Influence of the *trans* Substituent on N_2 Bonding in Iron(II)–Phosphane Complexes: Structure, Synthesis, and Properties of the Monomeric Adducts *trans*-$[FeXN_2(depe)_2]BPh_4$, X = Cl, Br**

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In our investigations on the bonding and activation of dinitrogen in transition metal complexes, we prepared the compound "*trans*-[{$FeCl(depe)_2$}$_2$(μ-N_2)]$(BPh_4)_2$" (depe = $Et_2PCH_2CH_2PEt_2$) according to a method described by Bellerby et al.[1] This compound is the only known example of an N_2-bridged iron(II) dimer with octahedral coordination of donor ligands, and thus is of interest as a potential phosphane-analogous N_2 precursor of diazene-bridged Fe^{II} dimers with an octahedral thiolate/thioether coordination environment.[2] We recently characterized the electronic and vibrational properties of these compounds.[3] The known dinuclear μ-N_2–Fe complexes include Fe^0 dimers with trigonal-bipyramidal coordination by P-donor and CO ligands besides N_2, as well as tetracoordinate Fe^{II} complexes with diphosphane and cyclopentadienyl co-ligands.[4] Otherwise, N_2-bridged octahedral complexes are only known for the higher homologues ruthenium(II) and osmium(II).

Doubts about the dimeric structure of the above-mentioned Fe–N_2–depe complex were raised in 1993 by Hughes et al. on the basis of a comparison with the analogous dmpe system (dmpe = $Me_2PCH_2CH_2PMe_2$), for which a monomeric structure was inferred from spectroscopic data.[5] Indeed, our X-ray crystallograpic characterization of the chloro and bromo depe complexes $[FeClN_2(depe)_2]BPh_4$ (**1**) and $[FeBrN_2(depe)_2]BPh_4$ (**2**) revealed a monomeric octahedral structure with end-on terminally bound dinitrogen *trans* to the halide ligand. This is the first X-ray structure of an $[FeXN_2P_4]^+$ complex with X = halide. Corresponding structures with X = H are known.[6]

The reaction of $[FeX_2(depe)_2]$ (X = Cl, Br)[7] with N_2 in methanol at room temperature yields an orange solution. After the addition of $NaBPh_4$, crystals of $[FeXN_2(depe)_2]BPh_4$ (X = Cl **1**[8], X = Br **2**[9]) precipitate. In the IR spectrum the N–N stretching mode is observed in a region typical for complexes in which N_2 is coordinated end-on (**1**: $\tilde{\nu}_{NN} = 2088$, **2**: $\tilde{\nu}_{NN} = 2091\ cm^{-1}$; cf. $\tilde{\nu}_{NN} = 2090\ cm^{-1}$ in $[FeHN_2(depe)_2]BPh_4$ (**3**)[7]) but at lower wavenumber than in the analogous, but not structurally characterized, compounds $[FeXN_2(dmpe)_2]BPh_4$ (X = Cl: $\tilde{\nu}_{NN} = 2105$, X = Br: $\tilde{\nu}_{NN} = 2107 cm^{-1}$).[10] A further band associated with the Fe(II)–N_2 unit is observed at 513 cm^{-1} (**1**) and 509 cm^{-1} (**2**). We succeeded in characterizing complexes **1** and **2** by Raman spectroscopy (30 K, 30 mW, excitation wavelength $\lambda = 514.5$ nm). The band for ν_{NN} was found at 2088 cm^{-1} for **1** and at 2090 cm^{-1} for **2**. Corresponding to the decrease in the intensity of the NN peak, rapid decay of the samples upon laser irradiation was observed.

