A Theoretical Study on the Co-ordination of Dinitrogen and Related Molecules to Nickel(0): '*Ab initio*' Calculations on the Model Compounds $[Ni(PH_3)_2(N_2)]$, $[Ni(PH_3)_2(N_2CH_2)]$, and $[Ni(PH_3)_2(N_2H_2)]$†

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'*Ab initio*' calculations have been performed on the systems $Ni(PH_3)_2L$, with L = N_2, N_2CH_2, or N_2H_2, to investigate the nature and the energetics of the interaction between nickel and dinitrogen or related molecules. The results indicate that the bonding between the fragment $Ni(PH_3)_2$ and the unsaturated molecule can be explained by the Chatt–Dewar–Duncanson model, although π back donation is much more relevant than σ donation. Dinitrogen prefers to bind to the fragment $Ni(PH_3)_2$ in a side-on fashion rather than in an end-on one, since the former mode implies a more pronounced π back donation than the latter. The most efficient electron transfer from the metal to the dinitrogen, therefore, is achieved by side-on bonding and this point is particularly relevant to nitrogen fixation. Also diazomethane prefers to bind in a side-on mode because of the increased π back donation. This molecule gives rise to a stronger bond than dinitrogen with the fragment $Ni(PH_3)_2$ since it is a better π-acceptor ligand. The species N_2H_2 prefers to bind in a η^2-di-imide form rather than in a σ-hydrazido(2−) one and this may account for the hydrogenation of side-on bonded dinitrogen, and provides some information on the problem of nitrogen reduction.

The dicovalent L_2M^0 (M = Ni, Pd, or Pt) fragment is the most appropriate for an experimental and theoretical study concerning the interaction with unsaturated diatomics X≡Y and X=Y. We will consider the interaction of the electron-rich carbenoid species $Ni(PH_3)_2$ with N_2. Two limiting bonding modes of N_2 have to be considered: end-on, as found in a number of complexes,[1–3] and side-on which has never been observed in any of the monometallic complexes so far identified, but spectroscopically detected in some matrix-isolated M–N_2 species.[2,4] The relative stabilities of the end-on and side-on co-ordination of N_2 in terms of σ donation and π back donation have been discussed by several authors.[5–9] The dinitrogen activation in dinitrogen-bridged transition-metal dimers has been analysed, too.[10–12] All the mononuclear complexes so far theoretically investigated prefer the end-on co-ordination of dinitrogen.[5–9] However, the co-ordination of dinitrogen to a metallic fragment which shows a strong Lewis basicity has never been analysed. The special attention we devoted to the side-on bonding mode, along with the comparison with end-on N_2, is justified by the fact that the most efficient electron transfer can be achieved in this bonding mode.[8,13] This results in the efficient reduction of the N_2 molecule. Our calculations, though on a relative energy scale, suggest that the failure to observe side-on bonding of the N_2 molecule is not associated with any intrinsic bonding instability. On the contrary, we found the side-on to be relatively more stable than the end-on bonding mode for the complex $[Ni(PH_3)_2(N_2)]$. Moreover, the results of our calculations confirm that the side-on bonding mode is the best way to transfer electrons from the metal to the N_2 molecule.

The comparison of the two limiting bonding modes was extended to diazomethane, which is an organic functionality closely related to the $M\overset{...}{-}N\overset{...}{-}N$ fragment. The diazo-fragment $>C{=}N^+{=}N^-$ may be viewed as a species with a polarized N_2 molecule. Significant differences have been found in the amount of electron transfer from the metal to the N_2 fragment, depending on the bonding mode, the most stable being the complex containing a side-on diazoalkane. Both bonding modes have been found in the co-ordination of $R_2C{=}N{=}N$ to a metal centre.[14–16]

Studies on the metal-bonded N_2 fragment have also been carried out by an investigation of the energetics of N_2H_2 bonded to the metal in the di-imide (diazene) HN=NH and hydrazido(2−) $N^-{=}N^+H_2$ form. Such a species has been considered as the first intermediate derived from the hydrogenation of N_2.[1,2,17–20] The higher stability of the η^2-N_2H_2 species may account for the hydrogenation of a side-on bonded dinitrogen.

