(Found: C 60.2; H 8.69; Cl 9.87; N 3.77; O 17.6. Calc. for $C_{19}H_{32}ClNO_4$: C 61.0; H 8.63; Cl 9.48; N 3.75; O 17.1.) IR spectrum: σ_{max} (KBr) 3190 (s), 1772 (s) cm^{-1}. NMR spectrum (DMSO-d_6) τ: 4.13 (t, 1 H, $J=5.0$ Hz, exchangeable in D_2O), 4.97 (d, 1 H, $J=4.5$ Hz), 5.21 (q, 1 H, $J_1=5.0$ Hz, $J_2=3.0$ Hz), 5.68 (d, 1 H, $J=3.0$ Hz), 5.90–6.30 (m, 2 H), 6.40–7.20 (m, 3 H), 6.86 (s, 6 H), 7.60–8.45 (m, 8 H), 8.54 (s, 3 H), 9.06 (d, 6 H, $J=6.0$ Hz).

Degradation of I with lithium hydride. A mixture of I (1.5 mg) and lithium hydride (5 mg) in *N*,*N*-dimethylformamide (0.5 ml) was heated at 100° for 18 h, and then cooled and acidified with aqueous hydrochloric acid. The solution was washed with ether (2 × 1 ml), neutralized with sodium hydrogen carbonate and extracted with ether (2 × 1 ml). The ether solution was dried and evaporated to dryness leaving II (1.0 mg). IR spectrum: σ_{max} ($CHCl_3$) 1778 (s) cm^{-1}. Pertinent mass spectral peaks *m/e* (rel. intensity): M^+ 293 (13), 292 (9), 249 (6), 220 (6), 177 (5), 175 (4), 138 (100), 124 (9), 111 (9), 93 (11), 91 (9), 74 (24).

Hydrogenation of II. A solution of II (1.8 mg) in aqueous hydrochloric acid (2 ml, 1 %) was hydrogenated over Adams catalyst (9 mg) at room temperature and atmospheric pressure. After 20 h the catalyst was filtered off and the solution made alkaline with sodium hydrogen carbonate and extracted with ether (3 × 1 ml). The ether solution was dried and evaporated to dryness leaving a quantitative yield of dihydronobilonine, indistinguishable (TLC, GLC, MS) from an authentic sample.

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On the Polarity of the Dinitrogen Ligand in a Dinitrogen Complex of Iron

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In a previous study,[1] infrared absorption intensities of the N–N stretching vibration in some dinitrogen complexes of rhenium and iridium were reported. It was found that the intensity of the N–N stretching vibration (A_{NN}) increases with decreasing frequency (ν_{NN}) (*cf.* Fig. 2 in Ref. 1). It was concluded that the lower the ν_{NN} and the higher the A_{NN}, the greater was the disturbance of the dinitrogen ligand. Furthermore, from ESCA measurements[2] on the above mentioned dinitrogen complexes, the charge distribution on the dinitrogen ligand was determined. The presence of two peaks in the N1*s* electron spectra shows that the dinitrogen ligand has an appreciable polarity. It has been found that both the nitrogen atoms in the complexes carry a negative charge. A connection between the magnitude of the shift in N1*s* binding energy and the N–N stretching frequency has been found, *viz.* the lower the ν_{NN}, the larger the chemical shift in binding energy. Thus, when the disturbance of the dinitrogen ligand is large, *i.e.* low ν_{NN}, the more pronounced is the charge separation on the nitrogen atoms.

