

Synthesis and properties of complexes $\text{Fe}(\text{CO})_2(\text{CNR})(1,4\text{-diaz-1,3-butadiene})$ obtained by heterogeneously (Pd/C) catalyzed substitution of a CO by an isocyanide ligand. Crystal structure of $\text{Fe}(\text{CO})_2(\text{t-BuNC})(N,N'\text{-}p\text{-tolyl-1,4-diaz-1,3-butadiene})$

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Abstract

A series of complexes **4**, (1,4-diaz-1,3-diene)isocyanide dicarbonyliron, $(R'\text{-DAB})(\text{RNC})\text{Fe}(\text{CO})_2$, with all combinations of $R' = i\text{-Pr}$ (**a**), $p\text{-Tol}$ (**b**), $p\text{-An}$ (**c**) and $R = \text{t-Bu}$ (**w**), sec-Bu (**x**), benzyl (**y**), $2,6\text{-xylyl}$ (**z**) has been prepared. The complexes were most conveniently prepared by heterogeneously (Pd 10%/C) catalyzed substitution of one CO ligand in $\text{Fe}(\text{CO})_3(R'\text{-DAB})$. The single crystal X-ray structure of $\text{Fe}(\text{CO})_2(\text{t-BuNC})(p\text{-Tol-DAB})$ (**4bw**) has been determined ($\text{FeC}_{23}\text{H}_{25}\text{N}_3\text{O}_2$, monoclinic, spacegroup $C2/c$, $a = 29.967(5)$, $b = 6.273(1)$, $c = 25.481(4)$ Å, $\beta = 110.37(2)^\circ$, $Z = 8$, $R = 0.064$, $R_w = 0.070$). The coordination geometry around the central iron is intermediate between trigonal bipyramidal and square pyramidal. The structure and the dynamic behaviour of the complexes in solution are discussed on the basis of IR, ^1H NMR and ^{13}C NMR spectroscopy.

Introduction

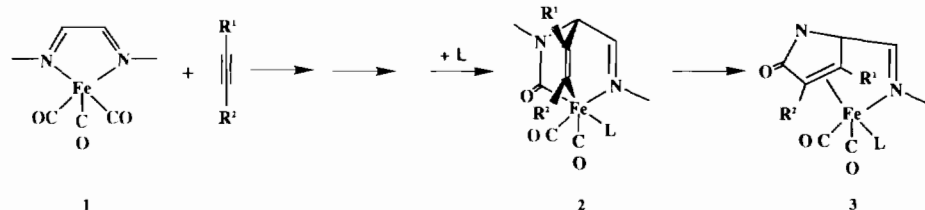
In previous papers [1] we have reported details of the reaction sequence shown in Scheme 1. In the initial step an electron deficient alkyne, as dipolarophile, adds across the 1,3-dipolar $\text{C}=\text{N}\text{-Fe}$ fragment [1] in $\text{Fe}(\text{CO})_3(R'\text{-DAB})^{**}$ (**1**) to give, after CO insertion,

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**The 1,4-diaz-1,3-dienes of formula $R'\text{N}=\text{C}(\text{H})\text{C}(\text{H})=\text{NR}'$ are abbreviated as $R'\text{-DAB}$.

incorporation of an additional ligand L and reductive elimination, the final product **3** [1].

In order to probe the influence on the initial cycloaddition step, and to study a possible competition between CO and CNR insertion in the subsequent step, we set out to substitute one or more of the CO ligands in **1** for a variety of better σ -donating/less π -accepting [2] isocyanides. In a recent communication [3] we have reported a dramatic increase in reactivity observed after



$R^1 = R^2 = \text{CO}_2\text{Me}$; $\text{C}(\text{O})\text{Ph}$

$R^1 = \text{H}$, $R^2 = \text{CO}_2\text{Me}$

$L = \text{CO}$; $\text{P}(\text{OMe})_3$

Scheme 1. 1,3-Dipolar cycloaddition of $\text{Fe}(\text{CO})_3(R'\text{-DAB})$ with an electron deficient alkyne.

substitution of one CO in the starting complex **1** by *t*-BuNC. In the present series of complexes, the R groups in the isocyanides and the R' groups in the diazadienes are varied systematically, using aliphatic and aromatic substituents. This gives the possibility to study in more detail the influence of electronic and steric properties of the CNR and R'-DAB.

Several synthetic routes are known to substitute a carbon monoxide ligand by an isocyanide ligand [4]. In addition to photochemical [5], thermal [6] and electrochemical [7] methods or via initial substitution of a weakly coordinating ligand [8], most of the synthetic routes make use of transition metal catalysts [9, 10]. Coville and co-workers have described many substitution reactions catalyzed by metal carbonyl dimers such as $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ or by (supported) metal catalysts such as CoCl_2 , Pd on carbon, Pt on CaCO_3 [10]. To our knowledge this is the first example where the transition metal catalyzed CO substitution is performed on a metal complex bearing, besides CO ligands, a chelating ligand. In this paper we present the results of our efforts to substitute a CO ligand by various aliphatic/aromatic isocyanides in $\text{Fe}(\text{CO})_3(\text{R}'\text{-DAB})$ (**1**) using a Pd/C catalyst. The single crystal X-ray structure of $\text{Fe}(\text{CO})_2(\text{t-BuNC})(p\text{-tolyl-DAB})$ (**4bw**) is described.

Experimental

^1H NMR 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.

Elemental analyses were carried out by the section Elemental Analysis of the Institute for Applied Chemistry, TNO Zeist, Netherlands.

For the irradiation a high pressure mercury lamp (Philips HPK 125 W) in a water-cooled quartz immersion well was used.

Solvents were carefully dried and distilled under nitrogen prior to use. All reactions were carried out under N_2 by standard Schlenk techniques.