Both **1** (Figure 1a, b) and **2** were studied by Mössbauer spectroscopy under nitrogen at various temperatures (Table 1). The spectrum of **1** at 300 K (Figure 1b) shows two doublets with quadrupole splittings ΔE_Q of 1.30 (I) and 2.66 $mm\,s^{-1}$ (II) and an isomer shift of $\delta = 0.21$ (I) and 0.41 $mm\,s^{-1}$ (II). Doublet (I) is assigned to complex **1**, which is in agreement with Mössbauer parameters given in the literature and a prediction by Silver.[11, 12] Correspondingly, ΔE_Q and δ were determined for complex **2** to be 1.34 and 0.23 $mm\,s^{-1}$, respectively (Table 1). Doublet (II) is attributed to the analogous N_2-free complex, because its intensity increases in a He atmosphere at room temperature (Figure 1c). Interestingly, this transformation is reversible: Repeating the measurement in an N_2 atmosphere again yields

Table 1. Mössbauer parameters of **1** and **2** under N_2 in $mm\,s^{-1}$ (δ vs. α-iron)

	T [K]	δ (I)	ΔE_Q (I)	δ (II)	ΔE_Q (II)
1	100	0.256(3)	1.398(5)	0.43(2)	2.64(3)
	150	0.244(4)	1.371(7)	0.38(3)	2.64(5)
	250	0.23(2)	1.31(3)	0.36(12)	2.65(24)
	300	0.21(1)	1.30(2)	0.41(3)	2.66(7)
2	150	0.268(8)	1.42(2)	0.39(1)	2.70(1)
	250	0.23(1)	1.39(3)	0.34(1)	2.61(3)
	300	0.23(2)	1.34(4)	0.33(1)	2.61(3)

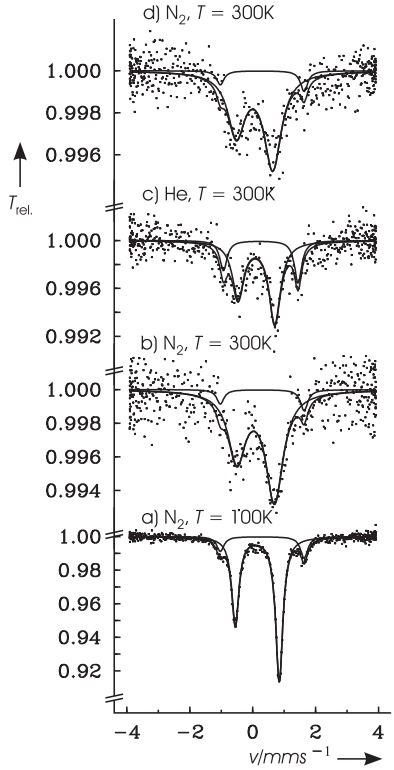

Figure 1. Mössbauer spectra of **1** under N_2 and He atmospheres. T_{rel} = relative transmission.

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the original spectrum (Figure 1d). Hence, the complex undergoes N_2 exchange at room temperature in the solid state, and the N_2-free product reversibly binds N_2 in the solid state. These observations demonstrate the lability of the Fe–N bond in these complexes.

The monomeric structure of **1** is shown in Figure 2. In the distorted octahedral environment of the iron atom, the end-on-bound N_2 is *trans* to the chloride ligand. One of the two