In order to further substantiate these observations, both infrared intensity and ESCA measurements have been performed on a dinitrogen complex of iron, *viz.* $FeH_2N_2(PPh_3)_3$. In view of the occurrence of iron in the nitrogen-fixing enzyme[3] in biological systems, such an investigation could be of added interest. $FeH_2N_2(PPh_3)_3$ was first prepared by Sacco and Aresta[4] and later by Borod'ko *et al.*[5] The complex investigated in this work has been prepared according to the procedure given by Borod'ko *et al.*[5] The purity of the compound was checked by elemental analysis and by its IR spectrum. (Found: C 74.0; H 5.69; N 3.16. Calc. C 74.3; H 5.43; N 3.21.) The IR spectrum shows a strong band at 2075 cm^{-1} (N–N stretching vibration) and a weak broad band at 1895 cm^{-1} (Fe–H stretching vibration). The intensity measurements on the N – N stretching vibration have been performed as before[1] both in the solid state and in solution. The intensity of the N – N band in solution was found to decrease with time, indicating the instability of the complex in solution. Therefore, the measurements were performed rapidly. Three spectra were recorded successively and the intensity was extrapolated to zero time. The results are given in Table 1.

Table 1. The results of the absorption intensity measurements on $FeH_2N_2(PPh_3)_3$.

Dispersion medium	ν_{NN} cm^{-1}	ε_{NN} $M^{-1} cm^{-1}$	$A_{NN} \times 10^{-4}$ $M^{-1} cm^{-2}$
KBr	2075	950 ± 100	4.5 ± 0.4
$C_6H_5CH_3$	2076	800 ± 100	4.3 ± 0.4

The good agreement of the intensity values (A_{NN}) determined in various dispersion media shows that the intensity is not dependent on the medium. There is further a good agreement between these intensity values and the value 4.4×10^4 M^{-1} cm^{-2}, which was reported by Borod'ko *et al.*[5] (the medium unspecified). The intensity values (A_{NN}) found for the Fe – N_2 complex are somewhat larger than corresponding A_{NN} for $IrClN_2(PPh_3)_2$ measured before.[1] This is expected as the frequency (ν_{NN}) is somewhat lower in the Fe – N_2 complex than in the iridium complex (2075 cm^{-1} and 2105 cm^{-1}, respectively). Indeed, the intensity values measured for the Fe – N_2 complex fall on the correlation curve between intensity (A_{NN}) and frequency (ν_{NN}) presented before (*cf.* Fig. 2 in Ref. 1). As mentioned above a high intensity value of the N – N stretching vibration means a great disturbance of the dinitrogen ligand and a decrease in the N – N bond order. Consequently, this means a strong metal-dinitrogen bond. The intensity values found for the Fe – N_2 complex are considerably smaller than the previously[1] determined values for the rhenium dinitrogen complexes. In agreement with this, it may be noted that the Fe – N bond is not so stable to chemical attack as the metal – N bond in the rhenium dinitrogen complexes.

The ESCA measurements were performed at low temperature, since it was found that the complex decomposes with evolution of dinitrogen under vacuum at room temperature. The nitrogen 1*s* electron spectrum of the complex obtained at – 50°C is given in Fig. 1. It is evident that the 1*s* electrons of coordinated dinitrogen did not give rise to two separate peaks, but only one broad peak. The half-width of the peak was 2.4 eV. The half-width of a separate N1*s* electron peak has been found to be 1.4 eV for the dinitrogen complexes of rhenium. The value 2.4 eV for $FeH_2N_2(PPh_3)_3$ thus gives an indication of two N1*s* electron peaks. To get the energy difference between the two peaks, the deconvolution procedure given in Ref. 6, Appendix D, has been used. Under the assumption that the half-width of a separate N1*s* electron peak in the iron dinitrogen complex is the same as the half-width of the N1*s* electron peaks found for the dinitrogen complexes of rhenium, the energy difference becomes 1.1 eV. The maxima of the two N1*s* electron peaks are then placed on each side of the maximum of the obtained peak. The N1*s* electron binding energies of the two nitrogen atoms then become 399.0 eV and 400.1 eV. Analogous to the earlier results,[1] the smallest N1*s* binding energy is assigned to the inner nitrogen atom, which thus is the most negative one. The charges on the nitrogen atoms can now be estimated from the binding energies with the aid of the correlation diagrams presented before (Figs. 3 – 5 in Ref. 2). It is evident that