The starting compounds *i*-Pr (**a**) [11], *p*-Tol (**b**) [12, 13] and *p*-An (**c**) [13] DAB and $\text{Fe}(\text{CO})_3(\text{R}'\text{-DAB})$ (**1a-c**) [14]* were prepared according to literature procedures. The catalyst, Pd(10%)/C was received from H. Drijfhout & Zoon's edelmetaalbedrijven N.V.; *t*-Bu isocyanide (**w**) and benzyl isocyanide (**y**) were purchased from Aldrich; 2,6-xylyl isocyanide (**z**) from Fluka AG; *sec*-Bu isocyanide (**x**) was synthesized by a published method [15].

*The best synthetic route to prepare compound **1** is presented in ref. 25b and refs. cited therein.

Synthesis of $\text{Fe}(\text{CO})_2(\text{CNR})(\text{R}'\text{-DAB})$ (**4**)

Formation of **4** with aliphatic R' groups (**4aw-z**)

To a solution of $\text{Fe}(\text{CO})_3(\text{i-Pr-DAB})$ (**1a**) (1.2 mmol) in 20 ml pentane, CNR (**w-z**) (1 equiv) was added. After addition of the Pd/C catalyst (about 10 mg) the solution was stirred at room temperature for 2–24 h, depending on the isocyanide used. The reaction was monitored by IR spectroscopy. After completion of the reaction (disappearance of the CO bands of the starting compound $\text{Fe}(\text{CO})_3(\text{i-Pr-DAB})$ (**1a**)) the solution was filtered over a G2 filter to remove the catalyst. After evaporation of the solvent, the product was purified by means of sublimation of both CNR and a possible excess of *i*-Pr DAB, by gentle heating, into a Schlenk tube cooled with liquid N_2 . The product could also be purified by crystallization from a concentrated pentane solution at -30°C . Yields range from 70 to 90%.

Formation of **4** with aromatic R' groups (**4bw-bz, 4cw-cz**)

To a solution of $\text{Fe}(\text{CO})_3(\text{R}'\text{-DAB})$ (**1b, c**) (0.5 mmol) and 1 equiv. CNR (**w-z**) in 15 ml THF was added a catalytic amount of Pd(10%)/C (about 10 mg). After 8–24 h stirring at room temperature IR spectroscopy indicated that the reaction was complete. After filtration over a G2 filter the solvent was removed under reduced pressure. The pure product was obtained by crystallization from a concentrated diethyl ether solution at -30°C with yields varying between 60 and 85%.

Photochemical substitution of a CO ligand by *t*-BuNC (**w**) in $\text{Fe}(\text{CO})_3(\text{i-Pr-DAB})$ (**1a**)

A solution of $\text{Fe}(\text{CO})_3(\text{i-Pr-DAB})$ (**1a**) (0.82 mmol) and 1 equiv. *t*-BuNC (**w**) in pentane was irradiated, while a slow stream of N_2 was used to purge the solution. The substitution was stopped after about 5 h when about 95% of the product was formed (indicated by IR spectroscopy). The product $\text{Fe}(\text{CO})_2(\text{t-BuNC})(\text{i-Pr-DAB})$ (**4aw**) was isolated as described above.

Elemental analyses of complexes **4bw-z****

4bw, $\text{FeC}_{23}\text{H}_{25}\text{N}_3\text{O}_2$. Found: C, 64.75; H, 6.20; N, 10.20. Calc.: C, 64.05; H, 5.84; N, 9.74%.

4bx, $\text{FeC}_{23}\text{H}_{25}\text{N}_3\text{O}_2$. Found: C, 62.98; H, 6.14; N, 9.56. Calc.: C, 64.05; H, 5.84; N, 9.74%.

4by, $\text{FeC}_{26}\text{H}_{23}\text{N}_3\text{O}_2$. Found: C, 65.86; H, 5.52; N, 8.70. C, 67.93; H, 4.86; N, 8.81%.

4bz, $\text{FeC}_{27}\text{H}_{25}\text{N}_3\text{O}_2$. Found: C, 67.17; H, 5.69; N, 8.40. Calc.: C, 67.65; H, 5.27; N, 8.77%.

Because the complexes presented here are within a series, the elemental analyses are only given for complexes **4bw-z. The purity of the other complexes has been checked spectroscopically. Complexes **4bx** and **4by** could not be crystallized and were probably less pure.

Crystal structure determination of Fe(CO)₂(t-BuNC)(p-Tol-DAB) (4bw)

A dark-blue block shaped crystal was mounted in a Lindemann-glass capillary and transferred to an Enraf-Nonius CAD4 diffractometer for data collection. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections with $9.2 < \theta < 14.3^\circ$. The unit cell parameters were checked for the presence of higher lattice symmetry [16]. The crystal quality was rather poor, as judged from broad reflection profiles. Data were corrected for L_p , for a linear decay (26%) of the intensity control reflections during the 129 h of X-ray exposure time and for the absorptions (using the DIFABS [17] method). The structure was solved with direct methods, the solution with the best figure of merit revealed all non-H atoms (SHELXS86 [18]). Refinement on F was carried out by full matrix least-squares techniques. H atoms were introduced on calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters, H atoms with one common isotropic thermal parameter ($U = 0.121(6)$ Å²).

Weights were introduced in the final refinement cycles, convergence was reached at $R = 0.064$. Crystal data and numerical details of the structure determination are given in Table 1. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2. Neutral atom scattering factors were taken from ref. [19] and corrected for anomalous dispersion [20]. All calculations were performed with SHELX76 [21] and the EUCLID package [22] (geometrical calculations and illustrations) on a MicroVAX cluster.

Results and discussion

The ligands and complexes employed in this investigation are shown in Fig. 1. The type of complex is identified by arabic numbers. The three diazadienes R'-DAB are indicated by letters a–c, while letters from the end of the alphabet, w–z, identify the different isocyanides.

