# On the Relevance of Mono- and Dinuclear Iron Carbonyl Complexes to the Fixation and Stepwise Hydrogenation of $N_2$[‡]

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*Dedicated to Professor Dieter Sellmann on the occasion of his 60th birthday*

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Density functional theory and high-level ab initio calculations are used to evaluate the influence of mono- and dinuclear iron carbonyl complexes to the fixation and stepwise hydrogenation of dinitrogen via diazene and hydrazine to ammonia. In comparison to the reaction of isolated $N_2$, only the first step in this reaction sequence (i.e. the reduction of $N_2$ to $N_2H_2$) experiences a significant change in its thermochemistry when coordinated to mono- or dinuclear iron tetracarbonyl fragments. The reaction enthalpy $\Delta H_R^0$ ($T$ = 0 K) for the endothermic hydrogenation of $(CO)_4Fe–N_2$ to give $(CO)_4Fe–N_2H_2$ is lower than for the corresponding metal-free process by 16.1 kcal mol$^{-1}$. The analogous step involving the dinuclear species $(CO)_4Fe–N_2–Fe(CO_4)$ and $(CO)_4Fe–N_2H_2–Fe(CO)_4$ is even less endothermic than the reduction involving only one iron tetracarbonyl complex by 13.1 kcal mol$^{-1}$. In comparison to that, the second and third step of this reduction sequence, namely the conversion of coordinated diazene to $(CO)_4Fe–N_2H_4$ and the subsequent reduction of coordinated hydrazine to $(CO)_4Fe–NH_3$ show only relatively small thermodynamic changes compared to the analogous reactions of isolated $N_2H_2$ and $N_2H_4$. The reduction of $(CO)_4Fe–N_2H_2$ to $(CO)_4Fe–N_2H_4$ is almost as exothermic as the analogue reaction involving isolated $N_2H_2$, whereas the hydrogenation of $(CO)_4Fe–N_2H_4$ to $(CO)_4Fe–NH_3$ is less exothermic by 4.0 kcal mol$^{-1}$. Finally, the reduction of $(CO)_4Fe–N_2H_2–Fe(CO)_4$ and $(CO)_4Fe–N_2H_4–Fe(CO)_4$ are both predicted to be less exothermic than their mononuclear analogues by 4.0 and 1.1 kcal mol$^{-1}$, respectively. Moreover, we find that only $N_2$ and $N_2H_2$, which already show a noticeable π-acceptor behavior in their complexes with $Fe(CO)_4$, experience important structural changes in their corresponding dinuclear complexes, i.e. a shortening of the Fe–N bonds and a lengthening of the N–N bonds on going from $(CO)_4Fe–L$ to $(CO)_4Fe–L–Fe(CO)_4$ (L = $N_2$, $N_2H_2$). This behavior is in line with a slightly increased π-acceptor ability of these ligands in their respective dinuclear complexes. Such structural changes are absent for $N_2H_4$, which only exhibits a comparatively weak π-acceptor character in $(CO)_4Fe–N_2H_4$.

## Introduction

The stepwise hydrogenation of dinitrogen to ammonia is one of the most important processes in biochemical research[1] and of utmost interest to chemical industry.[2] Besides the well-understood heterogeneously catalyzed reduction following the Haber−Bosch process,[3] deeper insight into the reduction of dinitrogen is necessary, particularly when dealing with biologically relevant systems. An example of this is the enzymatic fixation of $N_2$ catalyzed by nitrogenases.[4] Although the molecular structure of the Fe−Mo cofactor of a nitrogenase enzyme has been characterized by X-ray structure analysis,[5] details of the catalytically important features involved in the $N_2$ reduction have still not, however, been unequivocally answered.[6] To this end, the binding site, the binding mode of $N_2$ and the intermediates involved in the catalytic processes are still the source of much speculation.[4,6]

It is widely accepted that the initial binding of dinitrogen occurs at the iron rather than the molybdenum centers.[4] Theoretical studies based on different model systems of the Fe−Mo cofactor at various levels of theory are available.[7] However, due to the complexity of the overall reduction process and the structure of the Fe−Mo cofactor, a suitable model system for the Fe−Mo nitrogenases that reasonably mimics its catalytic activity may be too large for a quantum chemical treatment at a reasonable level of theory.[7] In addition to that, the nature of the actual intermediates of the enzymatic $N_2$ fixation process is still unknown.[8] Although there are numerous results indicating that biological $N_2$ fixation involves diazene and hydrazine species,[4] even the structure of the small four-atom diazene in solution was controversial until recently when Sellmann and Hennige isolated *trans*-$N_2H_2$ by complexation out of solution.[9] Beside the clarification of the nature of the intermediates involved in the stepwise hydrogenation of $N_2$ by nitrogenases, another pivotal question regarding the thermochemistry of these reduction steps is of utmost interest: Sellmann and

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co-workers suggested that all of the three reduction steps involved in the hydrogenation sequence should benefit energetically from the coordination of the nitrogen-containing ligands to iron(II) sulfur complexes.[6b]

Due to our interest in the structure and reactivity of iron carbonyl complexes,[10] the present study focuses on the influence and relevance of mono- and dinuclear iron carbonyl complexes of the general type $[\{Fe(CO)_4\}_nL]$ ($n$ = 1 for L = $NH_3$ and $n$ = 1, 2 for L = $N_2$, $N_2H_2$, $N_2H_4$) to the fixation and stepwise hydrogenation of $N_2$. We want to emphasize that this approach is not primarily intended to serve as a model study of the Fe−Mo cofactor, but to gain a deeper insight into the reduction steps of $N_2$ that are most affected by coordination to iron carbonyl fragments.[6] Particular interest is thus drawn to thermodynamic changes between the "metalated" reaction in which the nitrogen-containing ligands are either coordinated by one or two iron tetracarbonyl fragments and the isolated, metal-free hydrogenation of $N_2$. Moreover, we address the bonding situation of the Fe−L (L = $N_2$, $N_2H_2$, $N_2H_4$ and $NH_3$) bond in terms of σ-donor/π-acceptor abilities and the preferred coordination site of the ligands.

