Metal–Dinitrogen σ- and π-Bonding Roles in $[Fe(dmpe)_2H(N_2)]^+$, $[Fe(depe)_2(N_2)]$ and *trans*-$[V(dmpe)_2(N_2)_2]^-$ (dmpe = $Me_2PCH_2CH_2PMe_2$, depe = $Et_2PCH_2CH_2PEt_2$)

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The nature of the M–N and N–N bonding and the activation of co-ordinated N_2 towards protonation has been investigated theoretically using the extended Hückel molecular orbital (EHMO) method. Charges on the N_2 atoms and the M–N and N–N overlap populations for the model systems *trans*-$[V(PH_3)_4(N_2)_2]^-$, $[Fe(PH_3)_4H(N_2)]^+$ and $[Fe(PH_3)_4(N_2)]$ [the actual phosphine ligand being 1,2-bis(dimethylphosphino)ethane or its diethyl derivative] show an excellent correlation with experiment. The more reactive N_2 group of the vanadium complex has a much larger negative charge while both the V–N and N–N bonds in $[V(PH_3)_4(N_2)_2]^-$ are computed and observed to be relatively weak with the corresponding bonds in the Fe compounds being relatively strong. Both theory and experiment therefore demonstrate that the simple Dewar–Chatt–Duncanson (DCD) picture is not applicable since it predicts a strong M–N bond should be associated with a weak N–N bond and *vice versa*. For these first-row transition-metal complexes, the M–N bond is σ dominated while the N–N bond is π dominated and there is no synergic correlation between them. In contrast, EHMO calculations for $[Ru(NH_3)_5(N_2)]^{2+}$ and $[Os(NH_3)_5(N_2)]^{2+}$ correlate both with the experimental IR vibrational data and with the predictions of the DCD model. For these complexes, an increasing M–N interaction is associated with a decreasing N–N bond strength. The factors which lead to the departure away from the DCD picture for the vanadium and iron species are discussed in terms of the metal charges and co-ordination numbers.

Nitrogenase, a bacterial enzyme which can protonate dinitrogen to ammonia, is especially important as an inexpensive method of ammonia production.[1] Transition metals, particularly molybdenum, iron and vanadium, have long been known to be at the active site and an extensive co-ordination chemistry of N_2 has been developed in an attempt to understand the fundamental nature of the M–N_2 interaction and to develop relatively simple model complexes which can mimic the activity of the natural system.[2] The ongoing refinement of the crystal structure of nitrogenase[3] is set to stimulate further studies on the co-ordination chemistry of the dinitrogen ligand.

The general picture of N_2 bonding to metals derives largely from the familiar Dewar–Chatt–Duncanson (DCD) model of synergic σ donation/π back-donation in the isoelectronic carbonyl ligand.[4] There is therefore an expectation that the N–N stretching frequency observed in vibrational spectra should correlate with both the N–N and the M–N bond strengths. That is, a decreasing ν(N–N) implies greater M–N_2 π back-donation with a commensurate increase in the M–N bond strength. Greater π back-donation is also supposed to increase the activation of N_2 towards protonation.[5] This picture is supported by the vibrational spectra of, for example, $[Ru(NH_3)_5(N_2)]^{2+}$ and $[Os(NH_3)_5(N_2)]^{2+}$ which display an increasing ν(M–N) as ν(N–N) falls.[6] A stark exception to this behaviour occurs for the six-co-ordinate complexes *trans*-$[V(dmpe)_2(N_2)_2]^-$ and $[Fe(dmpe)_2H(N_2)]^+$ [dmpe = 1,2-bis(dimethylphosphino)ethane] and the five-co-ordinate $[Fe(depe)_2(N_2)]$ [depe = 1,2-bis(diethylphosphino)ethane].

The complex $[Fe(dmpe)_2H(N_2)]^+$ has a relatively high ν(N–N) of 2094 cm^{-1} [7] suggesting weak π back-donation and hence a weak Fe–N bond and yet the dinitrogen ligand is found to be relatively non-labile.[8] The neutral species $[Fe(dmpe)_2(N_2)]$ has been spectroscopically characterised during the protonation of the cationic complex and is believed to be the active species.[9] The crystallographically characterised depe analogue[10] also has a relatively high value for ν(N–N) (1955 cm^{-1}) and although there is evidence for protonation of the dinitrogen all the way through to ammonia, the yields obtained to date are small. The iron compounds therefore have high N–N stretching frequencies implying weak π back-donation and relatively unreactive N_2 yet the Fe–N bond appears relatively strong. In contrast, ν(N–N) for $[V(dmpe)_2(N_2)_2]^-$ is very low (1763 cm^{-1}) implying extensive π back-donation and thus a strong V–N bond and yet the N_2 can be easily pumped away at room temperature.[11] Thus ν(N–N) seems to be a reliable guide to activation of the dinitrogen towards protons but does not appear to correlate with the observed M–N bond strengths.