Computational Details

Basis Sets.—The *s,p* basis for nickel was taken from the (12*s*6*p*4*d*) set of ref. 21 with the addition of two basis functions to describe the 4*p* orbital,[22] while the Ni *d* basis was the reoptimized (5*d*) set of ref. 23, contracted (4/1). This leads to an (11*s*8*p*5*d*) primitive basis for nickel, contracted (8*s*6*p*2*d*). The MINI-1 basis[24] was used for the phosphorus atoms, while a double ζ expansion was used for all the other ligand atoms, with a (4*s*/2*s*) basis for hydrogen[25] and a (9*s*5*p*/4*s*2*p*) contraction for carbon and nitrogen.[25]

Methods.—Two levels of theory have been employed. '*Ab initio*' spin-restricted Hartree–Fock gradient calculations were used in partial geometry optimizations of the dinitrogen (with N_2 bonded both side-on and end-on to the metal), the di-imide

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† *Non-S.I. units employed:* cal = 4.184 J, Hartree = 4.36×10^{-18} J.

and hydrazido(2−) complexes, and in deriving estimates of the binding energies of all complexes with respect to free $Ni(PH_3)_2$ and N_2, N_2CH_2, or N_2H_2. Single- and multi-reference state configuration interaction calculations [hereafter referred to as single plus double configuration interaction (s.d.c.i.) and multi-reference single plus double configuration interaction (m.r.s.d.c.i.), respectively] were subsequently performed on the dinitrogen complex and associated fragments, including single and double excitations from the outer valence orbitals using the direct-c.i. method.[26] The SCF ground-state configuration was chosen as the reference function in the s.d.c.i. calculations. All the configurations with a coefficient greater than 0.05 in the s.d.c.i. wavefunction were chosen as reference functions in the m.r.s.d.c.i. calculations. Davidson's correction[27] was always added to correct for the effect of unlinked clusters in the s.d.c.i. calculations. A multi-reference analogue of Davidson's correction[28] was added in the m.r.s.d.c.i. calculations.

All computations were performed by using the GAMESS program package,[29] implemented on a CRAY XMP/48 computer.

Although the electronic states $^3D(3d^94s^1)$, $^3F(3d^84s^2)$, and $^1S(3d^{10})$ lie energetically close to each other in the free nickel atom, the ground state of a zerovalent nickel complex $Ni(PH_3)_2L$, with L an unsaturated ligand, is considered to be a closed-shell singlet.[30] Indeed the ground state of the fragment NiL (with L = N_2,[8] C_2H_4,[31] or CO[32,33]) is calculated to be a closed-shell singlet, when correlation effects are considered; moreover, the presence of the two PH_3 ligands should destabilize the more diffuse 4*s* and 4*p* orbitals to a larger extent than the 3*d*. Both factors justify the assumed d^{10} electronic configuration in $Ni(PH_3)_2L$. Dissociation of this complex to the fragments $Ni(PH_3)_2$ and L may lead to either singlet or triplet products. The ground state of dinitrogen,[34] diazomethane,[35] and *trans*-diazene[36] is experimentally known to be a singlet. To our knowledge, no experimental information is available on the ground state of hydrazido(2−), although it has been calculated to be the singlet $^1A_1$, when correlation is considered.[37] The ground state of the $Ni(PH_3)_2$ fragment, too, was recently calculated to be a singlet.[33] Fragmentation of the analysed complexes should therefore lead to singlet products. Consequently, the theoretical results which will be discussed in the following sections refer to the lowest singlet states of the molecular species investigated.