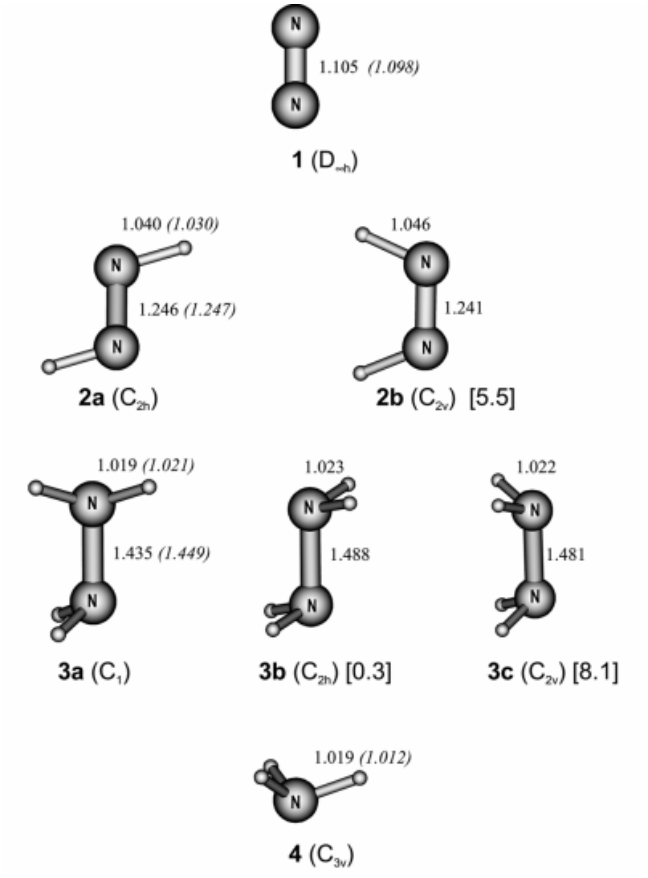


Figure 1. Optimized geometries of $N_2$ (**1**), $N_2H_2$ (**2**), $N_2H_4$ (**3**) and $NH_3$ (**4**); experimental values are given in italics; all bond lengths are in Å; the symmetry used for the geometry optimization is given in parentheses, while relative energies (kcal mol$^{-1}$) with respect to the most stable isomers are given in square brackets; angles are omitted for clarity and are provided separately in the Supplementary Information (Figure S1)

## Results and Discussion

### Stepwise Hydrogenation of Isolated Dinitrogen

The calculated geometries and structural parameters of dinitrogen **1**, diazene **2a** and **2b**, hydrazine **3a**−**3c** and ammonia **4** are shown in Figure 1. The reaction enthalpies obtained using a variety of energy evaluations based on the B3LYP/II geometries are summarized in Table 1. Details of the levels of theory necessary for a reasonable treatment of the stepwise hydrogenation of isolated dinitrogen to ammonia have been reported in a previous paper and the reaction enthalpies provided by this study serve as reference values for our present work.[21] Thus, for the individual hydrogenation steps shown in Equations (1)−(3), the benchmarks for the reaction enthalpies $\Delta H^0_R$ are 49.2 kcal mol$^{-1}$ [Equation (1)], −23.1 kcal mol$^{-1}$ [Equation (2)] and −44.7 kcal mol$^{-1}$ [Equation (3)].[21]

$$N_2 + H_2 \rightarrow N_2H_2 \quad (1)$$

$$N_2H_2 + H_2 \rightarrow N_2H_4 \quad (2)$$

$$N_2H_4 + H_2 \rightarrow 2\,NH_3 \quad (3)$$

Table 1. Hydrogenation enthalpies $\Delta H^0_R$ (in kcal mol$^{-1}$) for the stepwise reduction of isolated dinitrogen[a]

| | $N_2 + H_2 \rightarrow N_2H_2$ (1) | $N_2H_2 + H_2 \rightarrow N_2H_4$ (2) | $N_2H_4 + H_2 \rightarrow 2\,NH_3$ (3) |
|---|---|---|---|
| B3LYP/ | | | |
| 6−31G(d) | 46.9 | −18.0 | −37.2 |
| 6−31G(d,p) | 43.2 | −19.6 | −40.0 |
| 6−31+G(d,p) | 43.3 | −22.0 | −43.3 |
| 6−31+G(2df,p) | 44.1 | −22.6 | −43.4 |
| 6−31++G(2df,p) | 44.1 | −22.2 | −43.1 |
| 6−311G(d,p) | 47.1 | −20.9 | −41.6 |
| 6−311+G(d,p) | 45.3 | −22.4 | −44.1 |
| 6−311+G(2df,p) | 46.5 | −22.0 | −43.7 |
| 6−311++G(2df,p) | 46.4 | −22.0 | −43.7 |
| CCSD(T) | | | |
| 6−31G(d) | 55.8 | −11.7 | −37.3 |
| 6−31G(d,p) | 49.1 | −15.6 | −41.6 |
| 6−311G(d,p) | 44.1 | −16.7 | −41.7 |
| 6−311+G(d,p) | 51.9 | −18.3 | −43.5 |
| 6−311+G(2df,p) | 51.5 | −19.3 | −43.2 |
| 6−311++G(2df,p) | 51.4 | −19.3 | −43.3 |
| exp.[a] | 49.2 | −23.1 | −44.7 |

