Iron Bispentazole $Fe(\eta^5\text{-}N_5)_2$, a Theoretically Predicted High-Energy Compound: Structure, Bonding Analysis, Metal – Ligand Bond Strength and a Comparison with the Isoelectronic Ferrocene**

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Dedicated to the Memory of Privatdozent Doctor J. J. Wolff

Abstract: Quantum-chemical calculations with gradient-corrected (B3LYP) density functional theory have been carried out for iron bispentazole and ferrocene. The calculations predict that $Fe(\eta^5\text{-} N_5)_2$ is a strongly bonded complex which has D_{5d} symmetry. The theoretically predicted total bond energy that yields Fe in the ^5D ground state and two pentazole ligands is $D_o = 109.0\ \mathrm{kcal\,mol^{-1}}$, which is only $29\ \mathrm{kcal\,mol^{-1}}$ less than the calculated bond energy of ferrocene ($D_o = 138.0\ \mathrm{kcal\,mol^{-1}}$; experimental: $158 \pm 2\ \mathrm{kcal\,mol^{-1}}$). The compound $Fe(\eta^5\text{-}N_5)_2$ is $260.5\ \mathrm{kcal\,mol^{-1}}$ higher in energy than the experimentally known isomer $Fe(N_2)_5$, but the bond energy of the latter ($D_o = 33.7\ \mathrm{kcal\,mol^{-1}}$) is much less. The energy decomposition analyses of $Fe(\eta^5\text{-}N_5)_2$ and ferrocene show that the two compounds have similar bonding situations. The metal – ligand bonds are roughly half ionic and half covalent. The covalent bonding comes mainly from (e_{1g}) $\eta^5\text{-}N_5^- \rightarrow Fe^{2+}$ π-donation. The previously suggested MO correlation diagram for ferrocene is nicely recovered by the Kohn – Sham orbitals. The calculated vibrational frequencies and IR intensities are reported.

Keywords: bonding analysis · density functional calculations · donor – acceptor systems · ferrocene · pentazole complexes

Introduction

Currently the chemistry of binary nitrogen compounds is a topic of intensive experimental investigations, which has been crowned by the successful synthesis of novel unusual molecules. Highlights of the synthetic efforts in recent years have been the first structurally characterised hexaazidoarsenate anion $[As(N_3)_6]^-$[1] and the spectroscopically characterised N_5^+ cation,[2] which is only the third all-nitrogen compound to have been synthesised. Another interesting molecule that has recently been observed experimentally is $Fe(N_2)_5$, which is isoelectronic with $Fe(CO)_5$. The binary iron – dinitrogen complex was synthesised by co-depositing Fe cations with N_2 and electrons to form a matrix.[3] The molecule $Fe(N_2)_5$, which has five end-on bonded N_2 ligands, was identified by comparing the recorded FTIR spectrum with the results of DFT calculations.

In this paper we report on a theoretical study of a molecule which is an isomer of $Fe(N_2)_5$ but in which the ten nitrogen atoms are bonded as two pentazole ligands in $Fe(\eta^5\text{-}N_5)_2$. The compound iron bispentazole, which is isoelectronic with ferrocene, is, according to our calculations, a promising target for synthetic efforts. Although $Fe(\eta^5\text{-}N_5)_2$ is much higher in energy than $Fe(N_2)_5$ it has significantly stronger metal – ligand interactions; this makes it a possible candidate as a high-energy compound. If iron bispentazole could be made, it would introduce a new all-nitrogen ligand that has not been observed so far in transition metal chemistry. The heavier cyclic analogue P_5 is known as a ligand in compounds such as $Fe(Cp^*)(\eta^5\text{-}P_5)$.[4] Organic pentazole derivatives RN_5 with aryl substituents R have been known since 1956, when Huisgen and Ugi reported the first synthesis of phenylpentazole.[5, 6]

The parent compound 1*H*-pentazole and its anion N_5^- have been calculated by quantum-chemical methods before.[7–10] Two theoretical studies have addressed the question of whether the pentazole anion might be trapped as a ligand in metal complexes. Glukhotsev et al. reported on $Li(\eta^5\text{-}N_5)$, which was found to be a minimum on the potential energy surface.[9] Nguyen et al. carried out extended Hückel theory (EHT)calculations of $TM(CO)_3(\eta^5\text{-}N_5)$ with TM = Fe^+, Mn, Cr^-, which suggested that the pentazole complexes would be formed if the fragments could be brought together.[10] We do not know of a quantum-chemical study at ab initio or DFT

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levels of transition metal (TM) complexes with pentazole ligands. Our paper is the first theoretical study of a TM pentazole complex by using accurate quantum-chemical methods.

We report on DFT calculations of the equilibrium geometry, vibrational spectrum and metal–ligand bond-dissociation energy of iron bispentazole Fe(η^5-N_5)$_2$. The nature of the metal–ligand interactions has been analysed with the help of the ETS (Extended Transition State) energy-partitioning scheme, which was developed by Ziegler and Rauk.[11] For comparison we also calculated the complexes Fe(η^5-Cp)$_2$, Fe(N_2)$_5$ and Fe(CO)$_5$.

Computational Methods

The geometries were first optimised at the gradient-corrected DFT level by using the three-parameter fit of the exchange-correlation potential suggested by Becke[12] in conjunction with the LYP[13] exchange potential (B3LYP).[14] A nonrelativistic small-core ECP with a (441/2111/41) valence basis set for Fe[15] and 6-31G(d) basis sets[16] for C, N, O and H were employed in the geometry optimisations. This is our standard basis set II.[17] The nature of the stationary points was examined by calculating the Hessian matrix at B3LYP/II. Improved energy calculations at the B3LYP/II optimised geometries were carried out by using the larger basis set III+, which has triple-zeta quality augmented by an f function at Fe[18] and diffuse functions at C, N and O.[19] The valence basis set of Fe is (3311/2111/311/1). The basis sets for the other atoms is 6-311+G(d). Energy values in the text are discussed at B3LYP/III+//B3LYP/II unless otherwise specified. The atomic partial charges were estimated with Weinhold's NBO method.[20] The calculations were carried out with the program package Gaussian 98.[21]

The geometries were also optimised with the program ADF[22] by using Becke's exchange functional[23] and Perdew's correlation functional[24] (BP86) in conjunction with uncontracted Slater-type orbitals (STOs) as basis functions.[25] Relativistic effects were considered by the zero-order regular approximation (ZORA).[26] The basis sets for the metal atoms have triple-ζ quality augmented by one set of 6p functions. Triple-ζ basis sets augmented by two sets of d-type polarisation functions were used for the main group elements. The (n – 1)s^2 and (n – 1)p^6 core electrons of the main group elements and the (1s2s2p)^{10} core electrons of the transition metals were treated by the frozen-core approximation.[27a] An auxiliary set of s, p, d, f and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[27b]