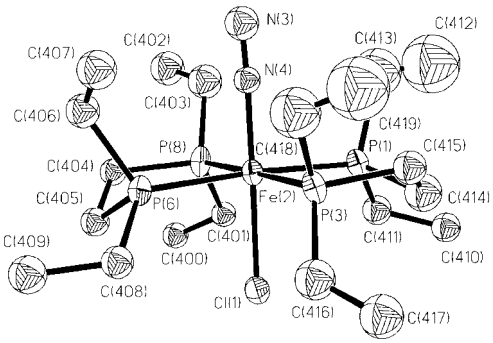

Figure 2. Structure of the cation of **1** (thermal ellipsoids are drawn at the 30% probability level; H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Fe(2)–P(1) 2.293(3), Fe(2)–P(3) 2.294(4), Fe(2)–P(6) 2.280(3), Fe(2)–P(8) 2.298(4), Fe(2)–Cl(1) 2.311(3), Fe(2)–N(4) 1.784(9), N(3)–N(4) 1.073(11), P(3)-Fe(2)-P(6) 96.58(12), P(3)-Fe(2)-P(1) 84.63(12), P(6)-Fe(2)-P(8) 84.18(12), P(1)-Fe(2)-P(8) 94.54(12), P(3)-Fe(2)-N(4) 89.3(3), P(3)-Fe(2)-Cl(1) 89.71(12), P(1)-Fe(2)-N(4) 92.5(3), P(6)-Fe(2)-Cl(1) 86.64(12), Fe(2)-N(4)-N(3) 177.5(10).

independent cations in the unit cell exhibits a partial disorder between the chloride and dinitrogen ligands.[13] In the following discussion of bond lengths we exclusively consider the geometry of the undisordered cation (Figure 2). The N–N bond length is comparable to that in the related complex $[FeH(N_2)(depe)_2]BPh_4$ (**3**),[14] the Fe–N bond is slightly shorter, and the Fe–P bonds are considerably longer (**3**: N–N 1.070(12), Fe–N 1.825(7), Fe–P (av) 2.240 Å). Furthermore, the Fe–Cl bond is slightly shorter than those in $[FeHCl(depe)_2]$ (**4**)[15] and $[FeCl_2(depe)_2]$ (**5**)[16] (**4**: Fe–Cl 2.404(2), Fe–P (av) 2.208; **5**: Fe-Cl 2.344(2), Fe–P (av) 2.260 Å). We also obtained single crystals of $[FeBr(N_2)(depe)_2]BPh_4$ (**2**) that were suitable for an X-ray structure analysis. Initial results confirm that the cations in **2** are structurally analogous to those of **1**. However, due to the strong disorder of the ligands in the two symmetry independent cations, a precise determination of the geometry was not possible up to now.[17]

In general iron(II)–dinitrogen complexes are stable if they contain tertiary phosphane and hydride ions as co-ligands.[18] This is demonstrated by the ability of $[FeH_4(PEtPh_2)_3]$ and $[FeH(Ph_2PCH_2CH_2PPh_2)_2]BPh_4$ to fix dinitrogen from air.[19] In contrast, the dinitrogen ligands in **1** and **2** are only weakly bound. A possible explanation for this difference is that the bond between the transition metal and dinitrogen is dominated by π backbonding into the π* orbitals of N_2. This interaction can be enhanced by co-ligands that lower the effective nuclear charge Z_{eff} of the metal and thus raise the energy of the backbonding d orbitals. The hydride ion is the strongest σ donor and therefore has the greatest influence in this respect. This is in accordance with the observation that the bis-hydrido unit has as strong a bonding capability for N_2 as the hydride-free ruthenium and osmium complexes.[20] In comparison, halides are in general weaker donors and also have π-donor character. The latter is an additional disadvantage as the π-donor ligand mixes with the t_{2g} orbitals which are responsible for backbonding, and hence the Fe–N overlap is reduced. Molecular orbital calculations seem to confirm this assumption,[21] which is of general significance for the stability of transition metal–N_2 adducts.

In view of the weakness of the Fe–N bond, it is not surprising that **1** has a monomeric stucture, as the bridging coordination of N_2 requires a certain stability of the Fe–N bond. Therefore, the existence of bridged, octahedrally coordinated iron(II)–N_2 systems at room temperature appears very unlikely.