[a] Ref. [21]

The data summarized in Table 1 clearly show that for all three hydrogenation steps convergence of the results is achieved when basis sets of at least 6−311+G(d,p) quality are used. At our highest level of theory, the enthalpies of reaction are 51.4 kcal mol$^{-1}$ for Equation (1), −19.3 kcal mol$^{-1}$ for Equation (2) and −43.3 kcal mol$^{-1}$ for Equa-

tion (3), which is in good agreement with the aforementioned reference data.[21] We note, however, that the predicted $\Delta H^0_R$ for the second reduction step [Equation (2)] is 3.8 kcal mol$^{-1}$ too high, while the reaction enthalpies of reactions (1) and (3) are too high by 2.2 and 1.4 kcal mol$^{-1}$, respectively. A more economic, yet reasonably accurate, alternative is given by CCSD(T) energy evaluations in combination with the 6−311+G(d,p) basis set. The deviations from the reference values are then between 4.8 and 1.2 kcal mol$^{-1}$, i.e. the $\Delta H^0_R$ values are 51.9 kcal mol$^{-1}$ for Equation (1), −18.3 kcal mol$^{-1}$ for Equation (2) and −43.5 kcal mol$^{-1}$ for Equation (3). For larger molecules, for which CCSD(T) is no longer affordable, B3LYP/{II & 6−311+G(d,p)} single-point energies are recommended. This approach leads to deviations from the reference that are particularly small for reactions (2) and (3). The calculated $\Delta H^0_R$ values of 45.3 kcal mol$^{-1}$ for Equation (1), −22.4 kcal mol$^{-1}$ for Equation (2) and −44.1 kcal mol$^{-1}$ for Equation (3) thus show that this approach offers a very economic way to reliable hydrogenation enthalpies.

The calculated N−N bond length of **1** is 1.105 Å, whereas the analogous bond lengths of **2a** and **2b** are calculated to be 1.246 and 1.241 Å, respectively. Compared to corresponding experimental data, the differences are quite small and in the range of 0.001 to 0.007 Å.[22,23] The same also holds for the N−H bond length of $NH_3$ (**4**), that is, a small deviation from the experimental data by 0.007 Å is found.[24] Relatively large deviations from the experimental values are, however, found for the structural parameters of **3a**−**3c**. The experimental N−N bond length of 1.449 Å is larger than the one we calculated for the most stable hydrazine isomer **3a** by 0.014 Å.[24] Our calculated value is, however, in perfect agreement with other high-level ab initio estimates,[21] implying that a re-examination of the experimental N−N bond length might be worthwhile. The calculated bond angles of **2**, **3** and **4** are generally in good agreement with the available literature data and we do not find significant deviations. Further details are given in the Supplementary Information (Figure S1).

At our standard level of theory, *viz*. CCSD(T)/II//B3LYP/II the *trans* isomer of diazene **2a** is predicted to be more stable than the *cis* isomer **2b** by 5.5 kcal mol$^{-1}$, which is in line with previous results.[21,25] Furthermore, our calculations predict the *gauche* isomer **3a** to be the most stable form of hydrazine, which is consistent with other data.[25] The energy difference to the corresponding *trans* isomer **3b** is, however, very small at only 0.3 kcal mol$^{-1}$, whereas the analogous *cis* hydrazine **3c** is significantly less stable than **3a** by 8.1 kcal mol$^{-1}$.

### Stepwise Hydrogenation in the Presence of Mononuclear Iron Carbonyl Complexes

The influence of mononuclear iron carbonyl complexes on the stepwise hydrogenation of coordinated $N_2$ is evaluated by comparing the individual reduction steps shown in Equations (4)−(6) with their metal-free analogues in Equations (1)−(3).