This apparent conflict cannot be explained in terms of the simple DCD model described above and has prompted Leigh[8] to conclude that 'ν(N–N) is a guide neither to activation to protonation nor to the eventual product'. To theoretical inorganic chemists, then, the question of interest is whether theory itself is at fault. This resolves into an issue of whether theory can reproduce the observed bonding and reactivity in these complexes.

Given the largely qualitative nature of the experimental data, especially where M–N bond strengths are concerned, we decided to use the equally qualitative extended Hückel molecular orbital (EHMO) method.[12] This approach has often been applied to problems in co-ordination chemistry with considerable qualitative success.[13] Moreover, our recent use of the density functional based discrete variational Xα (DVXα) scheme to a range of model Mo and W dinitrogen complexes was also only capable of a qualitatively reasonable description.[14] As described herein, EHMO calculations are quite consistent with the observed properties of *trans*-$[V(dmpe)_2(N_2)_2]^-$, $[Fe(dmpe)_2H(N_2)]^+$ and $[Fe(depe)_2(N_2)]$ and demonstrate that the apparent anomaly has more to do with the expectation that the simple DCD model is universally applicable rather than to an inadequacy in theory *per se*.

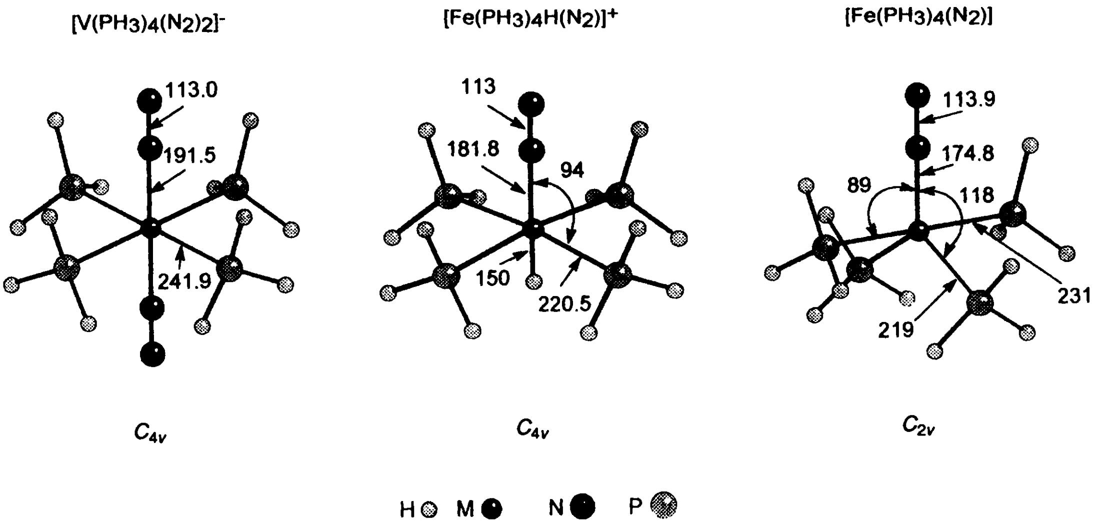


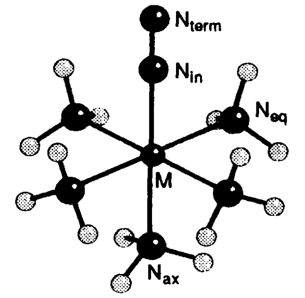
Fig. 1 Schematic representations of the model complexes used in this study. Only relevant bond lengths (pm) and bond angles (°) are shown (All P–H distances are 145 pm and all M–P–H angles are 107°)

Computational Details

All calculations were performed using the EHMO CACAO program system of Mealli and Proserpio.[15] This package implements the standard EHMO method as introduced by Hoffmann.[12] All atomic parameters used were as supplied.