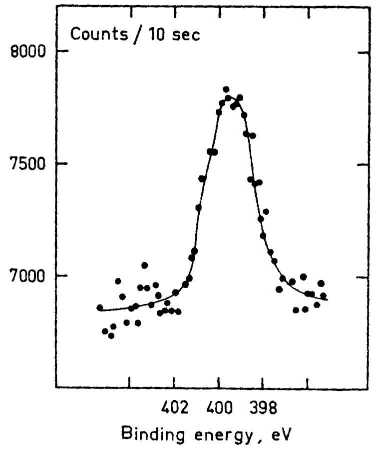

Fig. 1. Nitrogen 1*s* electron spectrum of $FeH_2N_2(PPh_3)_3$ obtained at – 50°C.

both the nitrogen atoms become negatively charged. The charges obtained from the correlation diagram based on CNDO calculated charges ($M-N_1-N_2$) are $q_{N_1} = -0.41$ a.u. and $q_{N_2} = -0.28$ a.u. The charge separation (0.13 a.u.) on the nitrogen atoms is thus smaller for this dinitrogen complex than the charge separation found for, *e.g.*, the dinitrogen complexes of rhenium[2] (0.23 a.u.). The $N-N$ bond in the iron dinitrogen complex thus shows smaller polarity than the $N-N$ bond in the dinitrogen complexes of rhenium, which also is expected from the IR results.

To get an idea about the charge on the iron atom in the dinitrogen complex some metal core electron spectra have also been recorded. Table 2 shows the Fe $2p_{3/2}$ and Fe $3p$ electron binding energies in the dinitrogen complex together with the corresponding binding energies for some other iron compounds. It is evident that the binding energies measured for the dinitrogen complex are closer to those found for Fe metal than those measured for other iron compounds of the same formal oxidation state. This indicates a low positive charge on the metal atom in the dinitrogen complex. On the other hand, it is expected that the π^*-acceptor ability of the dinitrogen ligand should cause a lower electron density around the metal atom and consequently a high binding energy and thereby a high positive charge on the metal atom. It must, however, be pointed out that the binding energy is dependent not only on the effective charge on the atom in question, but also on the potential at that atom originating from the effective charge of all the other atoms in the molecule. It is thus quite reasonable that the potential originating from the surrounding phosphines and especially the hydride ions in the dinitrogen complex causes a low binding energy at the metal atom and thereby seemingly a low positive charge. A low positive charge on the metal atom has earlier been found[2] for the dinitrogen complexes of rhenium and iridium.

Table 2. The binding energies of Fe $2p_{3/2}$ and Fe $3p$ electrons in some iron compounds.

Compound	E_b eV Fe $2p_{3/2}$	Fe $3p$
Fe metal	706.5	53.2
$FeH_2N_2(PPh_3)_3$	707.1	54.2
$FeCl_2$	710.9	56.0
$FeSO_4$	711.1	55.9

The shift in N1*s* binding energy earlier found for $IrClN_2(PPh_3)_2$ was 1.4 eV. This is to be compared with the shift (1.1 eV) now obtained for $FeH_2N_2(PPh_3)_3$. The $N-N$ stretching frequency is somewhat higher in $IrClN_2(PPh_3)_2$ than in $FeH_2N_2(PPh_3)_3$, so the shift found earlier is probably somewhat too large. It was also pointed out[2] that the intensity of the two N1*s* electron peaks in $IrClN_2(PPh_3)_2$ was small and therefore it was difficult to determine the exact position of the two peaks. The reported N1*s* binding energies for $IrClN_2(PPh_3)_2$ are consequently somewhat uncertain.

Another interesting observation is further confirmed through the measurements on the iron dinitrogen complex, *viz.* that the difference in N1*s* binding energy of the terminal nitrogen atom for various complexes (*cf.* Table 1 in Ref. 2) is not so pronounced as the difference in N1*s* binding energy of the inner nitrogen atom. Consequently, the charges on the terminal nitrogen atoms are more similar than the charges on the inner nitrogen atoms.

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