$$(CO)_4Fe{-}N_2 + H_2 \rightarrow (CO)_4Fe{-}N_2H_2 \quad (4)$$

$$(CO)_4Fe{-}N_2H_2 + H_2 \rightarrow (CO)_4Fe{-}N_2H_4 \quad (5)$$

$$(CO)_4Fe{-}N_2H_4 + H_2 \rightarrow (CO)_4Fe{-}NH_3 + NH_3 \quad (6)$$

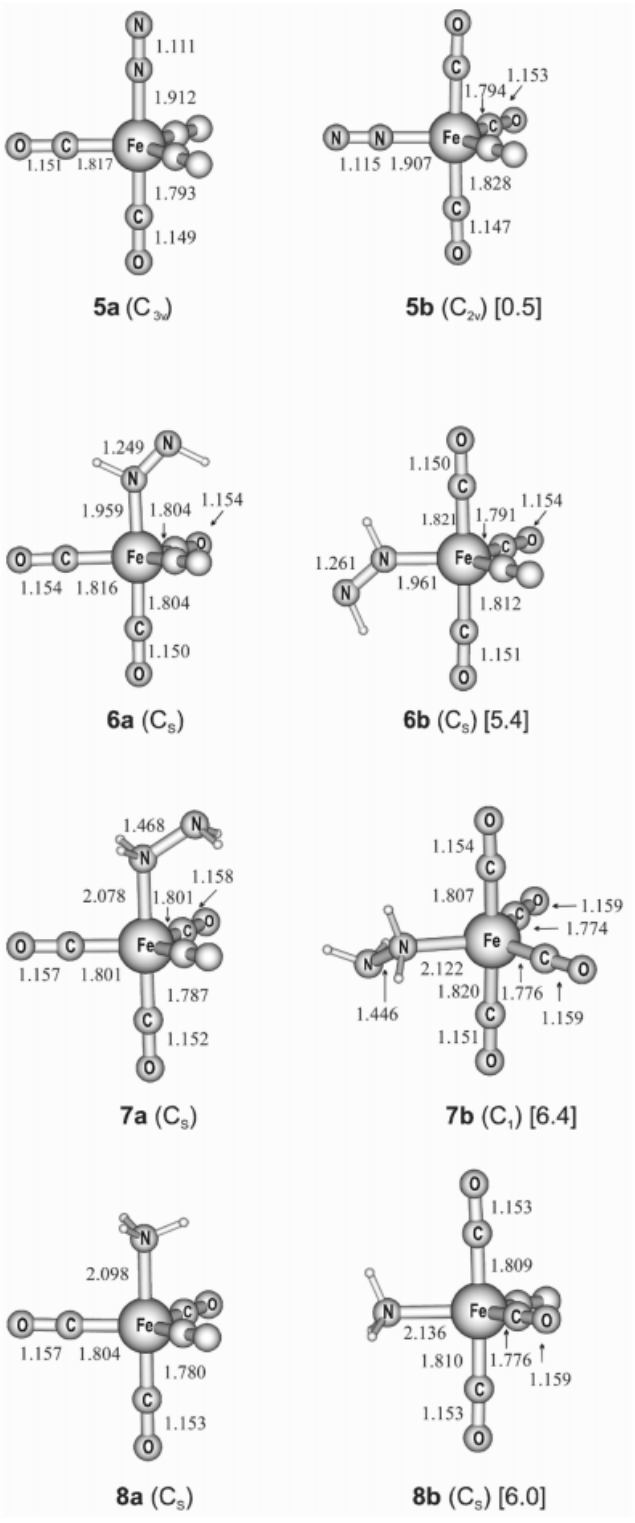


Figure 2. Optimized geometries of the complexes $(CO)_4Fe{-}N_2$ (**5**), $(CO)_4Fe{-}N_2H_2$ (**6**), $(CO)_4Fe{-}N_2H_4$ (**7**), and $(CO)_4Fe{-}NH_3$ (**8**); all bond lengths are in Å and the symmetry used for the geometry optimisation is given in parentheses; relative energies (kcal mol$^{-1}$) with respect to the most stable isomers are given in square brackets; angles and N−H bond lengths are omitted for clarity and are provided separately in the Supplementary Information (Figure S2)

Table 2. Hydrogenation enthalpies $\Delta H^0_R$ (in kcal mol$^{-1}$) for the stepwise reduction of $(CO)_4Fe-N_2$[a]

| | $(CO)_4FeN_2 + H_2 \rightarrow (CO)_4FeN_2H_2$ (4) | $(CO)_4FeN_2H_2 + H_2 \rightarrow (CO)_4FeN_2H_4$ (5) | $(CO)_4FeN_2H_4 + H_2 \rightarrow (CO)_4FeNH_3 + NH_3$ (6) |
|---|---|---|---|
| B3LYP | | | |
| 6−31G(d) | 32.4 | −18.6 | −35.4 |
| 6−31G(d,p) | 30.7 | −20.2 | −38.8 |
| 6−311+G(d,p) | 31.3 | −20.4 | −41.6 |
| CCSD(T) | | | |
| 6−31G(d) | 39.2 | −15.3 | −33.4 |
| 6−31G(d,p) | 35.9 | −18.8 | −39.0 |
| 6−311+G(d,p) | 35.8 | −18.5 | −39.5 |

[a] The basis sets given in the table refer to N and H, only. For all other main group elements the 6−31G(d) basis set is used.

The optimized geometries of the iron carbonyl complexes and the relative energies between the respective axial and equatorial isomers are shown in Figure 2. Table 2 summarizes the hydrogenation enthalpies $\Delta H^0_R$ for Equations (4)−(6) obtained at various levels of theory. Table 3 lists the calculated bond dissociation energies $D_0$ between the $Fe(CO)_4$ fragment and the nitrogen-containing ligands together with the NBO and CDA data.

Table 3. Bond dissociation energies $D_o$ (kcal/mol) and NBO/CDA data for mononuclear iron tetracarbonyl complexes $(CO)_4Fe-L$ obtained at the CCSD(T)/II//B3LYP/II level of theory

| | | | NBO[a] | | | CDA[a] | |
|---|---|---|---|---|---|---|---|
| Complex | $D_o$ | L | q[$Fe(CO)_4$][b] | q(π)→L | q(σ)→[TM] | *b* | *d* |
| **5a** | 22.9 | $N_2$ | −0.08 | 0.18 | 0.26 | 0.14 | 0.28 |
| **6a** | 39.3 | $N_2H_2$ | −0.18 | 0.15 | 0.33 | 0.10 | 0.30 |
| **7a** | 42.8 | $N_2H_4$ | −0.29 | 0.10 | 0.39 | 0.03 | 0.36 |
| **8a** | 38.9 | $NH_3$ | −0.27 | 0.13 | 0.40 | −0.01 | 0.33 |

[a] [TM] = [$(CO)_4Fe$]; q(σ)→[TM] σ-donation (*d*) and q(π)→L π-back donation (*b*) according to the NBO (*CDA*) analysis. − [b] Total charge of the $Fe(CO)_4$ complex fragment.

