Preliminary communication

Study of the interaction between iron(0) and dinitrogen: "ab initio" calculations on the model compound $Fe(PH_3)_4(N_2)$

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Abstract

"Ab initio" calculations have been carried out on the model system $Fe(PH_3)_4(N_2)$ to throw light on the nature and the energetics of the interaction between iron and dinitrogen. The results allow a complete description of the electronic structure of the compound: the coordinated bond between Fe and N_2 can be essentially described in terms of the Chatt–Dewar–Duncanson model, although π-back donation is much more relevant than σ-donation. The two possible coordination modes for N_2 to a monometallic fragment, i.e. end-on and side-on, have been considered. The results suggest that only the side-on coordination, which seems to be attainable for interaction with the basic fragment $Fe(PH_3)_4$, leads to incipient activation of dinitrogen.

Activation of dinitrogen by transition metal complexes can be strictly related to the bonding mode of N_2 to metal centres. Differences in the bonding mode lead to different polarizations and different degrees of reduction of dinitrogen both are fundamental factors by which coordination of N_2 becomes the prerequisite for its authentic activation. The end-on bonding mode for N_2 is the only one so far observed for mononuclear complexes, independent of the nature of the metal and other factors [1]. The small enhancement of reactivity of the N_2-metal bonded molecule may be attributed to the poor polarization and electron transfer associated with the end-on bonding mode. The electron transfer from the metal to N_2 to generate an incipient diimide dianion can be much more effective when the N_2 binds to the metal in a side-on fashion. Within this framework we can consider the difference in the degree of electron transfer from the metal to π-acids for end-on vs. side-on bonded species. The relative stabilities of the end-on and side-on coordination of N_2 in terms of σ-donation and π-back donation have been discussed by

several authors [2–6]. The activation of dinitrogen in dinitrogen-bridged transition metal dimers has also been analysed [7–9]. All the mononuclear complexes theoretically investigated so far prefer the end-on coordination of dinitrogen [2–6]. However, coordination of dinitrogen to a metallic fragment which has a strong Lewis basicity has never been investigated. In order to understand orbital requirements and differences in energy involved, we considered the two different modes for binding of N_2 to the metallic fragment $Fe(PH_3)_4$. Such a d^8 tetracoordinate iron-fragment has a carbenoid nature that is the most appropriate for the interaction with an unsaturated substrate. The $Fe(PH_3)_4$ fragment has previously been used in examination of interactions with formaldehyde [10] and carbon dioxide [11].

Computational details

"Ab initio" spin-restricted Hartree-Fock SCF gradient calculations were carried out for partial geometry optimization of the complex $Fe(PH_3)_4(N_2)$ having the dinitrogen side-on or end-on bonded to the iron, and in deriving estimates of the binding energies with respect to free N_2 and $Fe(PH_3)_4$. All computations were performed by use of the GAMESS program package [12] on a CRAY XMP/48 computer.

Two Gaussian basis sets described in ref. 11 were employed throughout this work. The first one, of double ζ valence quality for the iron, the nitrogen, and the hydrogen, and single ζ quality for the phosphorus atoms, was used for geometry optimization of the FeN_2 moiety. Subsequent single point SCF calculations at the optimized geometries were performed with a more extended basis set of double ζ quality.

The partially optimized structures of the $Fe(PH_3)_4(N_2)$ system with side-on or end-on bonded dinitrogen are shown in Fig. 1. The compound can be viewed as a distorted trigonal bipyramid with a 5-coordinate iron atom bonded to two mutually *trans* phosphines in axial sites and to two phosphines and dinitrogen in equatorial sites. The geometry of the $Fe(PH_3)_4$ fragment was taken from ref. 10 and kept frozen during the optimizations, while the Fe–N and N–N bond lengths were optimized for both coordination modes of the dinitrogen. The experimental geometry of N_2 was used for the free molecule [13], since the optimized structure is extremely close to the experimental one. In considering the electronic structure of the isolated fragment $Fe(PH_3)_4$, its geometry was assumed to be the same as that in the complex.