To simplify comparisons, the observed crystal structures of $[V(dmpe)_2(N_2)_2]^-$,[11] $[Fe(dmpe)_2H(N_2)]^+$ [7] and $[Fe(depe)_2(N_2)]$ [10] were idealised as follows. The diphosphine ligands were replaced by PH_3 groups and bond angles for $[V(PH_3)_4(N_2)_2]^-$ and $[Fe(PH_3)_4H(N_2)]^+$ were idealised to yield a C_{4v} geometry. The approximately trigonal-bipyramidal symmetry of $[Fe(PH_3)_4(N_2)]$ was idealised to C_{2v}. The relevant geometrical data are summarised in Fig. 1.

In addition EHMO calculations are reported for $[Ru(NH_3)_5(N_2)]^{2+}$ and $[Os(NH_3)_5(N_2)]^{2+}$ based on the reported structures of the Ru [16] and Os [2a] systems. Relevant geometrical details are shown in Fig. 2.



M	Ru	Os
M–N$_{in}$	210	184
M–N$_{eq}$	212	213.5
M–N$_{ax}$	214	215
N$_{in}$–N$_{term}$	112	112

Fig. 2 Schematic representations of $[Ru(NH_3)_5(N_2)]^{2+}$ and $[Os(NH_3)_5(N_2)]^{2+}$ with relevant bond lengths (pm). All N–M–N and M–N–H angles are 90 and 109° respectively and all N–H distances are 98 pm

Results and Discussion

Dinitrogen complexes have been the subject of widespread synthetic and theoretical interest. Much of the early work concentrated on Mo species[17] since this metal was believed to be the N_2 binding site in the nitrogenase cofactor, FeMoco. Subsequently, vanadium and iron cofactors were discovered but, more significantly, the details emerging from the actual structure of FeMoco suggest a co-ordinatively saturated Mo centre.[3] Hence, interest is shifting towards other metals like vanadium and, in particular, iron. The latter is the only metal common to all three types of nitrogenase cofactor characterised so far.

The diphosphine compounds $[V(dmpe)_2(N_2)_2]^-$, $[Fe(dmpe)_2H(N_2)]^+$ and $[Fe(depe)_2(N_2)]$ have been structurally characterised only relatively recently. We are aware of no theoretical studies on the vanadium compound or $[Fe(dmpe)_2H(N_2)]^+$ although there have been some EHMO studies of Fe–N_2 binding related to the nitrogenase active site[18] and the mode of co-ordination of N_2.[13] Rosi *et al.*[19] have reported Hartree–Fock (HF) calculations on the trigonal-bipyramidal model complex $[Fe(PH_3)_4(N_2)]$ and conclude that side-on co-ordination of N_2 is likely to lead to increased activation towards protonation. The current concensus disagrees with this proposal favouring end-on co-ordination of N_2.[1,18]

The HF approach is well known to give a relatively poor description of metal–phosphorus bonding[20] which presumably explains why Rosi *et al.*[19] did not attempt to optimise the Fe–P bonds although they do not state what distances were actually used. Bond lengths within the Fe–N_2 fragment were optimised although there is a large error in the calculated Fe–N distance which is about 25 pm longer than observed. Evidently the HF results on $[Fe(PH_3)_4(N_2)]$ are suspect. A similar conclusion was reached for $[Mo(PH_3)_4(N_2)_2]$ inasmuch as HF theory predicts[21] a positive rather than negative charge on the terminal nitrogen while both EHMO[13,18] and DVXα[14] calculations describe a more reasonable charge distribution with the terminal nitrogen carrying a net negative charge.

Focusing on end-on N_2 co-ordination, the problem to be solved here for $[V(PH_3)_4(N_2)_2]^-$, $[Fe(PH_3)_4H(N_2)]^+$ and $[Fe(PH_3)_4(N_2)]$ concerns the relative M–N and N–N bond strengths and the activation of dinitrogen toward protonation. Theoretically, we would expect the relevant electronic overlap populations to correlate with bond strengths while the build up of a net negative charge on N_2 would correlate with its activation towards protonation. Given the distinction between σ and π bonding arising from the DCD model, the computed overlap populations are also broken down into their σ and π components (Table 1).