The most intriguing effect of the $Fe(CO)_4$ fragment on the stepwise hydrogenation of coordinated $N_2$ is that the enthalpy of hydrogenation of 35.8 kcal mol$^{-1}$ for the first reduction step [Equation (4)] is significantly lower by $\Delta\Delta H^0_R = -16.1$ kcal mol$^{-1}$ compared to the analogous step of isolated $N_2$ [Equation (1)]. We do not observe a similarly drastic effect for the second and third reduction steps. To this end, the reduction of $(CO)_4Fe-N_2H_2$ [Equation (5)] is almost as exothermic as the corresponding hydrogenation [Equation (2)] of isolated $N_2H_2$ ($\Delta\Delta H^0_R = -0.2$ kcal mol$^{-1}$). For the hydrogenation of $(CO)_4Fe-N_2H_4$ [Equation (6)], we even find a less exothermic behavior than for the metal-free analogue [Equation (3)] and $\Delta\Delta H^0_R$ is calculated to be 4.00 kcal mol$^{-1}$.

Dinitrogen is both a weak σ-donor and π-acceptor ligand. The small energy difference between the two possible isomers **5a** and **5b** of the complex $(CO)_4Fe-N_2$, in which $N_2$ is either coordinated axially or equatorially, implies no pronounced coordination site preference.[26] The structures of **5a** and **5b** show $Fe-N_2$ bond lengths of 1.912 Å and 1.907 Å, respectively. This is in contrast to the results of Radius et al.,[27] who predicted the $Fe-N_2$ bond length of axial $N_2$ to be shorter than that of equatorial $N_2$. The energy difference of 0.5 kcal mol$^{-1}$ between **5a** and **5b** is in favor of the axial isomer, which is again in contrast to the results of the aforementioned group.[27] Note, however, that the chosen level of theory is surely beyond chemical accuracy (≤ 1.0 kcal mol$^{-1}$) and therefore our small energy difference is not conclusive. Interestingly, however, the uncertainty of the relative energy between **5a** and **5b** is also found in experimental chemistry. On the one hand, the reaction of $Fe(CO)_5$ with $N_2$ in polyethylene film implies that $N_2$ *may* occupy an equatorial rather an axial coordination site,[28] whereas photolysis experiments of $Fe(CO)_5$ in nitrogen-containing matrices[29] show an opposite behavior, that is, a more stable axial than equatorial isomer. The N−N distances of isomers **5a** and **5b** are both slightly longer than in isolated dinitrogen. The bond elongation upon coordination is in the range of 0.006 to 0.010 Å indicating that the N−N triple bond only experiences a weak "activation". In addition, the calculated Fe−N bond energy of 22.9 kcal mol$^{-1}$ also implies a relatively weak interaction between $N_2$ and the $Fe(CO)_4$ fragment.

The diazene complex formed by the first hydrogenation step [Equation (4)] shows a somewhat different behavior than the analogous dinitrogen complex. First, the energy difference of 5.4 kcal/mol$^{-1}$ between the axial (**6a**) and equatorial (**6b**) isomers is indeed significant and in favor of the axial isomer. Second, this preference towards axial coordination is also mirrored by the σ-donor/π-acceptor abilities of diazene.[26] NBO as well as CDA data both imply that $N_2H_2$ is at least as poor a π-acceptor as $N_2$, but at the same time a slightly better σ-donor (Table 3). Finally, the Fe−N bond dissociation energy of **6a** is calculated to be 39.3 kcal mol$^{-1}$, which is considerably higher than the corresponding value calculated for **5a**. The much stronger bond in $(CO)_4Fe-N_2H_2$ than that in $(CO)_4Fe-N_2$ is the reason why the first hydrogenation step of $N_2$ becomes energetically more favored upon $Fe(CO)_4$ complexation. Any structural changes of diazene on complexation are again very small and the N−N bond is lengthened by only 0.003 Å.

Further hydrogenation of coordinated $N_2H_2$ leads to the corresponding hydrazine complex [Equation (5)]. NBO and CDA data suggest that hydrazine is a significantly stronger σ-donor than diazene or dinitrogen (Table 3). Axial coordination of $N_2H_4$ should therefore be predominant, which is supported by the large energy difference of 6.4 kcal mol$^{-1}$ that favors the axial isomer **7a** over its equatorial analog **7b**. Interestingly, the former, more stable, isomer has hydrazine coordinated as *trans*-$N_2H_4$, which is not the most stable conformation for the isolated case. At the same time, the less-stable equatorial isomer has $N_2H_4$ coordinated in its most stable *gauche* conformation. Structural changes of $N_2H_4$ on coordination are significant as shown by the lengthening of the N−N bond in **7a** by 0.033 Å with respect to isolated $N_2H_4$. This relatively strong influence on the internal structure of $N_2H_4$ is also mirrored by the large Fe−N bond dissociation energy of 42.8 kcal mol$^{-1}$, which is, in fact, the highest $D_0$ value encountered in this study. Note, that at the same time the calculated Fe−N bond length of **7a** of 2.078 Å is significantly larger than the corresponding bond lengths found in complexes **5** and **6**, which exhibit weaker bonds between iron and the nitrogen-containing ligands.