The iron–ligand bonding interactions in Fe(η^5-N_5)$_2$ and Fe(η^5-Cp)$_2$ were analysed with the energy decomposition scheme ETS developed by Ziegler and Rauk.[11] The interaction energy ΔE_{int} was calculated and decomposed for the bonding between Fe^{2+} in the electronic reference state of the complexes, in which the valence orbitals 3d$_{xz}$, 3d$_{yz}$ and 3d$_{z^2}$ are doubly occupied, and two N_5^- or Cp$^-$ ligands in the frozen geometry of the complex. The instantaneous interaction energy ΔE_{int} can be divided into three components:

$$\Delta E_{\mathrm{int}} = \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{orb}} \qquad (1)$$

$\Delta E_{\mathrm{elstat}}$ is the electrostatic interaction energy between the fragments, which are calculated with a frozen electron-density distribution in the geometry of the complex. It can be considered to be an estimate of the ionic contribution to the bonding interactions.[28] The second term in Equation (1) $\Delta E_{\mathrm{Pauli}}$ is the repulsive four-electron interactions between occupied orbitals. The last term ΔE_{orb} is the stabilising orbital interactions, which can be considered to be an estimate of the covalent contributions to the bonding. Thus, the ratio $\Delta E_{\mathrm{elstat}}/\Delta E_{\mathrm{orb}}$ indicates the ionic/covalent character of the bond. The latter term can be partitioned further into contributions by the orbitals that belong to different irreducible representations of the interacting system. This makes it possible to calculate, for example, the contributions of σ- and π-bonding to a covalent multiple bond.[28] Technical details about the ETS method can be found in the literature.[30]

The bond dissociation energy (BDE) ΔE_e is given by the sum of ΔE_{int} and the fragment preparation energy ΔE_{prep}:

$$\Delta E_e = \Delta E_{\mathrm{prep}} + \Delta E_{\mathrm{int}} \qquad (2)$$

ΔE_{prep} is the energy which is necessary to promote the fragments from their equilibrium geometry and electronic ground state to the geometry and electronic state which they have in the optimised structure.

Results and Discussion

Geometries, bond dissociation energies and vibrational spectrum of Fe(η^5-N_5)$_2$: Figure 1 shows the optimised geometries at B3LYP/II and BP86/TZP of the calculated molecules. Calculated energies are given in Table 1.

The calculations predict that Fe(η^5-N_5)$_2$ has an equilibrium geometry which has D_{5d} symmetry, that is, the pentazole ligands have a staggered conformation. The eclipsed (D_{5h}) conformation, which is a transition state (number of imaginary frequencies $i = 1$) is predicted at B3LYP/II to be 1.4 kcal mol^{-1} higher in energy than the D_{5d} form. The energy difference becomes much smaller when larger basis sets are employed. The D_{5d} form is only <0.1 kcal mol^{-1} more stable than the D_{5h} form at B3LYP/III+ and BP86/TZP. This means that there is practically no barrier for rotation of the pentazole ligand about the C_5 axis.

The Fe–N bond lengths of Fe(η^5-N_5)$_2$ (D_{5d}) are 2.054 Å at B3LYP/II and 2.019 Å at BP86/TZP. This is significantly longer than the Fe–N bond lengths of Fe(N_2)$_5$ (Figure 1). The shorter bond lengths of the latter complex does *not* mean that the bonding interactions are stronger than in the former molecule. The donor and acceptor orbitals of the N_5^- pentazole ligands are the nitrogen p(π) orbitals, which are aligned towards the iron atom. In N_2, the ligand donor orbital is a sp-hybrid orbital, which is more contracted and higher in energy than a pure p orbital, while the π* acceptor orbital is aligned perpendicular to the Fe-ligand axis. This means that the metal–ligand donor–acceptor interactions in Fe(η^5-N_5)$_2$ take place at longer distances than in Fe(N_2)$_5$, and yet they are stronger. A similar reasoning has been given for other metal–ligand bonds before.[31] The N–N bond lengths of the pentazole ligands in Fe(η^5-N_5)$_2$ (1.357 Å at B3LYP and 1.373 Å at BP86/TZP) are ~0.03 Å longer than in free pentazole anion (Figure 1). The N–N bond lengthening suggests that there are significant metal–ligand interactions in the complex.

Figure 1 also shows the optimised geometries of ferrocene and iron pentacarbonyl. Because experimental values for the geometries of the two molecules are known, it is possible to estimate the accuracy of the theoretical predictions. The calculated Fe–C bond lengths of Fe(Cp)$_2$ (2.074 Å at B3LYP/II, 2.062 Å at BP86/TZP) are in excellent agreement with the electron diffraction data in the gas phase (2.064 Å).[32] Note that the calculations predict an eclipsed conformation for ferrocene which has a D_{5h} and not D_{5d} equilibrium geometry. This is in agreement with experimental results[32] and with recent calculations,[33] which also showed that the Cp ligands in ferrocene have an eclipsed conformation. The calculated internal rotational barrier is between 0.5 and 0.9 kcal mol^{-1}