For the N–N bonds, the most striking feature of the calculations is the large variation in π overlap while the σ overlap remains fairly constant. The variation of the total N–N bond strengths is clearly dominated by π effects and there is a good correlation between the increase in ν(N–N) and in the N–N π overlaps, both of which indicate an increasing N–N bond energy in the order: $[V(PH_3)_4(N_2)_2]^- < [Fe(PH_3)_4(N_2)] < [Fe(PH_3)_4H(N_2)]^+$. Conversely, the M–N bond energy is apparently dominated by σ effects inasmuch as the total overlaps for $[V(PH_3)_4(N_2)_2]^-$ and $[Fe(PH_3)_4H(N_2)]^+$ are virtually identical while there is a distinct increase in the

Table 1 Overlap populations (electrons), IR stretching frequencies (cm^{-1}) and net atomic charges, ρ (electrons)

	$[V(PH_3)_4(N_2)_2]^-$	$[Fe(PH_3)_4H(N_2)]^+$	$[Fe(PH_3)_4(N_2)]$
M–N(σ)	0.365	0.433	0.468
M–N(π)	0.188	0.130	0.228
M–N(total)	0.553	0.563	0.796
N–N(σ)	0.840	0.804	0.862
N–N(π)	0.460	0.728	0.645
N–N(total)	1.300	1.591	1.507
ν(N–N)	1763[a]	2094[b]	1955[c]
ρ(M)	2.22	0.29	−0.16
$\rho(N_{in})$	−0.02	0.57	0.51
$\rho(N_{term})$	−0.78	−0.43	−0.52
$\rho(N_2)$	−0.80	0.14	−0.01

[a] Ref. 11. [b] Ref. 7. [c] Ref. 9.

Table 2 Overlap populations (electrons) and IR stretching frequencies (cm^{-1}, ref. 6) for $[Ru(NH_3)_5(N_2)]^{2+}$ and $[Os(NH_3)_5(N_2)]^{2+}$ cations

	$[Ru(NH_3)_5(N_2)]^{2+}$	$[Os(NH_3)_5(N_2)]^{2+}$
M–N(σ)	0.400	0.500
M–N(π)	0.136	0.264
M–N(total)	0.536	0.764
N–N(σ)	0.863	0.870
N–N(π)	0.730	0.616
N–N(total)	1.521	1.486
ν(M–N)	500[a]	546[a]
	499[b]	540[b]
ν(N–N)	2105[a]	2012[a]
	2114[b]	2038[b]

[a] Dichloride salt. [b] Dibromide salt.

σ-overlap populations in line with the observation of an apparently stronger Fe–N than V–N interaction.

Hence, the experimental data can be rationalised if we recognise that the M–N interaction is σ dominated while the N–N interaction is π dominated. The former proposal has been made before.[22] The latter may be more peculiar to the molecules studied here since the value of ν(N–N), which is invariably used as an indicator of the N–N bond strength, will depend on the total N–N overlap. It just happens that in the present systems, the variation in the total arises mainly from changes in the π overlaps.

Evidently for these systems, there is not the clear connection between σ- and π-bonding effects implied by the DCD model and Leigh[8] is quite correct when he asserts that ν(N–N) does not provide a good indicator of the metal–nitrogen interaction. However, it does appear to correlate well with the activation of N_2 towards protonation.

Experimentally, the vanadium molecule protonates more readily than the iron species. This is consistent with the much larger negative charge computed for the terminal N atom in $[V(PH_3)_4(N_2)_2]^-$ (see Table 1). The terminal nitrogens in $[Fe(PH_3)_4H(N_2)]^+$ and $[Fe(PH_3)_4(N_2)]$ are also negatively charged but have a much smaller magnitude. Interestingly, the charge is slightly higher for the neutral Fe species suggesting that removal of H^+ enhances the activity of the co-ordinated N_2. Indeed, the protonation reaction of the cationic species $[Fe(PH_3)_4H(N_2)]^+$ has been studied[9] and it is believed that the active species corresponds to a neutral (model) $[Fe(PH_3)_4(N_2)]$ molecule, which is consistent with the calculations.

Overall, therefore, the EHMO calculations appear to correlate very well with the observed properties of these molecules. They describe a picture of metal–dinitrogen co-ordination in which the separate σ- and π-bonding effects are not necessarily linked in the manner prescribed by the DCD model. However, in order to confirm the reliability of these conclusions, we performed some additional EHMO calculations on the complexes which are widely quoted as providing the experimental support for the DCD picture of metal–dinitrogen bonding in $[Ru(NH_3)_5(N_2)]^{2+}$ and $[Os(NH_3)_5(N_2)]^{2+}$.* Relevant data are shown in Fig. 2 and Table 2. As ν(M–N) goes up from the Ru to the Os complex, ν(N–N) decreases.[6] Likewise, the M–N σ overlap increases (as, incidentally, does the π overlap) while the N–N π overlap decreases. Both theory and experiment are in complete accord with each other and, in this case, with the DCD predictions as well.