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[8] All reactions were carried out under dry N_2 in a glovebox or by standard Schlenk techniques. All solvents were distilled under Ar from an appropriate drying agent prior to use. The spectra were measured with the following instruments: IR spectra (CsI pellets): Matson Instruments 2030 Galaxy FTIR spectrometer, UV/Vis spectra (methanol, N_2 atmosphere): Bruins Omega 10 spectrophotometer, NMR spectra: Bruker DRX 400.
A solution of $[FeCl_2(depe)_2]$ (0.4 g, 0.74 mmol) in MeOH (50 mL) was stirred at room temperature under N_2 over night. After the addition of $NaBPh_4$ (0.37 g, 1.1 mmol) in MeOH (10 mL), orange cubes of **1** precipitated slowly and were collected by filtration under N_2. Yield: 0.6 g (95%); ^{1}H NMR (400 MHz, $CDCl_3$, 233 K): $\delta = 1.19$ (m, CH_3), 1.88 (m, CH_2), 7.13 (m, Ph); ^{31}P NMR (200 MHz, solid state, 303 K): $\delta = 61.5$ (quin); ^{31}P NMR(400 MHz, $CDCl_3$, 233 K): $\delta = 65.7$ (s); IR (CsI): $\tilde{\nu}_{NN} = 2088\ cm^{-1}$; UV/Vis: $\lambda_{max}(\varepsilon) = 280$ (7575), 333 (sh; 2272), 382 (2020), 420 nm (sh; 1818 $L\,mol^{-1}\,cm^{-1}$); elemental analysis calcd for $C_{44}H_{68}BClN_2P_4Fe$ (850.99): C 62.1, H 8.1, N 3.3; found: C 62.0, H 8.2, N 2.0. Small amounts of oxygen caused an immediate color change of the orange solutions of **1** and **2** to red (**1**) or green (**2**). After the

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addition of $NaBPh_4$, correpondingly colored needles precipitated, which regained an orange color under an N_2 atmosphere.

[9] A solution of $[FeBr_2(depe)_2]$ (0.35 g, 0.56 mmol) in MeOH (40 mL) was stirred at room temperature under N_2 overnight. After the addition of $NaBPh_4$ (0.28 g, 0.84 mmol) in MeOH (10 mL), orange prisms of **2** precipitated slowly and were collected by filtration under nitrogen. Yield: 0.45g (90%); ^{1}H NMR (200 MHz, CD_3OD, 303 K): $\delta = 1.19$ (m, CH_3), 1.98 (m, CH_2), 7.15 (m, Ph); ^{31}P NMR (400 MHz, CD_3OD, 233 K): $\delta = 63.8$ (s); IR (CsI): $\tilde{\nu}_{NN} = 2091\ cm^{-1}$; UV/Vis: $\lambda_{max}(\varepsilon) = 284$ (8666), 328 (sh; 4000), 394 nm ($1818\ L\,mol^{-1}\,cm^{-1}$); elemental analysis calcd for $C_{44}H_{68}BBrN_2P_4Fe$ (895.45): C 59.0, H 7.7, N 3.1; found: C 56.3, H 7.4, N 1.6.

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[11] $\delta = 0.26\ mm\,s^{-1}$ and $\Delta E_Q = 1.42\ mm\,s^{-1}$ at 77 K; see ref. [5].

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[13] X-ray structure analysis of **1**: An orange cube was mounted on a glass fiber by standard inert-gas techniques and cooled immediately. Crystal data for **1**: triclinic, $P\bar{1}$ ($\equiv$ no. 2), $a = 13.425(3)$, $b = 17.399(5)$, $c = 19.937(5)$ Å, $\alpha = 102.02(2)$, $\beta = 91.16(1)$, $\gamma = 95.7(3)^\circ$, $V = 4528(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.248\ g\,cm^{-1}$, $\mu(Mo_{K\alpha}) = 0.566\ mm^{-1}$. The data were collected on a Siemens P4 diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, graphite monochromator, $T = 203$ K) in the range $4 < 2\theta < 50^\circ$; 16528 (15785 symmetry independent) reflections were measured. The phase problem was solved by direct methods (SIR92), from which the heavy atoms were located. The other non-hydrogen atoms were found in subsequent cycles of refinements (SHELXL93) and difference Fourier maps. The hydrogen atoms were taken into account at idealized sites and with isotropic thermal parameters in the final cycle of refinement; 494 parameters, semiempirical absorption correction (ψ scan) $R1 = 0.077$ (3108 reflections with $F_o > 4\sigma(F_o)$), $wR2 = 0.202$ (all data). The unit cell contains two symmetrically independent cations. One of these cations shows some disorder of the chlorine and dinitrogen ligands. This disorder over the two *trans* positions (N_2, Cl) was modeled by partial occupation of these positions with Cl^- and N_2 with a fixed N – N bond length of 1.10 Å. The occupation ratio Cl^-:N_2 of the two positions was refined to 56:44 and 44:56, respectively. Anisotropic thermal parameters were refined for the heavy atoms (Fe, P, Cl); C and N atoms were refined isotropically. In the discussion of the molecular geomety, we exclusively describe the cation which is not disordered. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-407743.