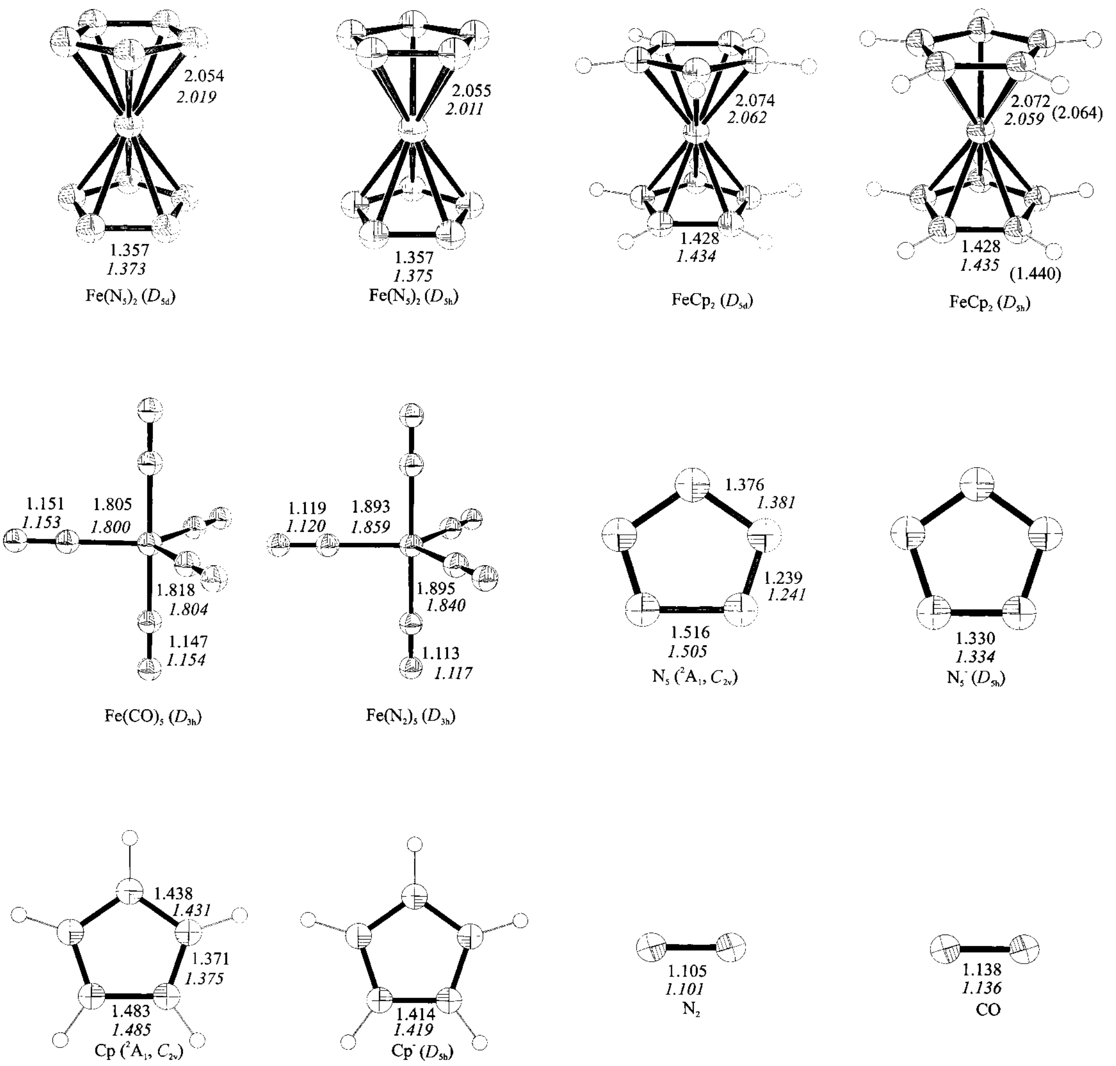

Figure 1. Calculated geometries of the complexes and ligands. Values calculated at B3LYP/II are in normal type, those at BP86/TZP are given in italics and experimental values are in parentheses. All bond lengths are in Å.

Table 1. Calculated energies of the compounds at different levels. Total energies E_{tot} [a.u.], relative energies [kcal mol^{-1}], zero-point vibrational energies (ZPE) [kcal mol^{-1}] and number of imaginary frequencies i.

Molecule	Symmetry	State	B3LYP/III+		B3LYP/II			
			E_{tot}	E_{rel}	E_{tot}	E_{rel}	ZPE	i
$Fe(N_5)_2$	D_{5h}	$^1A_1'$	– 670.83936	0.1	– 670.66430	0.2	27.9	1
$Fe(N_5)_2$	D_{5d}	$^1A_{1g}$	– 670.83944	0.0	– 670.66457	0.0	29.7	0
$Fe(Cp)_2$	D_{5h}	$^1A_1'$	– 510.62984	0.0	– 510.52091	0.0	106.3	0
$Fe(Cp)_2$	D_{5d}	$^1A_{1g}$	– 510.62892	0.6	– 510.51982	0.7	106.2	1
$Fe(N_2)_5$	D_{3h}	$^1A_1'$	– 671.24814		– 671.04939		25.5	0
$Fe(CO)_5$	D_{3h}	$^1A_1'$	– 690.36117		– 690.15656		26.7	0
N_5^-	D_{5h}	$^1A_1$	– 273.82582		– 273.72354		13.6	0
N_5	C_{2v}	$^2B_1$	– 273.63550		– 273.55603		9.9	0
N_2	$D_{\infty h}$	$^1\Sigma_g^+$	– 109.56055		– 109.52072		3.5	0
CO	$C_{\infty v}$	$^1\Sigma^+$	– 113.35025		– 113.30691		3.2	0
Fe	R^3	^5D	– 123.37881		– 123.38192		0.0	0
Fe^{2+}	R^3	^5D	– 122.49242		– 122.48463		0.0	0
Cp^-	D_{5h}	$^1A_1$	– 193.57243		– 193.49673		49.3	0
Cp	C_{2v}	$^2B_1$	– 193.50900		– 193.45833		49.1	0

when zero-point energy (ZPE) corrections are considered (Table 1). This is in excellent agreement with the experimental value of 0.9 ± 0.3 kcal mol^{-1}.[32] The theoretically predicted C–C bond lengths in $Fe(Cp)_2$ are also in very good agreement with experiment. The same holds true for the calculated and experimental geometry of $Fe(CO)_5$. The conclusion is that the optimised geometry of $Fe(\eta^5\text{-}N_5)_2$ shown in Figure 1 should be quite reliable.

Although the barriers for internal rotation of the cyclic ligands in ferrocene and $Fe(\eta^5\text{-}N_5)_2$ are very small, it is interesting to note that the latter complex has the pentazole ligands in a staggered conformation while the Cp ligands of the former complex are eclipsed. A theoretical analysis of ferrocene led to the conclusion that the eclipsed conformation is mainly due to the induction energy of the metal in the potential field of the rings.[34] A minor contribution, which favours the eclipsed form, comes from direct ring–ring electrostatic contributions in $FeCp_2$. We think that the repulsion of the nitrogen out-of-plane lone-pair electrons compensates for the above forces; this leads to a small preference for the D_{5d} geometry.

In order to estimate the strength of the iron–bispentazole interactions in $Fe(\eta^5\text{-}N_5)_2$, we calculated the dissociation energies of the homolytic and heterolytic bond cleavage; these are shown in Table 2.[35] Note that the calculated values of the exothermic reactions are negative, while the bond

Table 2. Calculated reaction energies [kcal mol^{-1}].

	Reaction	B3LYP/II	B3LYP/III+	Exp.
1	Fe (3d^{6}4s^2) ^{5}D + 2 N$_5$ → Fe(N$_5$)$_2$	−107.0 (−97.1)	−118.9 (−109.0)	
2	Fe (3d^{6}4s^2) ^{5}D + 2 Cp → FeCp$_2$	−139.4 (−131.3)	−146.1 (−138.0)	−158 ± 2[a]
3	Fe^{2+} (3d^6) ^{5}D + 2 N$_5^-$ → Fe(N$_5$)$_2$	−459.5 (−457.0)	−436.0 (−433.5)	
4	Fe^{2+} (3d^6) ^{5}D + 2 Cp$^-$ → FeCp$_2$	−653.9 (−646.2)	−622.4 (−614.7)	−635 ± 15[a]
5	Fe (3d^{6}4s^2) ^{5}D + 5 CO → Fe(CO)$_5$	−150.6 (−139.9)	−144.9 (−134.2)	−147.4[b]
6	Fe (3d^{6}4s^2) ^{5}D + 5 N$_2$ → Fe(N$_2$)$_5$	−40.1 (−32.1)	−41.7 (−33.7)	
7	Fe(N$_5$)$_2$ → Fe(N$_2$)$_5$	−241.3 (−245.5)	−256.3 (−260.5)	
8	Fe(N$_5$)$_2$ → Fe (3d^{6}4s^2) ^{5}D + 5 N$_2$	−201.2 (−213.4)	−214.6 (−226.8)	
9	Fe(N$_5$)$_2$ + 5 CO → Fe(CO)$_5$ + 5 N$_2$	−351.8 (−353.3)	−359.5 (−361.0)	

[a] Ref. [38]. [b] −D_e value, Ref. [41, 42].

dissociation energies D_e and D_o have positive values because the dissociation reactions are the reverse processes.