Geometries and Geometry Optimization.—In the complexes $Ni(PH_3)_2L$, with L = N_2, N_2CH_2, or N_2H_2, we have considered both side-on and end-on co-ordination of the ligand L. The Ni–P bond length and the starting value for the optimization of the P–Ni–P bond angle were derived from the experimental structure of $[Ni\{P(C_6H_4Me\text{-}p)_3\}_2(PhN{=}NPh)]$;[38] the experimental geometry of free PH_3 was used.[39]

For L = N_2, we have optimized the Ni–N, N–N, and P–Ni–P geometrical parameters for both side-on and end-on co-ordination modes; the results are shown in Figure 1. For the side-on complex both a planar and a pseudo-tetrahedral structure were examined: the latter is calculated to be less stable than the former by about 17 kcal mol^{-1} and, therefore, only the results relative to the planar compound have been reported. In the s.d.c.i. and m.r.s.d.c.i. calculations the Hartree–Fock optimized geometries were used, with P–Ni–P 118° for both dinitrogen complexes and the $Ni(PH_3)_2$ fragment.

For the diazomethane complexes, we derived the Ni–N and N–N bond lengths from the corresponding dinitrogen complexes; standard values were employed for N–C (1.34), C–H (1.08 Å), and H–C–H (120°). The N–N–C bond angle was 180° in the end-on complex and 140° in the side-on one. No geometry optimizations were performed for the diazo-complexes since the energy difference between the side-on and the end-on compounds at the fixed geometries was very high (about 36 kcal mol^{-1}).

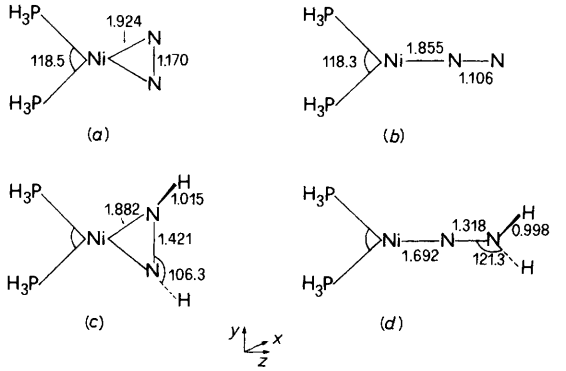

Figure 1. Optimized geometries of the η^2-N_2 (*a*), σ-N_2 (*b*), η^2-HNNH (*c*), and σ-NNH_2 (*d*) compounds. Bond lengths in Å, angles in °

For L = N_2H_2, we have considered the side-on co-ordination of *trans*-diazene and the end-on binding of hydrazido(2−). It is well established that *cis*-diazene is less stable.[40] The Ni–N, N–N, and N–H bond lengths and H–N–N bond angles were optimized and the results are shown in Figure 1; the P–Ni–P bond angle was fixed at 118° {value taken from the optimized structures of $[Ni(PH_3)_2(N_2)]$} for both compounds.

The geometry of the $Ni(PH_3)_2$ fragment was assumed equal to that of the corresponding $Ni(PH_3)_2L$ complexes, while the geometries of the free L ligands were optimized.

Results and Discussion

Interaction between $Ni(PH_3)_2$ *and* N_2.—The total SCF energies of the complexes under investigation, together with estimates of the binding energies, are listed in Table 1. We start our analysis with the complex $[Ni(PH_3)_2(N_2)]$, with dinitrogen bonded side-on and end-on to the metal. Bond formation between nickel and the unsaturated ligand can result either from a substitution reaction [equation (1)], or from addition to a 'hot' metallic fragment [equation (3)] thermally or photochemically generated in a previous stage [equation (2)]. The

$$Ni(PH_3)_2L' + L \longrightarrow Ni(PH_3)_2L + L' \qquad (1)$$

$$Ni(PH_3)_2L' \xrightarrow{h\nu \text{ or heat}} \text{'}Ni(PH_3)_2\text{'} + L' \qquad (2)$$

$$\text{'}Ni(PH_3)_2\text{'} + L \longrightarrow Ni(PH_3)_2L \qquad (3)$$

binding energy between the metal and the ligand L is that related to reaction (3). Since we use frozen-geometry fragments and partially optimized complex geometries, we expect our calculated binding energies to overestimate somewhat (in absolute value) the true fragmentation energies of the complexes, but this should not unduly affect our comparative analysis.