A singlet state, arising from the d^8 closed shell configuration for iron(0), was assumed for the system $Fe(PH_3)_4(N_2)$. Dissociation of this complex into the
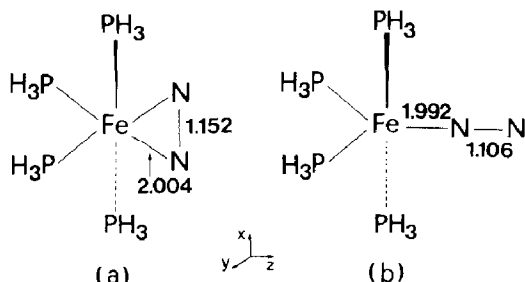

Fig. 1. Optimized geometries for side-on (a) and end-on (b) bonded dinitrogen. Bond lengths in Å.

fragments $Fe(PH_3)_4$ and N_2 may lead to either singlet or triplet products. In a previous study [10], configuration interaction calculations on the complex $Fe(CO)_4(\eta^2\text{-}CH_2O)$ led us to suggest that fragmentation of that complex leads to singlet products, given the $S_0 \rightarrow T_1$ value of 71.9 kcal mol^{-1} for free formaldehyde [14]. The $S_0 \rightarrow T_1$ value for free dinitrogen is 143.5 kcal mol^{-1} [13]. We thus assume that fragmentation of the complex $Fe(PH_3)_4(N_2)$ will lead to singlet products.

Results and discussion

The binding of an unsaturated ligand, such as the dinitrogen, to a carbenoid metallic fragment is usually described by the Chatt–Dewar–Duncanson model [15], with σ-donation from the ligand lone pair or π orbital to the metal atom and π-back-donation from the metal to the $\pi^\star$ orbital of the ligand. This picture holds also for $Fe(PH_3)_4(N_2)$, with the dinitrogen bonded both side-on or end-on, although π-back donation is much more relevant than σ-donation. Indeed the analysis of the molecular orbitals of $Fe(PH_3)_4(N_2)$ shows that the main bonding orbital between iron and dinitrogen is the highest occupied one (HOMO) for both coordination modes of N_2. This orbital can be viewed as the overlap between the occupied $3d_{xz}$ of the iron (hereafter denoted as d_π) and one of the two components of the virtual $1\pi_g$ orbital of N_2 (hereafter denoted as $\pi^\star$). The HOMO describes π-back donation from the iron to the dinitrogen. σ-donation takes place from the z-component of $1\pi_u$ orbital of N_2 for side-on coordination and from $3\sigma_g$ orbital for end-on coordination to a hybrid orbital of the iron (hereafter denoted as d_σ), formed mainly by $4p_z$, $3d_{x^2-y^2}$, $3d_{z^2}$.

The predominance of the role played by π-back donation over that by σ-donation, is confirmed by the Mulliken population analysis, the results of which are listed in Table 1. They show a strong decrease in the population of the d_π orbital of the iron (0.75 e for side-on; 0.20 e for end-on coordination) and, thus, an increase in the population of the $\pi^\star$ orbital of dinitrogen on going from the separate fragments toward the complexes. The increase of the population of the d_σ orbital of the iron is relevant, but it is mainly due to the electron-donor character of the phosphines ligands, particularly evident for side-on coordination of N_2. There is a flow of electron-density from the phosphines toward the iron upon coordination of the dinitrogen, especially when N_2 is bound in a side-on fashion: in this case the decrease in the population of the phosphines is 0.57 electron. The presence of the phosphine ligands enhances the electron-density at the iron atom and, so favors π-back donation toward the dinitrogen.

It is of interest that in the end-on dinitrogen complex the terminal nitrogen atom bears more negative charge than the coordinating one; the Mulliken populations (not shown in Table 1) are calculated to be 7.02 and 7.14 e with the smaller basis set; and 6.95 and 7.10 e with the bigger basis set for the coordinating and terminal nitrogen atoms, respectively. This result agrees with ESCA [16] and electron emission data [17], which indicate that the terminal nitrogen atom bears a larger negative charge than the coordinating one. Hoffmann et al. [18] have explained this in terms of allyl-type orbital mixing. Sakaki et al. [6] suggest that the orbital mixing and the positive charge of the central metal influence the N_2 electron distribution. In the case of complexes with a highly positively charged central metal the coordinating nitrogen atom is more negatively charged than the terminal one, as in Rh^I–N_2 complexes [6], while when the metal is in a low oxidation state, as in

Table 1

Mulliken populations (Mulliken population changes) and energies of the analysed systems. The interaction (INT) and deformation (DEF) contributions to the binding energy (BE) and the π^* orbital energy of the dinitrogen ligand are also reported.