Reaction 1 gives D_e and ZPE-corrected D_o values for the homolytic bond cleavage of Fe(η^5-N$_5$)$_2$, which yields the neutral fragments Fe in its (3d^{6}4s^2) ^{5}D ground state and two N$_5$ ligands. The neutral pentazole radical is Jahn–Teller distorted. Geometry optimisations of the D_{5h} symmetric form of N$_5$ in the $^2E_1''$ ground state gave two energetically nearly degenerate forms which have C_{2v} symmetry. One belongs to the $^2A_1$ state and the other to the $^2B_2$ state. A similar situation is found for the neutral Cp ligand (see below). The energetically slightly lower-lying (< 0.1 kcal mol^{-1}) $^2A_1$ state is shown in Figure 1.

Calculations at B3LYP/III+ predict a total bonding energy D_e = 118.9 kcal mol^{-1} for Fe(η^5-N$_5$)$_2$; after ZPE corrections this gives D_o = 109.0 kcal mol^{-1} and leads to an average Fe-(η^5-N$_5$) bond energy of 54.5 kcal mol^{-1}. Thus, the pentazole ligands are bonded rather strongly to Fe. The bond energy is much higher than in Fe(N$_2$)$_5$. Table 2 shows that the total bond energy of the latter complex yielding Fe and 5 N$_2$ (Reaction 6) is only D_o = 33.7 kcal mol^{-1}; this gives an average BDE of only 6.7 kcal mol^{-1} for the Fe–N$_2$ bonds,[36] and means that Fe(η^5-N$_5$)$_2$, if it can be prepared, could be more stable towards dissociation than its isomer Fe(N$_2$)$_5$.

In order to assess the accuracy of the calculated BDE of Fe(η^5-N$_5$)$_2$, we also calculated the bond energy of ferrocene for which experimental values are available. Table 2 gives the calculated BDE for homolytic dissociation of FeCp$_2$ into Fe and two Cp ligands (Reaction 2). This reaction has been the subject of other theoretical studies in recent years. Roos and co-workers reported a BDE of D_e = 156 kcal mol^{-1} using the CASPT2 method for the calculations.[37] A DFT study by Mayor-Lopez and Weber[33] led to a value of 158 kcal mol^{-1} after corrections for ZPE contributions were made. The experimental value for the BDE of homolytic bond cleavage of ferrocene is 158 ± 2 kcal mol^{-1}.[38] Our calculated value is D_o = 138.0 kcal mol^{-1}, which is ~20 kcal mol^{-1} too low. This means that our predicted value for the BDE of Fe(η^5-N$_5$)$_2$ could be too low by the same amount, because the bonding situation in the two complexes is similar (see below).

Table 2 also gives the calculated energies for the heterolytic bond cleavage of Fe(η^5-N$_5$)$_2$ and ferrocene yielding Fe^{2+} and 2 L$^-$ where L is the pentazole anion or Cp$^-$ (Reactions 3 and 4). An experimental value for the latter compound is available.[38] The ligands are closed-shell 6π-aromatic species and easy to calculate. For the calculation of Fe^{2+} which has a ^{5}D ground state[39] we took the lowest lying (4s^{2}3d^4) state as reference for the calculations. The heterolytic bond dissociation of ferrocene has recently been studied by other groups. Roos and co-workers reported a theoretical value D_e = 628 kcal mol^{-1}, which was obtained from CASPT2 calculations.[37] Klopper and Lüthi employed coupled-cluster as well as multireference perturbation theory and came to a calculated value of 655 ± 15 kcal mol^{-1},[40] which is ~20 kcal mol^{-1} higher than the experimental value of 635 ± 15 kcal mol^{-1}.[38] A recent DFT study came to an even higher value for the heterolytic BDE of ferrocene of 663 kcal mol^{-1}.[33] Table 2 shows that our calculations give a BDE of D_o = 614.7 kcal mol^{-1}, which is ~20 kcal mol^{-1} too low. Thus, our theoretical number, which has the same absolute error as the ab initio calculation by Klopper and Lüthi is not very different from the experimental value. It means that the theoretically predicted BDE for the heterolytic bond cleavage of Fe(η^5-N$_5$)$_2$ D_o = 433.5 kcal mol^{-1} should be quite reliable. By comparison with the calculated BDE of ferrocene it can be expected that it is ~20 kcal mol^{-1} too low.

Table 2 also gives the calculated BDE of Fe(CO)$_5$ D_e = 144.9 kcal mol^{-1}, which can be compared with the experimental value of D_e = 147.4 kcal mol^{-1}.[41, 42] This means that the theoretically predicted BDE of Fe(N$_2$)$_5$ D_o = 33.7 kcal mol^{-1} is probably slightly too low, but not very much.[36] The complex Fe(η^5-N$_5$)$_2$ is much higher in energy than its isomer Fe(N$_2$)$_5$. Table 2 shows that the latter complex is 260.5 kcal mol^{-1} more stable than Fe(η^5-N$_5$)$_2$ (Reaction 7). The lower energy of the dinitrogen complex comes from the N–N energy of the ligands, not from metal–ligand interactions, which are stronger in Fe(η^5-N$_5$)$_2$. Iron bispentazole is a truly energy-rich compound. The calculated reaction energy for the decay of Fe(η^5-N$_5$)$_2$ into the most stable products, iron atom and dinitrogen molecules (Reaction 8), is predicted to be −226.8 kcal mol^{-1}. The reaction of iron bispentazole with CO to yield iron pentacarbonyl and N$_2$ (Reaction 9) even has a reaction energy of −361.0 kcal mol^{-1} (Table 2). Thus, the calculated energies indicate that Fe(η^5-N$_5$)$_2$ has a rather high metal–ligand bond energy, which might be sufficiently large to allow the isolation of the molecule in a condensed phase. At the same time the compound is a high energy species that reacts in a strongly exothermic manner with ligands such as CO.