TABLE 1. Crystal data and details of the structure determination of Fe(CO)₂(t-BuNC)(p-Tol-DAB) (4bw)

<i>Crystal data</i>	
Formula	FeC ₂₃ H ₂₅ N ₃ O ₂
Molecular weight	431.32
Crystal system	monoclinic
Space group	C2/c (No. 15)
a, b, c (Å)	29.967(5), 6.273(1), 25.481(4)
β (°)	110.37(2)
V (Å ³)	4490.4(14)
Z	8
D_{calc} (g cm ⁻³)	1.276
$F(000)$	1808
μ (cm ⁻¹)	6.9
Crystal size (mm)	0.25 × 0.48 × 0.72
<i>Data collection</i>	
Temperature (K)	295
$\theta_{\text{min}}, \theta_{\text{max}}$	0.85, 25.38
Radiation	Mo K α (Zr-filtered), 0.71073 Å
Scan type	$\omega/2\theta$
$\Delta\omega$ (°)	$0.75 + 0.35 \tan\theta$
Horizontal and vertical aperture (mm)	3.0, 6.0
Distance crystal to detector (mm)	173
Reference reflections	– 6 0 0, – 7 – 1 4, – 3 1 2
Data set	$h - 36:0, k - 7:7; l 0:30$
Total data	9481
Total unique data	4142 ($R_{\text{int}} = 0.0615$)
Observed data	2203 ($I > 2.5\sigma(I)$)
DIFABS correction range	0.609–1.491
<i>Refinement</i>	
No. refined parameters	263
Weighting scheme	$w = 1.0/[\sigma^2(F) + 0.000751F^2]$
Final R, R_w, S	0.064, 0.070, 3.35
$(\Delta/\sigma)_{\text{av}}$ in final cycle	0.026
Min. and max. residual density (e/Å ³)	– 0.65, 0.55

TABLE 2. Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for Fe(CO)₂(t-BuNC)(p-Tol-DAB) (**4bw**)

Atom	x	y	z	U _{eq} ^a (Å ²)
Fe	0.11447(3)	0.50819(17)	0.40832(3)	0.0442(3)
O(1)	0.04607(19)	0.8453(10)	0.3580(2)	0.090(2)
O(2)	0.04316(16)	0.2388(9)	0.4296(2)	0.0781(19)
N(1)	0.14342(16)	0.6614(9)	0.47763(19)	0.0462(19)
N(2)	0.17904(16)	0.4062(9)	0.4274(2)	0.0462(17)
N(3)	0.09170(19)	0.3461(11)	0.2914(2)	0.066(2)
C(1)	0.0579(3)	1.2415(14)	0.5885(3)	0.095(4)
C(2)	0.0807(3)	1.0857(13)	0.5602(3)	0.063(3)
C(3)	0.0600(3)	0.8946(14)	0.5399(3)	0.067(3)
C(4)	0.0799(2)	0.7560(12)	0.5127(3)	0.057(3)
C(5)	0.1229(2)	0.8033(11)	0.5047(2)	0.047(2)
C(6)	0.1437(2)	0.9978(13)	0.5250(2)	0.058(2)
C(7)	0.1235(3)	1.1380(13)	0.5525(3)	0.065(3)
C(8)	0.1903(2)	0.6226(12)	0.5024(3)	0.057(3)
C(9)	0.2094(2)	0.4813(12)	0.4751(2)	0.052(2)
C(10)	0.1974(2)	0.2576(11)	0.3983(2)	0.046(2)
C(11)	0.2355(2)	0.3103(12)	0.3814(3)	0.058(3)
C(12)	0.2525(2)	0.1681(13)	0.3525(3)	0.064(3)
C(13)	0.2340(3)	-0.0334(12)	0.3401(3)	0.064(3)
C(14)	0.2536(3)	-0.1890(15)	0.3083(4)	0.103(4)
C(15)	0.1969(3)	-0.0894(12)	0.3580(3)	0.063(3)
C(16)	0.1788(2)	0.0537(11)	0.3866(3)	0.055(3)
C(17)	0.0732(2)	0.7168(12)	0.3788(3)	0.057(3)
C(18)	0.0726(2)	0.3349(11)	0.4228(3)	0.051(3)
C(19)	0.1002(2)	0.4053(12)	0.3368(3)	0.054(2)
C(20)	0.0835(3)	0.2684(15)	0.2362(3)	0.072(3)
C(21)	0.1259(3)	0.311(2)	0.2215(4)	0.160(7)
C(22)	0.0746(5)	0.0315(18)	0.2369(4)	0.152(6)
C(23)	0.0403(3)	0.3759(18)	0.1960(3)	0.108(4)

^aU_{eq} = $\frac{1}{3}$ of the trace of the orthogonalized U matrix.

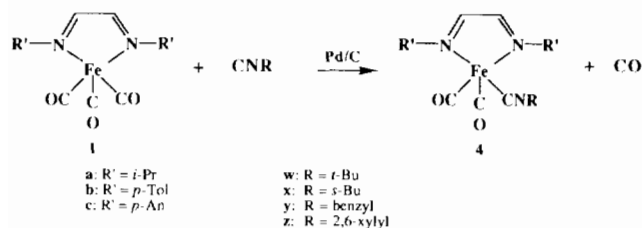


Fig. 1. Synthesis of Fe(CO)₂(CNR)(R'-DAB) via CO substitution in Fe(CO)₃(R'-DAB), catalyzed by Pd/C.

Formation of Fe(CO)₂(CNR)(R'-DAB)

CO ligand substitution with Pd/C catalyst

The complexes Fe(CO)₂(CNR)(R'-DAB) (**4**) are best prepared via a Pd/C catalyzed substitution of a CO ligand by a CNR ligand in Fe(CO)₃(R'-DAB) (**1**) (Fig. 1). IR monitoring of the reaction indicates that the substitution is quantitative and is completed within 2 h (for **4aw–y**) to almost 24 h (for **4bz** and **4cz**).