In our model the binding energy (b.e.) can be thought of as the sum of a positive deformation energy arising from the distortion of an unsaturated ligand and a negative interaction energy resulting from the interaction between the nickel fragment and the distorted ligand.[30] The deformation and interaction energies are also reported in Table 1.

The SCF binding energies are calculated to be −15.1 and −12.6 kcal mol^{-1} for side-on and end-on dinitrogen complexes, respectively (Table 1). To attempt an interpretation of these

Table 1. Total SCF energies (Hartree) and binding (b.e.), deformation, and interaction energies (kcal mol^{-1}) of the analysed systems; E_L and e_π* are the total SCF and the π*-orbital energies (Hartree) of the deformed unsaturated ligands N_2, N_2CH_2, or N_2H_2. The total SCF energy (Hartree) of the $Ni(PH_3)_2$ fragment is −2187.7252 and −2187.7183 for P–Ni–P 118 and 107.4°, respectively

	$[Ni(PH_3)_2(N_2)]$		$[Ni(PH_3)_2(N_2CH_2)]$		NH $Ni(Ph_3)_2$ NH	$Ni(PH_3)_2$-N-NH_2
	Side-on	End-on	Side-on	End-on		
E_{SCF}	−2 296.6275	−2 296.6236	−2 335.5684	−2 335.5115	−2 297.7491	−2 297.7167
E_L	−108.8635	−108.8782	−147.7547	−147.7780	−109.9138	−109.9358
b.e.	−15.1	−12.6	−42.9	−7.2	−45.9	−32.6
Deformation energy	9.3	0.06	18.4	3.8	23.2	2.3
Interaction energy	−24.4	−12.7	−61.3	−11.0	−69.1	−34.9
e_π*	0.1067	0.1394	0.0677	0.1253	0.0562	0.1246

Table 2. Mulliken population changes* for interaction between $Ni(PH_3)_2$ and L (L = N_2, N_2CH_2, or N_2H_2)

	$[Ni(PH_3)_2(N_2)]$		$[Ni(PH_3)_2(N_2CH_2)]$		NH $Ni(PH_3)_2$ NH	$Ni(PH_3)_2$-N-NH_2
	Side-on	End-on	Side-on	End-on		
Ni*s*	+0.11	+0.09	+0.10	+0.07	+0.16	+0.07
Ni*p*	+0.22	+0.12	+0.23	+0.07	+0.28	+0.26
p_x	+0.02	−0.01	+0.03	−0.01	+0.03	+0.06
p_y	+0.02	−0.01	+0.03	−0.03	+0.03	+0.01
p_z	+0.18	+0.14	+0.17	+0.11	+0.22	+0.19
Ni*d*	−0.43	−0.19	−0.67	−0.17	−0.67	−0.61
$d_{x^2-y^2}$	+0.05	+0.03	+0.06	+0.02	+0.07	+0.05
d_{z^2}	+0.03	−0.07	+0.05	−0.08	+0.06	+0.01
d_{xy}	+0.01	+0.01	+0.02	+0.01	+0.03	+0.02
d_{xz}	+0.04	−0.03	+0.04	−0.09	+0.04	+0.02
d_{yz}	−0.56	−0.13	−0.84	−0.03	−0.87	−0.71
$2PH_3$	−0.20	−0.04	−0.29	−0.01	−0.27	−0.15
L	+0.30	+0.02	+0.63	+0.04	+0.50	+0.43

* [Mulliken population of the complex] − [Mulliken population of fragment $Ni(PH_3)_2$ or L].