One referee pointed out that the stability of iron bispentazole will also depend on kinetic factors, such as the barrier for intramolecular rearrangement and the propensity to react with the environment. It is difficult to address this question in such an exact way as the geometry or bond energy of the molecule. Barriers for rearrangement can, in principle, be calculated by optimising transition state structures, but there are numerous reaction pathways which lead to a fragmentation of Fe(η^5-N$_5$)$_2$. However, the calculated geometry and the vibrational frequencies of the N–N stretching modes of the pentazole ligand led us suspect that the N_5 moiety of the iron complex is more resistant to fragmentation than the pentazole group in phenylpentazole compounds. The latter species has experimentally determined alternating N–N bond lengths between 1.30 and 1.35 Å.[49] Ab initio calculations of the parent system *cyc*-N_5H gave similar bond lengths.[7a] The lowest-lying transition state for the decomposition of *cyc*-N_5H into $N_2 + N_3H$ was calculated to be 19.8 kcal mol^{-1}. The equal N–N bond lengths of $Fe(\eta^5\text{-}N_5)_2$, which are predicted to be 1.36-1.37 Å, and the rather large wavenumbers of the N–N stretching modes suggest that the 6π-aromatic pentazole ligand of the iron complex is more stable towards fragmentation than the N_5 moiety in phenylpentazole. Concerning possible interactions with the environment, we give the energy levels of the frontier orbitals of $Fe(\eta^5\text{-}N_5)_2$ (HOMO: -8.09 eV; LUMO: -5.90 eV) and $FeCp_2$ (HOMO: -4.13; LUMO: -1.33 eV). The energetically much-lower-lying orbitals of iron pentazole indicate that the molecule is more prone to nucleophilic attack than ferrocene. This information might be useful for choosing proper reaction conditions for the experiments.

In order to assist the identification of $Fe(\eta^5\text{-}N_5)_2$, we present in Table 3 the calculated vibrational frequencies and the IR intensities. The most helpful IR-active mode should be the pentazole ligand E_{1u} in-plane stretching mode at 1139 cm^{-1}.

Table 3. Harmonic vibrational spectra [cm^{-1}], IR intensities [KM mol^{-1}] and Raman scattering activities [A^4 a.u.$^{-1}$] for D_{5d}-symmetric $Fe(N_5)_2$. B3LYP/II level of theory, unscaled. The intensities of degenerate modes have not been doubled.

Mode	$Fe(N_5)_2$, D_{5d}	IR	Raman	Comment
A_{1g}	244.8	0	2.4	N_5-Fe-N_5 symmetric stretch
A_{1g}	1100.5	0	68.4	N_5 symmetric ring breathing
E_{1g}	810.8	0	0.3	N_5 in-plane stretch
E_{1g}	1139.2	0	6.0	N_5 symmetric in-plane stretch
E_{2g}	323.2	0	4.7	N_5 out-of-plane topple
E_{2g}	703.0	0	0.04	N_5 out-of-plane deformation
E_{2g}	1066.9	0	6.7	N_5 symmetric in-plane stretch
A_{1u}	20.5	0	0	Ring rotation around main axis
A_{2u}	335.4	12.3	0	N_5-Fe-N_5 asymmetric stretch
A_{2u}	1106.8	1.4	0	N_5 asymmetric ring breathing
E_{1u}	156.8	0.02	0	N_5-Fe-N_5 bending
E_{1u}	449.0	9.7	0	Fe out-of-C_5 axis
E_{1u}	1138.6	6.0	0	N_5 in-plane stretch
E_{2u}	665.1	0	0	N_5 out-of-plane
E_{2u}	846.6	0	0	N_5 ring stretch
E_{2u}	1077.7	0	0	N_5 in-plane stretch

Bonding analysis: In order to get an insight into the metal–ligand interactions and to understand the bonding situation in $Fe(\eta^5\text{-}N_5)_2$, we carried out an energy decomposition analysis of the compound by the ETS method.[11] Before presenting the results, we want to point out the meaning and the goal of such a study. Inspection of textbooks of inorganic and organometallic chemistry shows that the bonding situation in transition metal compounds is usually discussed in terms of qualitative MO diagrams and heuristic models and assumptions which have proven to be helpful as an ordering scheme for the experimental observations. The missing link is the connection to the actual electronic structure of the molecule, which is at present an intensively investigated field in theoretical inorganic chemistry.[43] It is our goal to build a bridge between the quantitative electron-density distribution and the associated energy and qualitative chemical models, which are then not based on assumptions but on reliable data. This can be done in terms of electronic-charge distribution or in terms of energy decomposition. We begin with an analysis of the energy contributions to the bonding interactions.

Figure 2 shows an orbital-correlation diagram in D_{5d} symmetry for the interactions between a d^6 TM atom, with the reference electron configuration $(a_{1g})^2(e_{2g})^4(e_{1g})^0$, and a five-membered cyclic aromatic ligand. This is the standard MO correlation diagram for ferrocene, which is discussed in many textbooks.[44] It has been found to be reasonable to discuss the bonding situation of $FeCp_2$ in terms of interactions between closed-shell species Fe^{2+} with the above electron configuration and $2\,Cp^-$.[45] The same MO diagram will be applied for $Fe(\eta^5\text{-}N_5)_2$.

We do not want to discuss the qualitative features of the MO diagram shown in Figure 2 as this is done in many textbooks.[44] There is general agreement that the most important orbital interactions in ferrocene arise from the (e_{1g}) $Cp^- \rightarrow Fe^{2+}$ π-donation. The following questions shall be addressed in our analysis:

1) What is the ratio of covalent bonding to electrostatic bonding in $Fe(\eta^5\text{-}N_5)_2$ and ferrocene?
2) How strong are the individual orbital contributions to the total covalent bonding in both compounds?
3) What is the difference between the metal–ligand interactions in ferrocene and in $Fe(\eta^5\text{-}N_5)_2$?

Table 4 shows the results of the ETS analysis of both complexes. For didactic purposes we begin with ferrocene. The calculations give a strong interaction energy between Fe^{2+} and $2\,Cp^-$ in the frozen geometry of the complex of $\Delta E_{int} = -893.3$ kcal mol^{-1}. The repulsive contribution by the interactions between the occupied orbitals ΔE_{Pauli} is significantly smaller (272.2 kcal mol^{-1}) than the attractive terms. The electrostatic attraction (-598.0 kcal mol^{-1}) and orbital interactions (-567.5 kcal mol^{-1}) are about the same size. This means that the Fe^{2+}–Cp^- bonds are about half covalent and half electrostatic. The calculations also show that the e_{1g} orbitals give the largest contribution to the attractive orbital-interaction term ΔE_{orb}. The stabilisation by the (e_{1g}) $Cp^- \rightarrow Fe^{2+}$ π-donation is 64.7 % of the total orbital stabilisation term. The second largest contribution comes from the (e_{1u}) $Cp^- \rightarrow Fe^{2+}$ π-donation which comprises 10.8 % of the covalent bonding. Note that the latter term comes from the donation of the ligands into the iron p(π) orbitals, while the former comes from the donation into the d(π) orbitals. Also, the a_{2u} donation from the ligands into the p(π) orbital of Fe is rather weak (28.2 kcal mol^{-1}). Thus, the metal d orbitals are much more important as acceptor orbitals than the p orbitals, but the latter are not negligible. A similar conclusion was drawn from a recent bonding analysis of TM hexacarbonyls.[28a] The results are important because of the controversy about the importance of the TM valence p orbitals.[46, 47]