In the case of aliphatic isocyanides (**w–y**) the substitution is fast and clean, but in the case of the aromatic isocyanide (**z**) the situation is more complicated; in all cases the reaction time is prolonged. For the starting

complexes with aromatic R'-DAB substituents (**1b, c**) not only the substitution time is prolonged, but the reaction is also complicated by the occurrence of disubstitution. (The fact that aromatic isocyanides give rise to higher substituted products has been encountered before [10a, b, 23]). The disubstitution gives rise to very unstable FeCO(CNR)₂(R'-DAB) complexes with a carbonyl stretching vibration at about 1900 cm⁻¹. The formation of disubstituted complexes can be prevented or even suppressed by strictly avoiding the addition of more than one equivalent of **z**.

The Fe(CO)₂(CNR)(R'-DAB) (**4**) complexes formed are very sensitive to oxygen and moisture. The substitution proved to be irreversible. When complex **4aw** was subjected to 30 bar of CO pressure for a period of four days, no changes occurred.

Photochemical CO ligand substitution

Photochemical substitution of CO in complexes **1** by olefins [24b], dienes [25b] or phosphines [26] has been widely employed and is usually a fast and clean reaction. On irradiation of a mixture of Fe(CO)₃(i-Pr-DAB) (**1a**) and t-BuNC (**w**), in pentane, IR monitoring indicated the formation of **4aw** and the disappearance of *c.* 95% of the starting material after 5 h. However, besides a small tendency to form disubstituted products, variable amounts of a light pink insoluble unidentified precipitate were formed. When the mixture was irradiated for prolonged periods of time in order to obtain total conversion (as in the case with the Pd/C catalyst) more disubstitution and more pink precipitate was observed while also decomposition took place.

IR spectroscopy

IR data of the starting complexes (**1a–c**), the free isocyanides (**w–z**) and of the Fe(CO)₂(CNR)(R'-DAB) (**4**) complexes are collected in Table 3. The IR spectra of the complexes **4** show one CNR and two intense CO stretching bands. Compared with the Fe(CO)₃(R'-DAB) (**1**) precursors, the CO stretching vibrations of the Fe(CO)₂(CNR)(R'-DAB) complexes (**4**) have shifted *c.* 30–50 cm⁻¹ to lower frequency. This shift is a logical consequence of the introduction of the stronger σ -donating/less π -accepting CNR ligand [2] which causes a stronger π -backdonation to the two remaining CO ligands. The lower CO frequencies for complexes **4aw–z** are due to the less pronounced π -accepting properties of R'-DAB ligands containing aliphatic R' groups as compared to those containing aromatic R' groups [28].

The influence of the different R' and R groups on the CNR stretching frequencies can best be discussed by considering the three resonance structures for the M–CNR fragment in Fig. 2.

Resonance structure A, where the isocyanide σ -donation dominates, is most important for aliphatic

TABLE 3. IR data: wavenumbers (cm^{-1}) of stretching vibrations $\nu(\text{CO})$ and $\nu(\text{CN})$ (in italics) for starting complexes of $\text{Fe}(\text{CO})_3(\text{R}'\text{-DAB})$ (**1a-c**)^a, for isocyanides (**w-z**)^b and for the twelve combinations in the CNR substituted complexes **4**. Values are for solutions in pentane and tetrahydrofuran (in parentheses)

R' in R'-DAB	(1)	R in CNR			
		w: t-Bu 2130	x: sec-Bu 2133	y: benzyl 2145	z: 2,6-xylyl 2115
a: i-Pr	2025 (2017)	2108 (2114)	2105 (2115)	2109 (2126)	2072 (2088)
	1950 (1939)	1964 (1956)	1964 (1955)	1966 (1959)	1962 (1968)
		1916 (1904)	1916 (1903)	1920 (1906)	1923 (1909)
b: p-Tol	2038 (2033)	2130 (2133)	2126 (2133)	2136 (2140)	2095 (2100)
	1972 (1960)	1988 (1975)	1983 (1975)	1986 (1978)	1983 (1974)
	1963	1932 (1921)	1933 (1920)	1935 (1921)	1938 (1927)
c: p-An	2036 (2031)	2131 (2135)	2130 (2136)	2133 (2138)	2098 (2099)
	1971 (1956)	1982 (1976)	1979 (1975)	1980 (1971)	1986 (1973)
	1961	1927 (1919)	1927 (1918)	1928 (1916)	1939 (1925)

^aPartly taken from ref. 14b. ^bPartly taken from ref. 27.

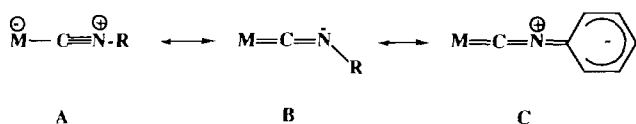


Fig. 2. Resonance structures of the $\text{M}-\text{C}\equiv\text{NR}$ unit.

CNR and aromatic R'-DAB. The higher π -accepting ability of the aromatic R'-DAB results in only marginal π -backdonation into the isocyanide ligand, and the $\nu(\text{CN})$ frequencies are in the range of the respective uncoordinated isocyanide.

Resonance structure B is most important for aliphatic CNR and aliphatic R'-DAB. There is substantial π -backdonation into the isocyanide ligand, resulting in a lowering of the $\nu(\text{CN})$ frequencies.