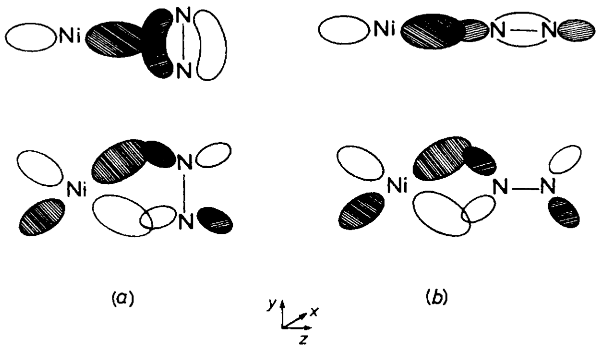

Figure 2. Schematic representation of orbital interactions involved in the Chatt–Dewar–Duncanson model for (*a*) side-on and (*b*) end-on bonded dinitrogen

data we must first analyse the bond structure of the complexes. The binding of an unsaturated ligand, such as dinitrogen, to a carbenoid metallic fragment is usually described by the Chatt–Dewar–Duncanson model[41] with σ donation from the ligand lone pair or π orbital to the metal atom and π back donation from the metal to the π* orbital of the ligand. A schematic representation of these interactions is shown in Figure 2. This picture holds also for $[Ni(PH_3)_2(N_2)]$ with the dinitrogen bonded both side-on or end-on, although π back donation is more relevant than σ donation. Indeed, the analysis of the molecular orbitals of $[Ni(PH_3)_2(N_2)]$ shows that the main bonding orbital between nickel and dinitrogen is the highest occupied one (h.o.m.o.) for both co-ordination modes of N_2. This orbital can be viewed as the overlap between the occupied $3d_{yz}$ orbital of the nickel (hereafter denoted as d_π) and one of the two components of the virtual $1\pi_g$ orbital of N_2 (hereafter denoted as π*). Thus the h.o.m.o. describes π back donation from the nickel to the dinitrogen. σ Donation takes place from one component of the $1\pi_u$ orbital of N_2 for side-on co-ordination and from the $3\sigma_g$ orbital for end-on co-ordination to an hybrid orbital of nickel (hereafter denoted as d_σ), formed mainly by $4s$,$4p_z$. The predominant role played by π back donation, with respect to σ donation, is confirmed by the Mulliken population analysis, whose results are reported in Table 2 as population changes, *i.e.* Mulliken population of the complex minus Mulliken population of the fragments. We notice a strong decrease of the population of the d_π orbital of the nickel (0.56 e for side-on, 0.13 e for end-on co-ordination) and, consequently, an increase of the population of the π* orbital of dinitrogen. The increase of the population of the d_σ orbital of the nickel is also substantial, but, for side-on co-ordination, it is mainly due to the electron-donor character of the phosphine ligands. The results of Table 2 show that there is a stronger interaction, and, particularly, a more pronounced π back donation, for side-on co-ordination of dinitrogen, in agreement with the binding energies of Table 1. Instead, the σ and π interactions are almost comparable for end-on co-ordination. The presence of a higher π back donation in the side-on complex is also confirmed by the energy of the π* orbital of N_2 in the distorted geometry of the complexes, reported in Table 1. This orbital overlaps with the d_π orbital of the nickel fragment whose energy is −0.2438 Hartree: the side-on co-ordination implies a better overlap and, therefore, an increased interaction. The energies of the π* orbital are related to the degree of deformation of dinitrogen upon co-ordination; from Figure 1, where we have reported the partially optimized structures of the

Table 3. Details and results of the c.i. calculations on $[Ni(PH_3)_2(N_2)]$ and the separated fragments; E in Hartree and b.e. in kcal mol^{-1}

	$Ni(PH_3)_2$	N_2	$[Ni(PH_3)_2(N_2)]$	
			Side-on	End-on
$N^{\text{active}}_{\text{orbitals}}$	39	16	55	55
$N^{\text{active}}_{\text{electrons}}$	26	10	36	36
$N^{\text{s.d.c.i.}}_{\text{configurat.}}$	14 867	260	57 797	58 029
$N^{\text{m.r.s.d.c.i.}}_{\text{configurat.}}$		2 225	298 247	115 363
E_{SCF}	−2 187.7252	−108.8783	−2 296.6275	−2 296.6236
$E_{\text{s.d.c.i.}}$	−2 188.1149	−109.0996	−2 297.2582	−2 297.2492
$E_{\text{m.r.s.d.c.i.}}$		−109.1110	−2 297.2799	−2 297.2574
b.e.$_{\text{SCF}}$			−15.1	−12.6
b.e.$_{\text{s.d.c.i.}}$			−27.4	−21.8
b.e.$_{\text{m.r.s.d.c.i.}}$			−33.9	−19.8