The ETS results suggest that the bonding situation in $Fe(\eta^5\text{-}N_5)_2$ is very similar to that in ferrocene. Table 4 shows

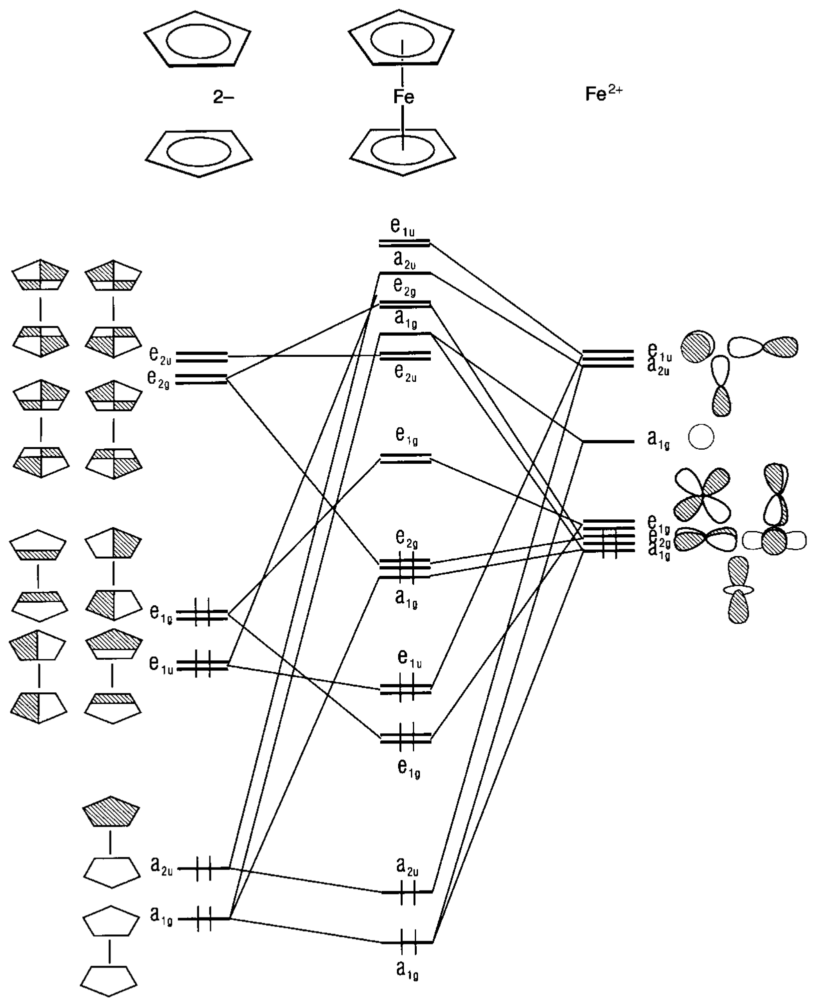

Figure 2. MO correlation diagram for the interactions between Fe^{2+} and a five-membered cyclic ligand X_5^- (X = CH, N).

Table 4. ETS analysis of $Fe(Cp)_2$ and $Fe(N_5)_2$ at BP86/TZP.[a]

Term	$Fe(C_5H_5)_2$	$Fe(N_5)_2$
ΔE_{int}[b]	− 893.3	− 706.7
ΔE_{Pauli}	272.2	244.0
ΔE_{elstat}	− 598.0 (51.3 %)[c]	− 492.6 (51.8 %)[c]
ΔE_{orb}	− 567.5 (48.7 %)[c]	− 458.1 (48.2 %)[c]
A_{1g}	− 48.5 (8.5 %)[d]	− 40.6 (8.1 %)[d]
A_{2g}	0.0	0.0
E_{1g}	− 367.2 (64.7 %)[d]	− 285.4 (65.5 %)[d]
E_{2g}	− 46.1 (8.1 %)[d]	− 44.7 (8.0 %)[d]
A_{1u}	0.0	0.0
A_{2u}	− 28.2 (5.0 %)[d]	− 22.3 (4.8 %)[d]
E_{1u}	− 61.1 (10.8 %)[d]	− 44.5 (10.6 %)[d]
E_{2u}	− 16.4 (2.9 %)[d]	− 20.6 (2.9 %)[d]

[a] All values are in kcal mol^{-1}. [b] Fe^{2+} (t_{2g}^6) + 2 L^-. [c] Percentage of attractive interactions ΔE_{elstat} + ΔE_{orb}. [d] Percentage of orbital interactions ΔE_{orb}.

that the intrinsic interaction energy of iron bispentazole (− 706.7 kcal mol^{-1}) is, as expected, less than in ferrocene. The contributions by the three terms ΔE_{Pauli}, ΔE_{orb} and ΔE_{orb} become smaller by about the same extent. Thus, the (Fe^{2+})−(η^5-N_5^-) bond has about the same percentage covalent bonding (48.2 %) as the (Fe^{2+})−(Cp^-) bond. The strongest contribution to the covalent bonding in $Fe(\eta^5\text{-}N_5)_2$ comes from the (e_{1g}) η^5-N_5^- → Fe^{2+} π-donation (62.3 %).

An explanation as to why the (e_{1g}) η^5-N_5^- → Fe^{2+} π-donation is the strongest contributor to the stabilising orbital interactions in $Fe(\eta^5\text{-}N_5)_2$ and ferrocene is as follows. The a_{1g} ΔE_{orb} term describes the interactions of four electrons that are stabilised only by the mixing with the empty 4s orbital of iron, which is not as important an acceptor orbital as the empty 3d orbitals (Figure 2). The a_{2u} and e_{1u} ligand → Fe^{2+} donations involve the higher-lying 4p orbitals of iron. The (e_{2g}) Fe^{2+} → ligand back-donation is not very strong because the iron carries a large positive charge of +2. This leaves the (e_{1g}) η^5-N_5^- → Fe^{2+} π-donation as the only term which strongly contributes to ΔE_{orb}. We want to point out that the stabilisation that is calculated for the ΔE_{orb} term does not only come from the mixing of the orbitals of the interacting fragments. Part of the orbital relaxation is caused by the electrostatic effect of the fragments, mainly through the stabilisation of the occupied orbitals of the ligand by the positive charge of the metal ion. The stabilisation by the charge of Fe^{2+} can be estimated as ~20 kcal mol^{-1}.[48]