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[17] Preliminary crystal data of **2**: triclinic, P1 (no. 1), $a = 11.5727(3)$, $b = 13.3353(4)$, $c = 16.6220(3)$ Å, $\alpha = 108.23(1)$, $\beta = 101.235(2)$, $\gamma = 104.545(2)^\circ$, $V = 2251(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.321\ g\,cm^{-1}$, $\mu(Mo_{K\alpha}) = 1.40\ mm^{-1}$.

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A Kinetically Stabilized [1.1]Paracyclophane: Isolation and X-Ray Structural Analysis**

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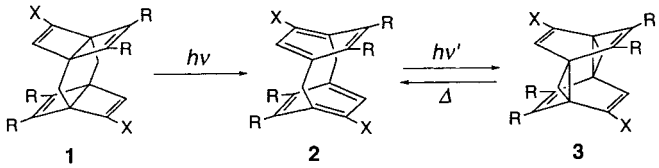
In 1993 we reported preparation of the first [1.1]paracyclophane, the bis(methoxycarbonyl) derivative **2b**.[1] The low thermal stability of **2b** and of the subsequently synthesized **2a**[2]—both persistent only below $-20\,^\circ C$ in dilute solution—virtually precluded exploration of their physical and chemical properties. The lability of [1.1]paracyclophanes seems to arise from susceptibility of the bridgehead carbon atoms toward addition of numerous reagents, upon which the steric strain inherent in the system is largely relieved. In other words, it seems plausible that the [1.1]paracyclophane skeleton might be kinetically stabilized by the introduction of substituents that sterically shield all four bridgehead sites. Although fulfillment of such a requirement appears formidable at first, examination of molecular models suggests that kinetic stabilization of the [1.1]paracyclophane system might be achieved through **2c**, for which the appropriate precursor **1** should also be accessible. Here we report the isolation and X-ray structural analysis of **2c** as well as its interconversion with the corresponding transannular addition product **3c**.



a: R = X = H **b**: R = H, X = CO_2Me **c**: R = CH_2SiMe_3, X = $CONMe_2$

The synthesis of precursor **1c** is outlined in Scheme 1. Although addition of **5**[3] to **6** was significantly slower than that of **5** to **4**,[2] *anti*-bis-adduct **7** was obtained after prolonged irradiation of **6** in a saturated solution of **5** in CH_2Cl_2. The conversion of **7** into **10** via **8**[4] and **9** proceeded uneventfully, and **10** was transformed into diamide **13** by addition of $LiNMe_2$ followed by hydrolysis. However, the carbon atoms adjacent to the amide groups in **13** are already so sterically hindered that initial attempts to prepare **11** (e.g. by reaction of **12**[5] with PhSeBr, and of **13** with KH/$PhSe_2$[6]) proved fruitless. Taking a hint from the reaction of (phenylselenyl)-amines with unsaturated carbonyl compounds,[7] we obtained **11** by the reaction of **10** with $PhSeNMe_2$.[8] Oxidation of **11** to the selenoxide and subsequent elimination of PhSeOH proceeded smoothly to afford **1c**.

Irradiation of **1c** in degassed *n*-decane with a low-pressure mercury lamp at $-20\,^\circ C$ led to formation of the corresponding

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