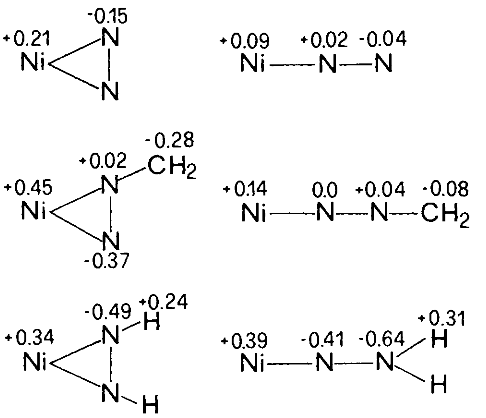

Figure 3. Net atomic charges (electronic units) obtained by accumulating the Mulliken populations

complexes, we can see that the N–N bond is elongated in the side-on complex (1.170 Å), but not in the end-on one (1.106 Å) (the experimental N–N bond distance is 1.097 68 Å).[34] The deformation energy of the side-on complex (9.3 kcal mol^{-1}) is much higher than that of the end-on one (0.06 kcal mol^{-1}), but it is more than compensated by the increased interaction energy (−24.4 for side-on, −12.7 kcal mol^{-1} for end-on).

It is interesting that in the end-on dinitrogen complex the terminal nitrogen atom is more negatively charged than the co-ordinating one. Indeed the charges on the atoms, obtained by accumulating the Mulliken populations and reported in Figure 3, are computed to be −0.04 e on the terminal nitrogen atom and +0.02 e on the co-ordinating one. This result is in agreement with ESCA (electron spectroscopy for chemical analysis) studies[42] and electron emission spectra,[43] which suggest that the terminal nitrogen atom presents a higher negative charge than the co-ordinating one. Hoffmann *et al.*[44] have explained this fact by considering the allyl-type orbital mixing. Sakaki *et al.*[9] suggest that two factors, 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 co-ordinating nitrogen atom is more negatively charged than the terminal one, as is observed in Rh^{I}–N_2 complexes,[9] while when the metal is in a low oxidation state, as in $[Ni(PH_3)_2(N_2)]$, the orbital mixing is more important and the terminal nitrogen atom is the nucleophilic centre, which could react with electron-acceptor molecules.[45]

The charge distribution on the dinitrogen end-on bonded to a low-valent metal, M–$N^{\delta+}$–$N^{\delta-}$, allows an interesting comparison with the diazoalkane functionality, $R_2C{=}N^{+}{=}N^{-}$. This result suggests that an end-on metal-bonded dinitrogen can engage in the same reactions as diazoalkanes with metal complexes.[46] Such a reaction will produce complexes of dinitrogen interacting with two different metals, which is a major prospect in this field.[47]

The preference for side-on co-ordination, with respect to the end-on one, for the dinitrogen interacting with the $Ni(PH_3)_2$ fragment is a rather unexpected result, since it is well known that dinitrogen interacting with an isolated nickel atom prefers end-on co-ordination.[6,8,48] Since correlation effects may play a fundamental role and even reverse the relative stabilities of the analysed systems because of the small energy difference between them, configuration interaction calculations have been performed on the two dinitrogen complexes and relative fragments, by using the direct-c.i. method.[26] To reduce the size of the c.i. problem (39 doubly occupied orbitals and 88 basis functions) for the $[Ni(PH_3)_2(N_2)]$ complexes, 42 electrons have been frozen. In the evaluation of the energies of $Ni(PH_3)_2$ and N_2, the orbitals correlating with those frozen in the complex have also been frozen. For the $Ni(PH_3)_2$ fragment only s.d.c.i. calculations have been performed since no configurations with a coefficient greater than 0.05 were present in the s.d.c.i. wavefunction. The preference for the side-on co-ordination of dinitrogen, with respect to the end-on one, in the case of the $Ni(PH_3)_2$ fragment is confirmed by the c.i. calculations, whose results are reported in Table 3. We notice an increase of the binding energy for both co-ordination modes of dinitrogen; this increase, however, is more pronounced for side-on co-ordination and it is particularly relevant in the m.r.s.d.c.i. calculations.