The reader may wonder why we did not discuss the atomic partial charges of ferrocene and $Fe(\eta^5\text{-}N_5)_2$ until now. The calculated NBO charges of the iron atom are +0.204 in ferrocene and +0.650 in $Fe(\eta^5\text{-}N_5)_2$. The more positive charge of Fe in the latter compound could be expected because of the higher electronegativity of nitrogen compared with carbon. We want to emphasise that atomic partial charges can be misleading as an indicator of the nature of the chemical bond. The more positive charge of iron and the more negative charge of the ligand could lead to the erroneous conclusion that the Fe−pentazole bond is more ionic than the Fe−Cp bond. The ETS results show that this is not the case. The reason is that the charge distribution in a molecule also strongly influences the energy levels of the interacting orbitals and, thus, it also determines the covalent bonding. We recently showed in an analysis of the metal−CO bonding in $TM(CO)_6^q$ (TM^q = Hf^{2-}, Ta^-, W, Re^+, Os^{2+}, Ir^{3+}) that the most highly charged hexacarbonyls $Hf(CO)_6^{2-}$ and $Ir(CO)_6^{3+}$ have the most covalent TM−CO bonds while the neutral complex $W(CO)_6$ has the least covalent bond.[28a] This is because Hf^{2-}

has very high lying occupied orbitals and Ir^{3+} very low lying vacant orbitals; this yields very strong donor–acceptor orbital interactions. Another very important aspect is that atomic partial charges give no information about the topography of the charge distribution. The three-dimensional electronic-charge distribution can be very anisotropic, and there may be local negative-charge concentrations at atoms which overall carry a positive charge. The latter has been found to be crucial for an understanding of TM–ligand bonds that have dominantly σ-bonded ligands.[28b]

We analysed the electronic-charge distribution of $Fe(\eta^5\text{-}N_5)_2$ and ferrocene in order to see if the qualitative orbital diagram shown in Figure 2 can be reproduced by the shape of the Kohn–Sham (KS) molecular orbitals. It has recently been suggested that KS orbitals may be used for the analysis of chemical bonding in the same way as Hartree–Fock (HF) orbitals.[30] It is important to know if the actual shape of the KS orbitals correlates with qualitative MO schemes which were originally suggested for HF and EHT orbitals.[44b]

Figure 3 shows the contour-line diagrams of the KS orbitals of $Fe(\eta^5\text{-}N_5)_2$ and ferrocene, which are the results of the DFT calculations. The LUMO and HOMO of both compounds are degenerate e_{1g} and e_{2g} MOs, which closely resemble each other. They also match the shape of the LUMO and HOMO; this can be expected from the qualitative MO diagram (Figure 2). The same holds true for the a_{1g} HOMO-1 orbitals of the two molecules, which have a strong contribution from the d_z2 AO of iron (Figure 3). The next-lower-lying bonding orbital according to the MO diagram should be the e_{1u} orbital. Figure 3 shows that the HOMO-2 of ferrocene and the HOMO-6 of iron bispentazole nicely correlate with the expected shape of the orbital. Note that the coefficient of the p(π) acceptor orbital of Fe is very small; this is in agreement with the calculated low stabilisation energy. The orbitals from HOMO-2 up to HOMO-5 of $Fe(\eta^5\text{-}N_5)_2$ are nitrogen lone-pair orbitals.

The HOMO-3 of ferrocene and HOMO-7 of $Fe(\eta^5\text{-}N_5)_2$ are the degenerate e_{1g} orbitals, which are the strongest contributors to the orbital interaction term. Figure 3 shows that the orbitals have large coefficients at iron ($3d_{xz}$ and $3d_{yz}$) and the ligand atoms, which are connected in a bonding fashion. This correlates with the calculated high stabilisation energy of the e_{1g} ΔE_{orb} term. The remaining orbitals are the a_{2u} MOs, which were found as the HOMO-4 of ferrocene and HOMO-10 of $Fe(\eta^5\text{-}N_5)_2$, and the a_{1g} MOs, which are the HOMO-11 of ferrocene and HOMO-9 of $Fe(\eta^5\text{-}N_5)_2$. The a_{1g} and a_{2u} MOs of iron bispentazole are in reverse order compared with ferrocene. Figure 3 shows that the coefficient of the p(σ) AO of Fe in the a_{2u} orbitals is very small, while the extension of the iron d_{z^2} AO in the a_{1g} orbital is somewhat larger. The other occupied orbitals, which are not shown, are mainly nitrogen lone-pair MOs in case of $Fe(\eta^5\text{-}N_5)_2$ and ligand orbitals in case of ferrocene. The conclusion is that the shape of the actual KS orbitals nicely correlates with the qualitative MO diagram, which is established in inorganic chemistry. It shows that it is possible to use accurate quantum-chemical calculations as the basis for qualitative chemical models of chemical bonding. It is exciting to see that qualitative reasoning may thus now be supplemented by quantitative arguments without that the simplicity of the model is lost.

Conclusion

The results of this work can be summarised as follows.

Iron bispentazole is a strongly bonded molecule with staggered pentazole ligands. The theoretically predicted total bond energy is $D_o = 109.0\,\text{kcal mol}^{-1}$, which is only $\sim 30\,\text{kcal mol}^{-1}$ less than the BDE of ferrocene. Although $Fe(\eta^5\text{-}N_5)_2$ is $260.5\,\text{kcal mol}^{-1}$ higher in energy than the isomer $Fe(N_2)_5$ it has significantly stronger metal–ligand bonds.

The energy decomposition analyses of $Fe(\eta^5\text{-}N_5)_2$ and ferrocene show that the bonding situation in the two compounds is very similar. The metal–ligand bonds are approximately half ionic and half covalent. The covalent bonding comes mainly from (e_{1g}) $\eta^5\text{-}N_5^- \rightarrow Fe^{2+}$ π-donation. The qualitative MO correlation diagram, which was introduced for analysing the chemical bonds in ferrocene, is mirrored by the calculated KS orbitals.

From the calculated results, it can be concluded that iron bispentazole is a promising target for synthesis. We think that the chances for a successful synthesis are not bad; although the search for a suitable iron compound that properly reacts with a pentazole compound and the design of the experimental setup will be a formidable challenge for experimentalists. The remarkable success in synthesising compounds in recent years,[1–3] which have previously been elusive for experimentalists allow us to feel optimistic that $Fe(\eta^5\text{-}N_5)_2$ might soon become an observable molecule.