For the aromatic isocyanides resonance structure C, which enhances the electron withdrawing properties, also plays a significant role [2a, c, d, 8a, 9, 29]. This becomes evident for the complexes with aromatic R'-DAB and aromatic CNR, where the $\nu(\text{CN})$ frequencies are substantially lowered with respect to the free isocyanides. Steric effects can also influence the frequency of $\nu(\text{CN})$ [2c, 27, 30], i.e. a decrease in the CNR frequency can be the consequence of a bulky isocyanide substituent. The bulky group pushes the isocyano group away or forces the isocyano group to bend. The first effect elongates or weakens the bond between the isocyano group and the substituent. The second effect will lead to a rehybridization of the nitrogen atom from sp to sp^2 , i.e. to a lower CN bond order. Both effects will lead to a decrease of the CNR frequency [27]. These steric arguments can perhaps explain why in the complexes **4bz** and **4cz** the CNR frequency is substantially lowered, compared with the other aliphatic isocyanide containing complexes, while the CO frequencies are of the same order of magnitude.

Comparable influences of the aliphatic/aromatic R' groups of the DAB ligand and of the aliphatic/aromatic isocyanide ligands have been found in the case of the related $\text{Cr}(\text{CO})_3(\text{CNR})(\text{R}'\text{-DAB})$ complexes [8b].

NMR spectroscopy

¹H NMR and ¹³C NMR data of the free R'-DAB ligands (**a-c**), the starting complexes $\text{Fe}(\text{CO})_3(\text{R}'\text{-DAB})$ (**1**) and the $\text{Fe}(\text{CO})_2(\text{CNR})(\text{R}'\text{-DAB})$ (**4**) complexes are listed in Tables 4 and 5. The imine protons of the free DAB (**a-c**), the $\text{Fe}(\text{CO})_3(\text{R}'\text{-DAB})$ (**1**) and the $\text{Fe}(\text{CO})_2(\text{CNR})(\text{R}'\text{-DAB})$ complexes (**4**) appear as a singlet at 7.62–8.49 ppm which is within the 7–9 ppm range commonly observed for chelating $\sigma\text{-N}$, $\sigma\text{-N}'$ coordinated R'-DAB ligands [31]. Comparing the imine proton chemical shifts of free DAB, $\text{Fe}(\text{CO})_3(\text{R}'\text{-DAB})$ (**1**) and $\text{Fe}(\text{CO})_2(\text{CNR})(\text{R}'\text{-DAB})$ (**4**), the increased shielding results in a shift to higher field. Decreased paramagnetic deshielding is observed for the imine carbon atoms which absorb near 158, 144 and 140 ppm for free DAB, $\text{Fe}(\text{CO})_3(\text{R}'\text{-DAB})$ and $\text{Fe}(\text{CO})_2(\text{CNR})(\text{R}'\text{-DAB})$, respectively. This high field shift of imine carbon atoms has also been encountered for $\text{Ru}(\text{CO})_3\text{DAB}$ [28] and $\text{Fe}(\text{CO})_3\text{DAB}$ [32]. The largest shift ($\Delta\delta$ about 14 ppm) has been observed upon coordination of a R'-DAB ligand to the metal. Substitution of a CO by a CNR ligand results only in a small additional shift of about 4 ppm.

The two CO ligands of complexes **4** give rise to a ¹³C signal at about 218 ppm. This low field shift, relative to the starting complexes **1** (cf. Table 5), is a consequence of the enhanced π -backdonation to the CO ligands [33]. The ¹³C signals of the CO ligands of the complexes with aliphatic R' groups (**4aw-z**) have been found at a somewhat higher δ value compared to those with aromatic R' groups (**4bw-z** and **4cw-z**). This is in

TABLE 4. ^1H NMR data of R'-DAB (a-c), $\text{Fe}(\text{CO})_3(\text{R}'\text{-DAB})$ (1) and $\text{Fe}(\text{CO})_2(\text{CNR})(\text{R}'\text{-DAB})$ (4)^a

Compound	Imine H ^b	R' group ^b	CNR group ^b
a	7.94 (s, 2H)	3.14 (sept, 2H, 6 Hz), 1.08 (d, 12H, 6 Hz)	
b	8.44 (s, 2H)	7.15 (d, 4H, 8 Hz), 6.81 (d, 4H, 8 Hz), 2.06 (s, 6H)	
c	8.48 (s, 2H)	7.22 (d, 4H, 9 Hz), 6.68 (d, 4H, 9 Hz), 3.24 (s, 6H)	
1a	7.95 (s, 2H)	4.48 (sept, 2H, 6 Hz), 1.23 (d, 12H, 6 Hz)	
1b	7.23 (s, 2H)	7.33 (d, 2H, 7 Hz), 6.94 (d, 4H, 7 Hz), 2.08 (s, 6H)	
1c	7.18 (s, 2H)	7.35 (d, 2H, 8 Hz), 6.70 (d, 4H, 8 Hz), 3.28 (s, 6H)	
4aw	7.38 (s, 2H)	4.83 (sept, 2H, 6 Hz), 1.48 (d, 12H, 6 Hz)	0.90 (s, 9H)
4ax	7.39 (s, 2H)	4.83 (sept, 2H, 7 Hz), 1.48 (d, 12H, 7 Hz)	2.96 (m, 1H), 1.11–0.66 (m, 8 H)
4ay	7.42 (s, 2H)	4.80 (sept, 2H, 7 Hz), 1.45 (d, 12H, 7 Hz)	7.06–6.94 (m, 5H) 3.70 (s, 2H)
4az	7.39 (s, 2H)	4.88 (sept, 2H, 7 Hz), 1.45 (d, 12H, 7 Hz)	6.75–6.62 (m, 3H), 2.17 (s, 6H)
4bw	7.41 (s, 2H)	7.63 (d, 4H, 8 Hz), 6.94 (d, 4H, 8 Hz), 2.12 (s, 6H)	0.54 (s, 9H)
4bx	7.42 (s, 2H)	7.61 (d, 4H, 8 Hz), 7.00 (d, 4H, 8 Hz), 2.12 (s, 6H)	2.68 (m, 1H), 0.90–0.61 (m, 5H), 0.48–0.44 (m, 3H)
4by	7.42 (s, 2H)	7.59 (d, 4H, 7 Hz), 6.95 (d, 4H, 7 Hz), 2.06 (s, 6H)	6.70–6.57 (m, 5H), 3.61 (s, 2H)
4bz	7.43 (s, 2H)	7.62 (d, 4H, 8 Hz), 6.95 (d, 4H, 8 Hz), 1.83 (s, 6H)	6.68–6.51 (m, 3H), 2.08 (s, 6H)
4cw	7.41 (s, 2H)	7.63 (d, 4H, 7 Hz), 7.20 (d, 4H, 7 Hz), 3.35 (s, 6H)	0.66 (s, 9H)
4cx	7.41 (s, 2H)	7.61 (d, 4H, 7 Hz), 7.22 (d, 4H, 7 Hz), 3.34 (s, 6H)	2.71 (m, 1H), 0.86–0.29 (m, 8H)
4cy	7.41 (s, 2H)	7.59 (d, 4H, 7 Hz), 7.23 (d, 4H, 7 Hz), 3.32 (s, 6H)	6.74–6.61 (m, 5H), 3.64 (s, 2H)
4cz	7.41 (s, 2H)	7.61 (d, 4H, 8 Hz), 7.22 (d, 4H, 8 Hz), 3.30 (s, 6H)	6.74–6.51 (m, 3H), 1.87 (s, 6H)