In the final step [Equation (6)] of the overall reduction process, coordinated hydrazine is reduced to ammonia. The $NH_3$ ligand is found by CDA and NBO to be an equally strong σ-donor as $N_2H_4$, whereas its π-acceptor capability is close to zero (Table 3). Again we find a dominant preference of the axial $(CO)_4Fe-N_2$ isomer **8a** over the equatorial isomer by 6.0 kcal mol$^{-1}$, which is in line with crystallographic data and IR spectra.[30] Our estimate for the Fe−N bond dissociation energy is 38.9 kcal mol$^{-1}$ and the calculated Fe−N bond length is 2.098 Å. Both values show slight deviations from those found for the analogous hydrazine complex **7a**. These differences are, however, small, thus indicating a close resemblance of these two complexes.

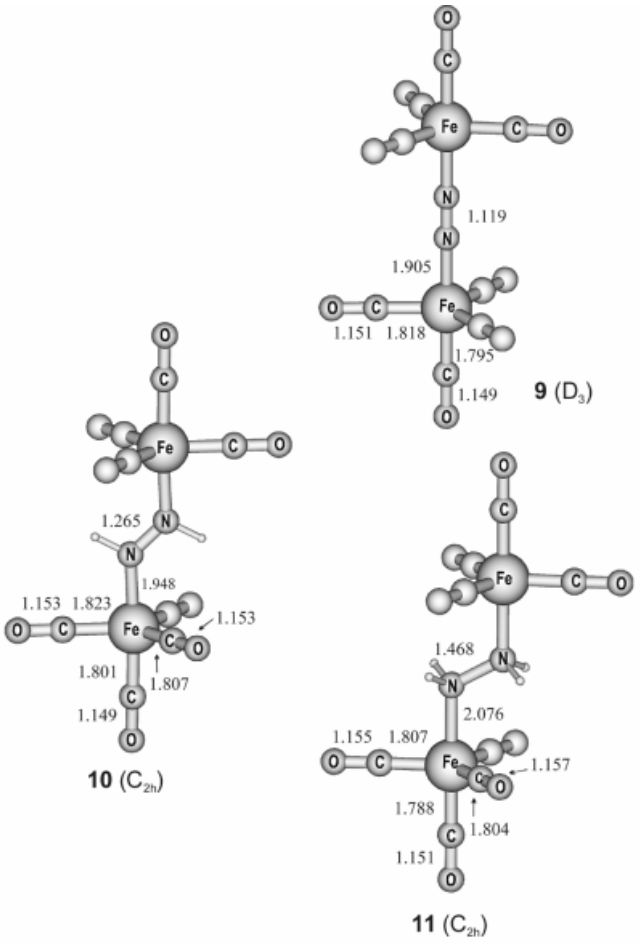


Figure 3. Optimized geometries of the dinuclear iron tetracarbonyl complexes $(CO)_4Fe-N_2-Fe(CO)_4$ (**9**), $(CO)_4Fe-N_2H_2-Fe(CO)_4$ (**10**), and $(CO)_4Fe-N_2H_4-Fe(CO)_4$ (**11**); all bond lengths are in Å; the symmetry used for the geometry optimization is given in parentheses; for more details regarding structural parameters see the Supporting Information (Figure S3)

### Stepwise Hydrogenation in the Presence of Dinuclear Iron Carbonyl Complexes

Figure 3 shows the optimized geometries of the dinuclear complexes $(CO)_4Fe-N_2-Fe(CO)_4$ (**9**), $(CO)_4Fe-N_2H_2-Fe(CO)_4$ (**10**) and $(CO)_4Fe-N_2H_4-Fe(CO)_4$ (**11**), considered in the hydrogenation steps according to Equations (7)−(9). Table 4 and 5 summarize the hydrogenation enthalpies for the individual steps and the bond dissociation energies, as well as the NBO/CDA data, respectively.

$$(CO)_4Fe-N_2-Fe(CO)_4 + H_2 \rightarrow (CO)_4Fe-N_2H_2-Fe(CO)_4 \quad (7)$$

$$(CO)_4Fe-N_2H_2-Fe(CO)_4 + H_2 \rightarrow (CO)_4Fe-N_2H_4-Fe(CO)_4 \quad (8)$$

$$(CO)_4Fe-N_2H_4-Fe(CO)_4 + H_2 \rightarrow 2\,(CO)_4Fe-NH_3 \quad (9)$$

The coordination of dinitrogen by two iron tetracarbonyl fragments results in a further significant decrease of the hydrogenation enthalpy of the first reduction step [Equation (7)] by $\Delta\Delta H^0_R = -13.1$ kcal mol$^{-1}$ compared to the analogous step [Equation (4)] involving only one $Fe(CO)_4$ fragment.[31] The overall decrease of the hydrogenation enthalpy with respect to the metal free reaction [Equation (1)] thus becomes 27.1 kcal mol$^{-1}$.[31] This considerable change of the thermochemistry is so much more interesting as it only affects the first reduction step. To this end, the second [Equation (8)] and third [Equation (9)] hydrogenation steps are even less exothermic than their mononuclear analogues [Equation (5) and (6)]. The $\Delta\Delta H^0_R$ values calculated on going from Equation (5) to (8) and from Equation (6) to (9) are 4.0 and 1.1 kcal mol$^{-1}$, respectively.