Of course, these two complexes have the same structure, number of valence electrons and, even more significantly, the same formal metal oxidation state. In contrast, $[V(PH_3)_4(N_2)_2]^-$, $[Fe(PH_3)_4H(N_2)]^+$ and $[Fe(PH_3)_4(N_2)]$ have different formal oxidation states *viz.* −1, +2 and 0 respectively. One would anticipate a low or even negative formal oxidation state to be associated with an electron-rich metal centre. On the basis of Pauling's electroneutrality principle, the metal would therefore be seeking to lose electron density which would tend to discourage σ donation from the ligand but encourage π back-donation. Conversely, a positive metal oxidation state would tend to encourage σ donation and discourage π back-donation. This simple picture is certainly consistent with the properties of $[V(PH_3)_4(N_2)_2]^-$, $[Fe(PH_3)_4H(N_2)]^+$ and $[Fe(PH_3)_4(N_2)]$ where the decreasing π back-donation [as measured by an increasing ν(N–N)] varies in the order of decreasing formal oxidation state $V^{-1} < Fe^0 < Fe^{2+}$.

The same argument would predict M–N σ bond strengths to increase with the oxidation state and yet they vary in the order $V^{-1} < Fe^{2+} < Fe^0$. Evidently, σ bonding is rather more complicated. Interestingly, the N–N bond lengths in all three molecules are remarkably similar while the M–N distance decreases in the same order as the σ-overlap populations increase (see Fig. 1). The formal oxidation state is not enough to rationalise the M–N bonding. Superimposed on this effect, one could consider two further influences on the nature of the metal–ligand bonding.

First, there is a general increase in the effective nuclear charge, Z_{eff}, on crossing the transition series from left to right. This leads to shorter M–L bonds with enhanced ligand-to-metal charge donation and, presumably, weakened metal-to-ligand charge back-donation. Secondly, the changing nature and number of ligands can affect the M–N_2 bond. In the vanadium complex, there are two dinitrogens in competition with each other while for $[Fe(PH_3)_4H(N_2)]^+$ the N_2 competes with a non-π-bonding H^- ligand. Lastly, $[Fe(PH_3)_4(N_2)]$ is only five-co-ordinate facilitating an even stronger, shorter M–N bond. Apparently, this effect outweighs the change from +2 to 0 in formal oxidation state. Of course, the formal charge is only a rough guide to the actual charge. On the basis of the present

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* EHMO results on these systems have been reported previously.[2a,23] We have repeated the calculations here to maintain internal consistency.

EHMO calculations, the Fe charges on $[Fe(PH_3)_4H(N_2)]^+$ and $[Fe(PH_3)_4(N_2)]$ are 0.29 and −0.16 respectively. The former is certainly more positive but the difference between the actual charges is well removed from two.

Conclusion

Extended Hückel MO calculations on the model complexes *trans*-$[V(PH_3)_4(N_2)_2]^-$, $[Fe(PH_3)_4H(N_2)]^+$ and $[Fe(PH_3)_4(N_2)]$ successfully rationalise the apparent conflict between the observed M–N and N–N bond strengths and the predictions of the Dewar–Chatt–Duncanson synergic bonding model. In these molecules, the apparent increase in π back-bonding, as measured by the decreasing N–N stretching frequency from $[Fe(PH_3)_4H(N_2)]^+$ to $[Fe(PH_3)_4(N_2)]$ to $[V(PH_3)_4(N_2)_2]^-$, is not accompanied by a commensurate increase in the M–N bond strength. The EHMO overlap populations are in accord with experiment and show that the M–N bond is dominated by σ effects while the N–N bond is dominated by π effects. Both the experimental observations and the theoretical calculations reveal that, contrary to the DCD model, a decreasing N–N bond strength need not be accompanied by an increasing M–N bond strength. Thus, $[V(PH_3)_4(N_2)_2]^-$ has both a relatively weak N–N and a relatively weak V–N bond while the corresponding interactions in the iron compounds are both relatively strong.

The gross features of these data can be rationalised in terms of the formal metal charges. The high electron concentration on the formally V^{-1} complex encourages metal-to-ligand π back-donation and discourages ligand-to-metal σ donation while the relatively positive Fe centres encourage σ donation and discourage π back-donation. The iron compounds are, however, subject to further effects. In particular, the change to five-fold co-ordination for $[Fe(PH_3)_4(N_2)]$ appears to be more important than the decrease in formal oxidation state and leads to an overall strengthening of the Fe–N bond.

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