^aThe chemical shift values, in ppm relative to Me_4Si , are measured in C_6D_6 at 293 K and 300.15 MHz. ^bs=singlet, d=doublet, m=multiplet.

agreement with the observed trend for (L-L) $\text{Fe}(\text{CO})_3$ compounds where the CO ligands shift to lower field with decreasing π -acceptor capacity of the bidentate (L-L) ligand [34]. Interestingly, the two CO ligands of $\text{Fe}(\text{CO})_2(\text{CNR})(\text{R}'\text{-DAB})$ (4) appear as one sharp ^{13}C signal at 243 K except for the sec-Bu isocyanide complexes (4a–cx) for which a difference of 0.1 ppm between the two CO signals is found.

In acetone- d_6 at 243 K (and in C_6D_6 at 293 K) the two N-substituents give rise to only one set of signals in ^1H NMR as well as in ^{13}C NMR. A striking effect of this identity is visible for the methyl groups of the i-Pr DAB groups. The diastereotopic methyl groups would be expected to appear as a set of two signals in ^1H NMR as well as in ^{13}C NMR, in view of the molecular geometry in the solid state (*vide infra*). A similar observation has been reported by Leibfritz and tom Dieck for the starting complex $\text{Fe}(\text{CO})_3(\text{R}'\text{-DAB})$

(1) [32a]. Obviously a dynamic process which scrambles the two COs and equilibrates the two N-substituents, i.e. the diastereotopic methyl groups, takes place. This process can be explained by Berry pseudorotations [35], as shown schematically for $\text{Fe}(\text{CO})_2(\text{CNR})(\text{R}'\text{-DAB})$ (4) in Fig. 3.

The N and N' and the C₁ and C₂ of the R'-DAB and the carbonyl ligands, respectively, interconvert as evidenced by the magnetical equivalency of the CO ligands and the two N-substituents. In contrast to the situation with the $\text{Fe}(\text{CO})_3(\text{R}'\text{-DAB})$ (1) complexes it is possible to reach the slow exchange limit in the case of the $\text{Fe}(\text{CO})_2(\text{CNR})(\text{R}'\text{-DAB})$ (4) complexes. When $\text{Fe}(\text{CO})_2(\text{t-BuNC})(\text{i-Pr-DAB})$ was cooled to 190 K, the two CO ligands gave rise to two separate ^{13}C signals, separated by 0.1 ppm. This rather small difference in chemical shift has not been observed for the two N-substituents. In the case of the sec-Bu isocyanide com-

TABLE 5. ^{13}C NMR data^a of CNR (**w–z**) (with $J(\text{NC})$ in Hz in parentheses), $\text{R}'\text{-DAB}$ (**a–c**), $\text{Fe}(\text{CO})_3(\text{R}'\text{-DAB})$ (**1**) and $\text{Fe}(\text{CO})_2(\text{CNR})(\text{R}'\text{-DAB})$ (**4**)

Compound	CO	CNR	Imine C	R' group	CNR group
w		154.8 (4.2)			30.6, 54.3 (5.1)
x		156.1 (4.9)			9.8, 21.2, 29.8, 51.6 (5.5)
y		157.6 (4.9)			44.3 (6.9), 126.1, 127.5, 128.2, 132.6
z		169.1 (5.0)			17.8, 126.3 (12.3), 127.9, 128.7, 134.3
a			158.5	22.5, 60.5	
b			159.1	21.3, 121.8, 130.4, 138.7, 147.6	
c			157.1	54.4, 114.6, 122.3, 143.1, 159.8	
1a	215.6		142.8	24.2, 62.7	
1b	212.4		145.0	19.3, 122.2, 128.7, 135.2, 153.7	
1c	212.6		145.0	54.0, 112.9, 123.3, 149.5, 157.1	
4aw	218.9	161.0	138.6	23.3, 60.2	29.3, 55.5
4ax	219.3, 219.4	162.9	137.7	24.4, 61.3	9.2, 20.6, 29.7, 53.9
4ay	219.4	158.7	138.1	24.8, 61.8	47.5, 126.4, 127.1, 128.1, 133.8
4az	218.3	178.9	138.9	24.4, 61.6	17.3, 126.5, 127.1, 128.2, 132.9
4bw	218.8	159.1	143.2	23.6, 124.7, 139.6, 134.9, 155.2	39.2, 58.1
4bx	216.2, 216.3	155.9	140.8	19.1, 122.4, 128.3, 133.3, 154.7	8.7, 19.3, 28.1, 53.8
4by	216.4	161.1	141.0	19.1, 122.6, 128.9, 133.4, 154.5	46.9, 126.7, 127.2, 128.6, 132.6
4bz	217.1	189.3	142.2	18.9, 122.9, 128.5, 133.0, 155.7	18.3, 126.6, 127.1, 128.6, 131.9
4cw	217.8	161.0	141.6	55.9, 115.3, 125.8, 151.9, 158.7	30.3, 57.8
4cx	216.3, 216.4	158.6	140.8	53.9, 112.6, 123.8, 150.5, 156.4	8.7, 19.4, 27.4, 52.9
4cy	216.2	161.5	140.1	53.6, 112.5, 123.2, 150.2, 155.9	46.8, 125.7, 126.9, 127.7, 132.5
4cz	217.4	180.6	141.8	53.9, 113.3, 122.9, 151.6, 155.2	18.1, 125.7, 127.8, 133.2