The $Fe(CO)_4$ fragments in **9** are twisted against each other by 8.7°. The rotation barrier is extremely low and we find several different isomers that are energetically not distinguishable from each other. In comparison to the mononuclear analogue **5a** we do not observe further significant alterations of structural parameters. Note that the Fe−N bond length becomes shorter by 0.007 Å, which is paralleled by the lengthening of the N−N bond by 0.008 Å. The CDA and NBO data in Table 5 show that the σ-donor properties of $N_2$ embraced by two iron tetracarbonyl fragments is hardly changed compared to **5a** — only the π-

Table 4. Hydrogenation enthalpies $\Delta H^0_R$ (in kcal mol$^{-1}$) for the stepwise reduction of $(CO)_4Fe-N_2-Fe(CO)_4$[a]

| | $[(CO)_4Fe]_2N_2 + H_2 \rightarrow [(CO)_4Fe]_2N_2H_2$ (7) | $[(CO)_4Fe]_2N_2H_2 + H_2 \rightarrow [(CO)_4Fe]_2N_2H_4$ (8) | $[(CO)_4Fe]_2N_2H_4 + H_2 \rightarrow 2(CO)_4FeNH_3$ (9) |
|---|---|---|---|
| B3LYP | | | |
| 6−31G(d) | 19.9 | −16.2 | −39.2 |
| 6−31G(d,p) | 17.6 | −17.0 | −42.0 |
| 6−311+G(d,p) | 18.2 | −16.4 | −40.5 |

[a] The basis set given in the table refers to N and H, only. All of the other elements use the 6−31G(p) basis set.

Table 5. Bond dissociation energies $D_o$ (kcal/mol) and NBO/CDA data for dinuclear iron tetracarbonyl complexes $(CO)_4Fe-L-Fe(CO)_4$ obtained at the B3LYP/II//B3LYP/II level of theory

| Complex | $D_o$[b]/$D_o$[c] | L | $q$[Fe(CO)$_4$][d] | NBO[a] q(π)→L | NBO[a] q(σ)→[TM]$_2$ | CDA[a] *b* | CDA[a] *d* |
|---|---|---|---|---|---|---|---|
| **9** | 16.0/32.5 | $N_2$ | −0.05 | 0.40 | 0.50 | 0.28 | 0.50 |
| **10** | 28.6/59.6 | $N_2H_2$ | −0.11 | 0.38 | 0.60 | 0.24 | 0.57 |
| **11** | 26.1/57.7 | $N_2H_4$ | −0.24 | 0.18 | 0.66 | 0.11 | 0.63 |

[a] [TM] = [(CO)$_4$Fe]; q(σ)→[TM] σ-donation (*d*) and q(π)→L π-back donation (*b*) according to the NBO (*CDA*) analysis with respect to both Fe(CO)$_4$ fragments. Half of this value equals the charge transferred per Fe(CO)$_4$ unit. − [b] Fe−L bond dissociation energy per Fe(CO)$_4$ fragment according to: $[TM]_2L \rightarrow [TM]L + TM$. − [c] Total Fe−L bond dissociation energy according to: $[TM]_2L \rightarrow TM + TM + L$. − [d] Total charge of the Fe(CO)$_4$ complex fragment.

acceptor characteristics are somewhat enhanced. The overall $Fe-N_2-Fe$ bond dissociation energy is calculated to be 32.5 kcal mol$^{-1}$, which translates to a Fe−N bond dissociation energy per Fe(CO)$_4$ fragment of 16.0 kcal mol$^{-1}$. Comparison of these data with the bond dissociation energy obtained for **5a** implies a decreased bond strength between an *individual* Fe(CO)$_4$ subunit and $N_2$.

Further hydrogenation of **9** results in the formation of the corresponding diazene complex $(CO)_4Fe-N_2H_2-Fe(CO)_4$ (**10**). The Fe−N as well as the N−N bond lengths of **10** are calculated to be 1.948 Å and 1.265 Å, respectively. These values are in good agreement with the structural data of the related [μ-$N_2H_2${Fe(PPr$_3$)('S$_4$')}$_2$] ['S$_4$'$^{2-}$ = 1,2-bis(2-mercaptophenylthio) ethane(2-)] complex reported by Sellmann and co-workers.[32] The small deviations of less than 0.052 Å are noteworthy as such Fe$^{II}$('S$_4$') complexes involving multidentate organosulfur ligands are often used as model compounds for the Fe-Mo, Fe−V and Fe−Fe nitrogenases.[4,6,32] We note a non-negligible shortening of the Fe−N bond by 0.011 Å and a lengthening of the N−N bond by 0.016 Å on going from **6a** to its dinuclear pendant **10**. Interestingly, CDA and NBO data indicate that the ability of diazene to act as σ-donor is almost unaltered. Only a slight increase of the π-acceptor capabilities of $N_2H_2$ is observed. The Fe−N bond dissociation energy of **10** follows the same trend as shown above for the corresponding dinitrogen complex; that is, the bond strength per Fe(CO)$_4$ fragment is smaller than in the mononuclear case, whereas the overall binding energy obtained by complexation with two Fe(CO)$_4$ fragments is significantly larger.

In the second step of the overall reduction process [Equation (8)], the analogous hydrazine complex $(CO)_4Fe-N_2H_4-Fe(CO)_4$ (**11**) is formed by hydrogenation of coordinated diazene. The comparison with complex **7a** shows hardly any shortening of the Fe−L bond length or lengthening of the N−N bond. We want to point out that the NBO data imply that both the σ-donor as well as the π-acceptor abilities of $N_2H_4$ decrease slightly on going from the mononuclear complex to **11**. With respect to the σ-donor character this is also supported by the corresponding CDA values. Although the analogue π-acceptor value implies a stronger π back-donation of $N_2H_4$ in the dinuclear complex **11**, the predicted magnitude is too small to account for a significant π-acceptor character of $N_2H_4$.