	$(PH_3)_4Fe + N_2$	$(PH_3)_4Fe\diagup\!\!\!\!{\displaystyle\mathop{N}_{N}}$	$(PH_3)_4Fe-N-N$
Fe4s	0.18	0.29 (+0.11)	0.20 (+0.02)
Fe4p	0.22	0.49 (+0.27)	0.37 (+0.15)
4p_x	0.08	0.13 (+0.05)	0.09 (+0.01)
4p_y	0.04	0.12 (+0.08)	0.06 (+0.02)
4p_z	0.10	0.24 (+0.14)	0.22 (+0.12)
Fe3d	7.63	7.39 (−0.24)	7.56 (−0.07)
3$d_{x^2-y^2}$	0.74	0.85 (+0.11)	0.85 (+0.11)
3d_{z^2}	1.17	1.47 (+0.30)	1.19 (+0.02)
3d_{xy}	1.89	1.94 (+0.05)	1.91 (+0.02)
3d_{xz}	1.90	1.15 (−0.75)	1.70 (−0.20)
3d_{yz}	1.91	1.98 (+0.07)	1.91 (0.00)
N_2s	7.66	7.58 (−0.08)	7.53 (−0.13)
N_2p	6.34	6.85 (+0.51)	6.52 (+0.18)
p_x	2.34 (2.00) [a]	2.28 (−0.06)	2.21 (+0.21)
p_y	2.00	1.98 (−0.02)	2.03 (+0.03)
p_z	2.00 (2.34) [a]	2.59 (+0.59)	2.28 (−0.06)
PH_3 (eq.)	36.11	35.74 (−0.37)	36.00 (−0.11)
PH_3 (ax.)	35.86	35.66 (−0.20)	35.82 (−0.04)
E_{SCF} [b]	−2740.2765	−2740.3112	−2740.3042
INT [c]		−26.6	−17.5
DEF [c]		4.8	0.06
BE [c]		−21.8	−17.4
π^* [b]	0.1436	0.1171	0.1394

[a] For end-on coordination. [b] Hartree. [c] kcal mol^{-1}.

$Fe(PH_3)_4(N_2)$, the orbital mixing is more important and the terminal nitrogen atom is the nucleophilic centre.

The total SCF energies of the analysed systems are listed in Table 1, together with the estimated binding energies, which have been computed as the difference between the energies of the complexes and those of the separated fragments. Since in computing these energies we have used partially optimized geometries for the complexes and nonoptimized geometry for the free iron-fragment, we expect our data to somewhat overestimate (in absolute value) the true fragmentation energies of the complexes. However, this should not affect the main qualitative conclusions of our comparative analysis. In our model the binding energy (BE) can be thought of as the sum of a positive deformation energy (DEF), arising from the distortion of the unsaturated ligand, and a negative interaction energy (INT) resulting from the interaction between the iron fragment and the distorted ligand [19]. The deformation and interaction energies are also shown in Table 1.

The binding energies are calculated to be −21.8 and −17.4 kcal mol^{-1} for side-on and end-on coordination of the dinitrogen, respectively. Although our results should be viewed as preliminary, since correlation effects were not taken into account, side-on is slightly preferred over end-on coordination by dinitrogen bonded

to $Fe(PH_3)_4$. In the side-on bonded dinitrogen complex there is a more pronounced π-back donation from the iron to the unsaturated ligand, as it is indicated by the Mulliken populations and by the energy of the $\pi^\star$ orbital of N_2 at the distorted geometry of the complex. This orbital overlaps with the d_π orbital of the iron fragment whose energy is -0.2249 hartree: the side-on coordination involves a better overlap and so increased interaction. The side-on coordination also involves a larger electrostatic attraction between the negatively charged dinitrogen molecule and the positively charged $Fe(PH_3)_4$ fragment.

It is well established [3,5,20] that the end-on is markedly preferable over the side-on approach for interaction of N_2 with an isolated iron atom. In the presence of donor ligands at the metal centre the stabilities of the two bonding modes of N_2 become comparable, and, at least at the Hartree–Fock level the side-on approach seems to be attainable. This point is of particular interest owing to its implications for the problem of nitrogen fixation. In the side-on bonded dinitrogen complex there is a larger electron transfer from the metal to N_2: the negative charge on the dinitrogen molecule is 0.43 e in the side-on complex and only 0.05 e in the end-on one. Moreover, from Fig. 1 we can see that the N–N bond is lengthened in the side-on complex (1.152 Å), but not in the end-on one (1.106 Å) (the experimental N–N bond distance is 1.09768 Å [13]). The deformation energy of the side-on complex (4.8 kcal mol^{-1}) is higher than that of the end-on one (0.06 kcal mol^{-1}), but this is more than compensated by the increased interaction energy (-26.6 for side-on; -17.5 kcal mol^{-1} for end-on). We conclude that only side-on coordination results in activation of the dinitrogen; this point was previously established for interaction of N_2 with an isolated iron atom [5,21]. However, in the presence of donor ligands on the metal centre the side-on coordination also seems to be attainable, while for an isolated iron atom it is strongly destabilized [5].

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