^aThe chemical shift values, in ppm relative to Me_4Si , have been measured in acetone- d_6 at 243 K and 75.47 MHz.

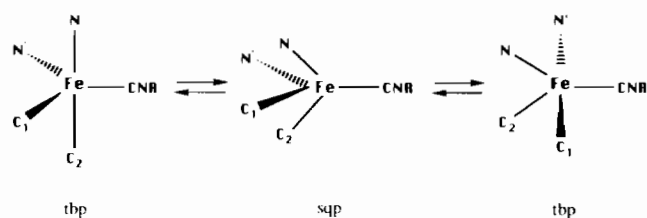


Fig. 3. Proposed dynamic process for **4** via Berry pseudorotations.

plexes (**4a–cx**), the slow exchange limit was already reached at 243 K as shown by the appearance of two separate CO signals. Upon heating $\text{Fe}(\text{CO})_2(\text{sec-BuNC})(i\text{-Pr-DAB})$ (**4ax**) to 293 K the two CO signals coalesce to one signal. Neither steric nor electronic

considerations can give a straightforward explanation why the rotation barrier with isocyanide **x** should be higher as compared to **w**, **y** and **z**.

Upon coordination, the terminal carbon nucleus of the CNR ligand becomes more deshielded resulting in a low field shift in the ^{13}C NMR. The aliphatic isocyanide complexes **4aw–cw** and **4ay–cy** show rather small coordination shifts of 0–8 ppm (see Table 5), while it is somewhat larger for the aromatic isocyanide complexes **4az–cz** (c. 10 ppm). This can be interpreted as a consequence of more π -backdonation to the (aromatic) isocyanide as was also concluded from the IR data. The ^{13}C – ^{14}N coupling which varies from 4.2 to 12.3 Hz [27] for the free isocyanides becomes too small to be observed for the $\text{Fe}(\text{CO})_2(\text{CNR})(\text{R}'\text{-DAB})$ (**4**) com-

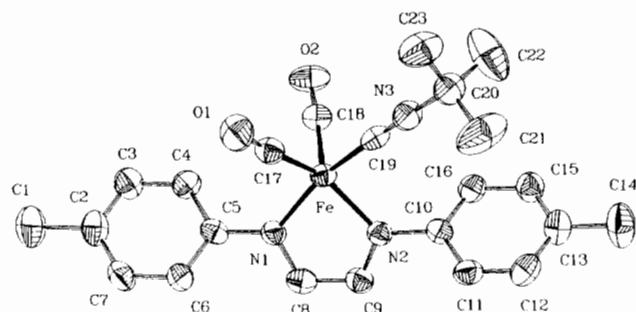


Fig. 4. Thermal ellipsoid plot of $\text{Fe}(\text{CO})_2(\text{t-BuNC})(p\text{-Tol-DAB})$ (**4bw**), drawn at the 40% probability level, with the adopted atom labelling. H atoms were left out for clarity.

TABLE 6. Bond lengths (Å) of the non-hydrogen atoms of $\text{Fe}(\text{CO})_2(\text{t-BuNC})(p\text{-Tol-DAB})$ (**4bw**) (e.s.d.s in parentheses)

Fe–N1	1.931(5)	Fe–N2	1.933(5)	Fe–C17	1.778(7)
Fe–C18	1.793(7)	Fe–C19	1.840(7)	O1–C17	1.137(9)
O2–C18	1.131(8)	N1–C5	1.393(8)	N1–C8	1.347(8)
N2–C9	1.326(7)	N2–C10	1.416(8)	N3–C19	1.153(9)
N3–C20	1.429(9)	C1–C2	1.512(12)	C2–C3	1.366(12)
C2–C7	1.402(13)	C3–C4	1.371(11)	C4–C5	1.405(9)
C5–C6	1.386(10)	C6–C7	1.388(11)	C8–C9	1.369(10)
C10–C11	1.393(9)	C10–C16	1.386(10)	C11–C12	1.363(10)
C12–C13	1.372(11)	C13–C14	1.512(13)	C13–C15	1.386(13)
C15–C16	1.381(11)	C20–C21	1.467(13)	C20–C22	1.511(15)
C20–C23	1.501(12)				

plexes. The signals of the carbon atom of the $\text{C}\equiv\text{N}$ unit and the carbon atom of the $\text{C}\equiv\text{N}-\text{C}$ unit appear as small and slightly broadened signals, apparently due to a shorter T_1 of the quadrupole ^{14}N nucleus. This has also been encountered in the case of other isocyanide metal complexes [9, 36].