## Conclusion

Density functional and ab initio calculations were used to evaluate the influence of iron tetracarbonyl complexes on the stepwise hydrogenation of dinitrogen. In comparison to the metal-free reduction process, we find that complexation by one or two Fe(CO)$_4$ fragments results in a pronounced change of the thermochemistry of the first hydrogenation step, namely the reduction of coordinated $N_2$ to $N_2H_2$. The effects on the second and third hydrogenation steps, *viz* the hydrogenation of coordinated $N_2H_2$ and $N_2H_4$, are much weaker, and even less-exothermic reduction processes compared with the metal-free hydrogenation are predicted. The decrease of the hydrogenation enthalpy is larger for the reduction of $(CO)_4Fe-N_2-Fe(CO)_4$ than it is for the reduction of $(CO)Fe-N_2$. In conclusion, our calculations thus clearly demonstrate that only one, namely the first, reduction step in the hydrogenation sequence of $N_2$ is

in fact favored in terms of the reaction enthalpy by complexation with iron tetracarbonyl fragments. Although the systems used in our study are not intended to primarily serve as model complexes for the mode of action of nitrogenase, we suggest that these results should be considered in further discussions of the thermochemistry of $N_2$ fixation and activation processes.

The binding characteristics of $N_2$, $N_2H_2$, $N_2H_4$ and $NH_3$ to $Fe(CO)_4$, analyzed in terms of the NBO and CDA partitioning schemes, imply a consistent trend of the σ-donor/π-acceptor behavior of these ligands that correlates with the relative energies between the respective isomers. Thus, ligands with comparatively high σ-donor capabilities like $N_2H_4$ and $NH_3$ give iron tetracarbonyl complexes in which the axial isomers are considerably more stable than their equatorial analogues. In addition to that, only ligands like $N_2$ and $N_2H_2$ that show noticeable π-acceptor quantities in their respective $Fe(CO)_4$ complexes are affected by the formation of dinuclear complexes. Thus, the Fe−N bond lengths are shorter and the N−N bonds are longer in the dinuclear complexes than in their mononuclear analogues. This behavior is also mirrored by a slight increase of the π-acceptor ability on going from $(CO)_4Fe-X$ to $(CO)_4Fe-X-Fe(CO)_4$ (X = $N_2$, $N_2H_2$) complexes. Such structural changes are absent for $N_2H_4$, and both its σ-donor as well as its π-acceptor behavior are less pronounced in $(CO)_4Fe-N_2H_4-Fe(CO)_4$ than in $(CO)_4Fe-N_2H_4$.

## Experimental Section

**Computational Details:** Geometry optimizations were performed with Becke's three-parameter hybrid functional in combination with the correlation functional according to Lee, Yang and Parr (B3LYP).[11] A small core pseudopotential and a (441/2111/41) split-valence basis set according to Hay and Wadt were used for iron,[12] whereas an all-electron 6−31G(d) basis set was chosen for the main-group elements.[13] It was shown previously that this combination of basis sets (further abbreviated as basis set II) in combination with the aforementioned functional predicts equilibrium geometries of transition metal complexes reasonably well.[14] All structures discussed in this paper were verified to represent local minima on their potential energy surfaces by harmonic frequency calculations at the same level of theory. Refined estimates of relative energies were obtained by single-point calculations of the B3LYP/II geometries using both the B3LYP functional and coupled-cluster theory with singles, doubles and perturbative estimates of triple substitution [CCSD(T)].[15] CCSD(T) and basis set II were used for estimating relative energies between isomeric forms of diazene, hydrazine and all iron carbonyl complexes. Refined reaction enthalpies $\Delta H^0_R$ (T = 0 K) for the individual hydrogenation reactions, however, were predicted using basis sets that consisted of the aforementioned basis set for the metal and the elements C and O, but were extended by either the 6−31G(d,p) or the 6−311+G(d,p) basis sets for N and H. These combinations of basis sets are further abbreviated as {II & 6−31G(d,p)} and {II & 6−311+G(d,p)}, respectively.

The $\Delta H^0_R$ values obtained for the hydrogenation steps of the metal-free reactions were compared with their analogous steps involving mononuclear iron carbonyl fragments. The resulting $\Delta\Delta H^0_R$ values indicate whether the $\Delta H^0_R$ of an individual reduction step decreases ($\Delta\Delta H^0_R < 0$) or increases ($\Delta\Delta H^0_R > 0$) on going from the reactions of the isolated to the coordinated species. The corresponding $\Delta\Delta H^0_R$ values obtained for the individual reduction steps involving mono- and dinuclear iron carbonyl fragments were used likewise. Unless otherwise noted, relative enthalpies obtained at the CCSD(T)/{II & 6−311+G(d,p)}//B3LYP/II level of theory were the basis for the comparison between the metal-free hydrogenation steps of $N_2$ and the reactions following the reduction of $(CO)_4Fe-N_2$. With respect to the large resources needed for a proper description of the reactions involving dinuclear species, the comparisons between the hydrogenation steps involving mono and dinuclear iron carbonyl complexes were based on the B3LYP/{II & 6−311+G(d,p)}//B3LYP/II energies only. For the evaluation of the reaction enthalpies only the most stable isomers within a reaction sequence were considered.

Reaction enthalpies and relative energies are corrected by zero-point vibrational energy (ZPE) contributions obtained at the B3LYP/II level of theory. The nature of the Fe−N and N−N bonds was examined using the natural bond orbital (NBO)[16] partitioning scheme and the charge decomposition analysis (CDA).[17] All calculations used the program packages Gaussian94/98,[18] MOLPRO96/2000,[19] and CDA2.1.[20]

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