{-1} [ν(CO)]. − $C_{36}H_{62}FeN_4O_2$ (638.8): calcd. C 67.69, H 9.78, N 8.77, Fe 8.74; found C 67.56, H 9.67, N 8.58, Fe 8.60.

Preparation of [*t*BuC(N*i*Pr)$_2$]$_2$Fe(CO)$_2$ (2b): For this preparation, compound **1b** was first generated by reaction of FeCl$_2$ (0.150 g, 1.18 mmol) with Li[*t*BuC(N*i*Pr)$_2$] (0.450 g, 2.36 mmol) in THF (15 mL) as described above, and the product was extracted with hexane (20 mL). A flask charged with this hexane extract was attached to a vacuum line and the solution was degassed; thereafter CO (1 bar) was admitted. After allowing the solution to stand for two days (protected from light), it was filtered, concentrated, and cooled to −25 °C. This led to the deposition of 0.158 g (0.33 mmol, 28% overall) of orange crystalline **2b**; m.p. 112−113 °C. − ^{1}H NMR ([D$_6$]benzene, 25 °C): δ = 4.58 (quint., $^3J_{HH}$ = 5.8 Hz, 2 H, *i*Pr CH), 3.95 (quint., $^3J_{HH}$ = 6.3 Hz, 2 H, *i*Pr CH), 1.50 and 1.19 (d, $^3J_{HH}$ = 5.8 Hz, 6 H each, *i*Pr Me), 1.27 and 1.15 (d, $^3J_{HH}$ = 6.3 Hz, 6 H each, *i*Pr Me), 1.17 (s, 18 H, *t*Bu). − ^{13}C (APT) NMR ([D$_6$]benzene, 25 °C): δ = 219.4 (CO), 177.1 (NCN), 49.6 and 48.5 (NCH), 41.1 [*C*(CH$_3$)], 30.7 [C(*C*H$_3$)$_3$], 27.5, 26.3, 24.7, and 22.8 [CH(*C*H$_3$)$_2$]. − IR (Nujol, KBr): $\tilde{\nu}$ = 2009, 1942 cm^{-1} [ν(CO)].

X-ray Crystal Structure Determinations: Diffraction data were collected on an Enraf−Nonius CAD4-F diffractometer. Pertinent crystallographic data and information concerning the data collection and residuals can be found in Table 3. For **1a**, the cell parameters were derived from the setting angles of 22 reflections in the range 16.37° ≤ θ ≤ 21.54°; for **2b** from 22 reflections in the range 17.95° ≤ θ ≤ 20.39°. Intensity data were corrected for Lorentz and polarization effects, but not for absorption. The structures were solved by Patterson methods and the models were extended by direct methods applied to difference structure factors using the program *DIRDIF*.[13] In both structures, all hydrogen atoms were located and refined with isotropic displacement parameters. Final refinement on F^2 was carried out by full-matrix least-squares techniques. Calculations were performed with the program packages *SHELXL*[14] (least-squares refinement) and *PLATON*[15] (geometric data). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-147087 for **1a** and -147086 for **2b**. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The authors wish to thank J. Baas for performing the solid-state susceptibility measurements on **1a**, and Montell Italia S.p.A. and the University of Ferrara for grants (to G.P. and B.V.).

[1] [1a] F. T. Edelmann, *Coord. Chem. Rev.* **1994**, *137*, 403. – [1b] J. Barker, M. Kilner, *Coord. Chem. Rev.* **1994**, *133*, 219–300.

[2] [2a] F. A. Cotton, L. M. Daniels, C. A. Murillo, *Inorg. Chem.* **1993**, *32*, 2881–2885. – [2b] D. I. Arnold, F. A. Cotton, D. J. Maloney, J. H. Matonic, C. A. Murillo, *Polyhedron* **1997**, *16*, 133–141. – [2c] F. A. Cotton, L. M. Daniels, X. Feng, D. J. Maloney, J. H. Matonic, C. A. Murillo, *Inorg. Chim. Acta* **1997**, *256*, 291–301.

[3] [3a] S. Hao, S. Gambarotta, C. Bensimon, J. J. H. Edema, *Inorg. Chim. Acta* **1993**, *213*, 65–74. – [3b] S. Hao, P. Berno, K. M. Ravinder, S. Gambarotta, *Inorg. Chim. Acta* **1996**, *244*, 37–49.

[4] [4a] D. Herskovics-Korine, M. S. Eisen, *J. Organomet. Chem.* **1995**, *503*, 307–314. – [4b] R. Gómes, R. Duchateau, A. N. Chernega, J. H. Teuben, F. T. Edelmann, M. L. H. Green, *J. Organomet. Chem.* **1995**, *491*, 153–158. – [4c] C. Averbuj, E. Tish, M. S. Eisen, *J. Am. Chem. Soc.* **1998**, *120*, 8640–8646. – [4d] V. Volkis, M. Shmulinson, C. Averbuj, A. Lisovskii, F. T. Edelmann, M. S. Eisen, *Organometallics* **1998**, *17*, 3155–3157.

[5] M. P. Coles, R. F. Jordan, *J. Am. Chem. Soc.* **1997**, *119*, 8125–8126.

[6] E. A. C. Brussee, A. Meetsma, B. Hessen, J. H. Teuben, *Chem. Commun.* **2000**, 497–498.

[7] F. A. Cotton, L. M. Daniels, J. H. Matonic, C. A. Murillo, *Inorg. Chim. Acta* **1997**, *256*, 277–282.

[8] J. R. Hagadorn, J. Arnold, *Inorg. Chem.* **1997**, *36*, 132–133.

[9] M. P. Coles, D. C. Swenson, R. F. Jordan, V. G. Young, Jr., *Organometallics* **1997**, *16*, 5183–5194.

[10] P. Braunstein, G. C. Cea, A. DeCian, J. Fischer, *Inorg. Chem.* **1992**, *31*, 4203–4206.

[11] J. Takács, L. Markó, P. Kiprof, E. Herdtweck, W. A. Herrmann, *Polyhedron* **1989**, *8*, 1503–1507.

[12] P. Kovacic, N. O. Brace, *Inorg. Synth.* **1960**, *6*, 172–173.

[13] P. T. Beurskens, G. Beurskens, R. de Gelder, S. García-Granda, R. O. Gould, R. Israël, J. M. M. Smit, *The DIRDIF-99 Program System*, Crystallography Laboratory, University of Nijmegen, The Netherlands, **1999**.

[14] G. M. Sheldrick, *SHELXL-97 – A Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[15] A. L. Spek, *PLATON – A Program for the Automated Analysis of Molecular Geometry*, University of Utrecht, The Netherlands, **1999**.

Received July 31, 2000
[I00300]