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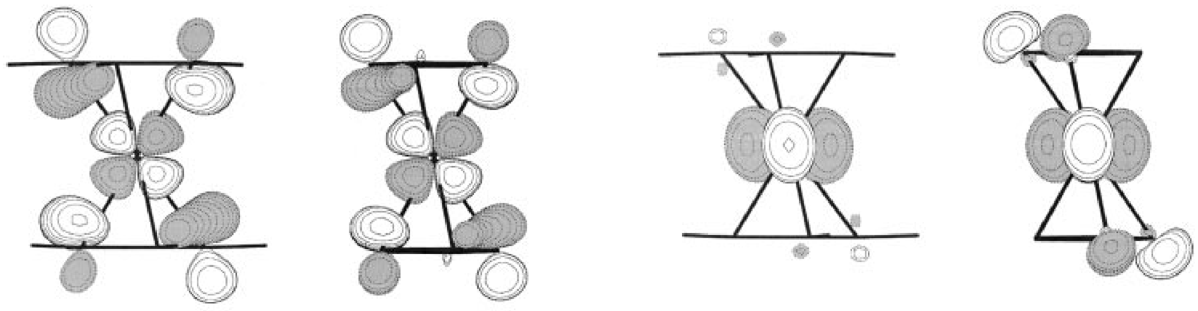
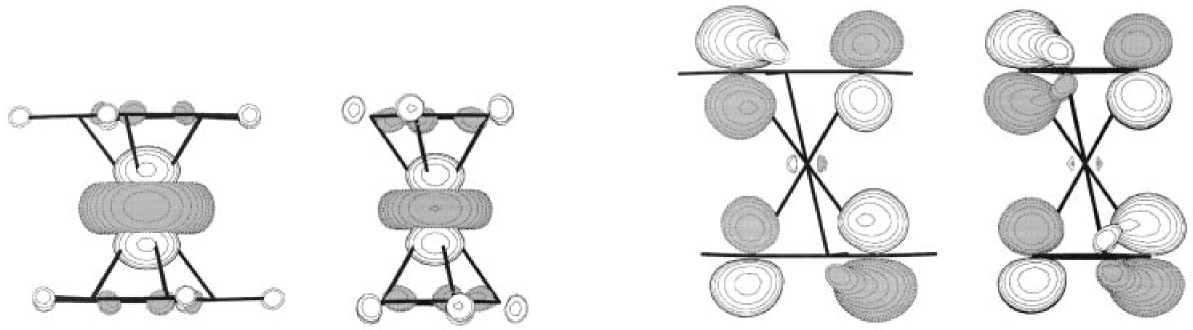
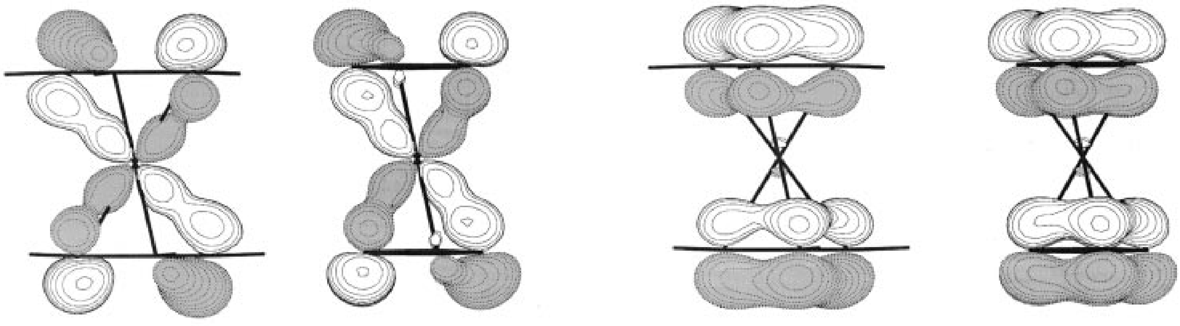


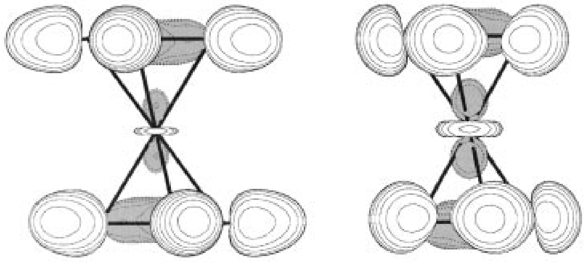
Fe(Cp)$_2$ LUMO e1g Fe(N$_5$)$_2$ LUMO e1g Fe(Cp)$_2$ HOMO e2g Fe(N$_5$)$_2$ HOMO e2g



Fe(Cp)$_2$ HOMO-1 a1g Fe(N$_5$)$_2$ HOMO-1 a1g Fe(Cp)$_2$ HOMO-2 e1u Fe(N$_5$)$_2$ HOMO-6 e1u



Fe(Cp)$_2$ HOMO-3 e1g Fe(N$_5$)$_2$ HOMO-7 e1g Fe(Cp)$_2$ HOMO-4 a2u Fe(N$_5$)$_2$ HOMO-10 a2u



Fe(Cp)$_2$ HOMO-11 a1g Fe(N$_5$)$_2$ HOMO-9 a1g

Figure 3. Plot of the Kohn–Sham orbitals of ferrocene and iron bispentazole at B3LYP/II, which correspond to the MO diagram shown in Figure 2.

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[36] The total bonding energy of Fe(N$_2$)$_5$, which is reported in ref. [3b] is much higher ($D_e = 101.5$ kcal mol^{-1}) than in our work. However, the value in the latter work, which focussed on the vibrational frequencies of Fe(N$_2$)$_n$ isomers, was obtained with a DFT functional that leads to strong overbinding. H. A. Duarte, D. R. Salahub, personal communication to G.F.

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[45] a) One referee objected to the discussion of the metal–ligand bonding in terms of interactions between Fe^{2+} and 2L$^-$, because the dissociation products are a neutral Fe atom and neutral ligands. We want to point out that the bonding situation in the complexes more closely resembles interactions between the negatively charged Cp$^-$ or cyc-N$_5$$^-$, which have D_{5h} symmetry, and Fe^{2+} than bonding between neutral ligands, which are Jahn–Teller distorted species with C_{2v} symmetry, and Fe. A discussion of the metal–ligand bonding in ferrocene and iron bispentazole between open-shell ligands in the doublet ground state and Fe in a triplet state (which is not the ground state) would be cumbersome and not appropriate to the actual electronic structure in the complex. It is sometimes the case that the fragments in a molecule are electronically excited with respect to the ground state of the free species. b) We prefer to present the MO diagram of ferrocene like most textbooks[44] with D_{5d} symmetry, although the molecule has D_{5h} symmetry, because it facilitates the comparison with iron bispentazole.

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[48] The ETS analysis of Os(CO)$_6$$^{2+}$ showed that the t$_{1g}$ and t$_{2u}$ ligand orbitals are stabilised by Os^{2+} with 19.4 and 23.9 kcal mol^{-1}, respectively. There are no AOs of Os that have t$_{1g}$ or t$_{2u}$ symmetry.[28a]

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