Molecular structure of $\text{Fe}(\text{CO})_2(\text{t-BuNC})(p\text{-Tol-DAB})$ (**4bw**)

The molecular structure of $\text{Fe}(\text{CO})_2(\text{t-BuNC})(p\text{-Tol-DAB})$ (**4bw**) together with the atomic numbering is

shown in Fig. 4. Selected bond distances and bond angles are presented in Tables 6 and 7. Compared to the structure of free *c*-Hex DAB [37] there is a significant lengthening (see Table 6) of the two imine bonds (1.258(3) versus 1.34(2) Å (mean)) and shortening of the central C–C bond (1.457(3) versus 1.369(10) Å*). This is a consequence of π -backdonation into the R'-DAB LUMO which is antibonding in C–N and bonding in C–C [37–39]. The DAB bond lengths of **4bw** compare well with those found in the related structure of $\text{Fe}(\text{CO})_5(2,6\text{-di-}i\text{-PrC}_6\text{H}_3\text{-DAB})$ [24a] (1.329(5) and 1.390(5) Å for the C=N and the central C–C bonds, respectively). From this it may be concluded that the electronic changes in the molecule by substituting a CO for a CNR ligand are more clearly reflected in the IR and NMR spectroscopic properties than by bond length variations in the single crystal X-ray structure.

The angles 178.1(7) and 177.2(7)° of Fe–C19–N3 and C19–N3–C20, respectively (see Table 7) are close to 180°. The bond lengths C19–N3 and N3–C20 of the *t*-Bu isocyanide ligand are 1.153(9) and 1.429(9) Å, respectively. This is in accordance with a triple bond and a single bond, respectively, indicating that in $\text{Fe}(\text{CO})_2(\text{t-BuNC})(p\text{-Tol-DAB})$ (**4bw**) resonance structure A (Fig. 2) has a larger contribution to the description of the actual bonding situation; the isocyanide mainly acts as a σ -donating ligand. Comparable bond lengths and angles have also been encountered in numerous other *t*-Bu isocyanide complexes [2d, 4a, 30, 40]. For a regular five-coordinate d^8 -complex, a trigonal bipyramidal or a square pyramidal structure might be expected [41]. The coordination geometry of $\text{Fe}(\text{CO})_2(\text{t-BuNC})(p\text{-Tol-DAB})$ (**4bw**) however, is understandably neither a perfect tbp nor a sqp. Judging from the angles

*It has to be taken into account that in complex **4bw** the R'-DAB group is aromatic and that the R' substituent of the free ligand is aliphatic.

TABLE 7. Bond angles (°) of the non-hydrogen atoms of $\text{Fe}(\text{CO})_2(\text{t-BuNC})(p\text{-Tol-DAB})$ (**4bw**) (e.s.d.s in parentheses)

N1–Fe–N2	81.0(2)	N1–Fe–C17	92.6(3)	N1–Fe–C18	103.7(3)
N1–Fe–C19	163.1(3)	N2–Fe–C17	147.0(3)	N2–Fe–C18	117.3(3)
N2–Fe–C19	90.0(3)	C17–Fe–C18	95.7(3)	C17–Fe–C19	87.2(3)
C18–Fe–C19	93.1(3)	Fe–N1–C5	129.5(4)	Fe–N1–C8	113.7(4)
C5–N1–C8	116.8(5)	Fe–N2–C9	114.9(4)	Fe–N2–C10	128.6(4)
C9–N2–C10	116.5(5)	C19–N3–C20	177.2(7)	C1–C2–C3	121.8(8)
C1–C2–C7	120.2(7)	C3–C2–C7	118.0(8)	C2–C3–C4	121.9(8)
C3–C4–C5	121.5(7)	N1–C5–C4	121.5(6)	N1–C5–C6	121.9(6)
C4–C5–C6	116.6(6)	C5–C6–C7	121.9(6)	C2–C7–C6	120.2(7)
N1–C8–C9	115.5(6)	N2–C9–C8	114.9(6)	N2–C10–C11	121.0(6)
N2–C10–C16	121.3(6)	C11–C10–C16	117.7(6)	C10–C11–C12	120.8(7)
C11–C12–C13	122.0(7)	C12–C13–C14	121.1(8)	C12–C13–C15	117.6(7)
C14–C13–C15	121.2(7)	C13–C15–C16	121.1(7)	C10–C16–C15	120.7(6)
Fe–C17–O1	177.2(7)	Fe–C18–O2	173.8(6)	Fe–C19–N3	178.1(7)
N3–C20–C21	108.7(7)	N3–C20–C22	107.0(7)	N3–C20–C23	109.2(7)
C21–C20–C22	110.8(10)	C21–C20–C23	111.3(7)	C22–C20–C23	109.7(8)

around the central iron atom (see Table 7), the structure resembles slightly more a sqp geometry. An ideal sqp or tbp structure is not possible for this sort of complexes since the bite angle of the DAB ligand never exceeds $80 \pm 1^\circ$ [24, 25, 28]. The angle between the two CO ligands is $95.7(3)^\circ$. In solution, the CO–Fe–CO angle has been determined from the relative intensities of the symmetrical and anti-symmetrical stretching modes by the method of Kettle and Paul [42] and amounts to 99° . So the structure description is not only valid in the solid state but also in solution. For a number of five-coordinate Fe(α -diimine) complexes the X-ray structures have been determined, indicating that the geometries range from approximately tbp to sqp via intermediate structures with increasing π -acceptor properties of the DAB ligand [24, 25, 28]. When regarding the structure as a tbp the two CO ligands and one N atom of the DAB ligand are in equatorial positions, while the other N atom of the DAB and the t-Bu isocyanide ligand are in axial positions. If one considers the structure as sqp, the DAB ligand, the t-Bu isocyanide and a CO ligand are in the basal plane while the other CO ligand is in an apical position. These geometries are in agreement with the theoretical predictions which place the σ -donor ligand (here the t-Bu isocyanide) in an axial position for the tbp geometry and in the basal positions for the sqp geometry [41b].

Supplementary material

A full list of crystallographic details (31 pages) can be supplied by the authors on request.

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