At this point we can suggest with some confidence that the dinitrogen molecule prefers to bind to the $Ni(PH_3)_2$ fragment in a side-on fashion, rather than in an end-on mode. This point is particularly interesting for its implications in the problem of nitrogen fixation. In the side-on bonded dinitrogen complex we have a higher electron transfer from the metal to N_2: the negative charge in the dinitrogen molecule is 0.30 e in the side-on complex and just 0.02 e in the end-on one. Moreover, the N–N bond is stretched only in the side-on complex. Therefore, we can conclude that only side-on co-ordination leads to an activation of dinitrogen. Such a co-ordination seems to be possible in the presence of appropriate ligands. The preference of Ni^0 in $[Ni\{P(C_6H_{11})_3\}_2(N_2)]$ and $[\{Ni[P(C_6H_{11})_3]_2\}_2N_2]$[49] may be associated with a more complex energetic balance. The end-on bonding mode allows the co-ordination of a fourth ligand,[50] *i.e.* solvent, *etc.*, or the formation of a dimer.[49]

Interaction between $Ni(PH_3)_2$ *and* N_2CH_2.—The total SCF energies of the $[Ni(PH_3)_2(N_2CH_2)]$ complex, with the diazomethane bonded both side-on and end-on to the metal centre, are reported in Table 1, together with estimates of the binding energies. These energies are computed to be -42.9 and -7.2 kcal mol^{-1} for side-on and end-on co-ordination of N_2CH_2, respectively: therefore, the diazomethane prefers to bind to the $Ni(PH_3)_2$ fragment in a side-on fashion. This result is in agreement with the known structures of nickel(0) complexes containing diazoalkanes,[15] which show an η^2 co-ordination of the diazo-molecule. The analysis of the molecular orbitals shows that the bonding between the nickel fragment and the diazo-molecule can be described, as in the case of the dinitrogen molecule, by the Chatt–Dewar–Duncanson model,[41] with ligand-to-metal σ donation and metal-to-ligand π back donation. However, π back donation is much more relevant than σ donation and this is confirmed by the Mulliken population analysis, whose results are shown in Table 2. π Back donation is particularly important for side-on co-ordination of N_2CH_2: the decrease in population of the d_π orbital, upon co-ordination, is 0.84 e. We notice also a non-negligible increase in population of the d_σ orbital in the case of side-on co-ordination, but this is mainly due to the donor character of the phosphine ligands: there is a decrease of 0.29 e in the population of the phosphines upon co-ordination of N_2CH_2. The diazomethane prefers to bind to the $Ni(PH_3)_2$ fragment in a side-on fashion, rather than in an end-on one, since this co-ordination mode implies an increased π back donation and, therefore, a stronger interaction with the metal centre. The π^*-orbital energies of the deformed N_2CH_2 molecule, Table 1, also suggest that π back donation is higher in the side-on complex, because of the smaller energy gap with the d_π orbital. The deformation energy required by side-on co-ordination of N_2CH_2 is higher, with respect to the end-on one (18.4 and 3.8 kcal mol^{-1}, respectively), but it is more than compensated by the increased interaction energy (-61.3 and -11.0 kcal mol^{-1} for side-on and end-on bonding, respectively).

Of interest is the polarizing effect exhibited by the CH_2 group. The nitrogen atom bonded to the CH_2 group shows a small positive charge, as we can see from Figure 3 where we have reported the charges obtained by accumulating the Mulliken populations, while the other nitrogen atom presents a more nucleophilic character, particularly evident in the side-on complex, where the negative charge on this nitrogen atom is 0.37 e. In the free diazomethane molecule, too, the terminal nitrogen atom is more nucleophilic than the CH_2-bound one, but the side-on co-ordination of N_2CH_2 to the nickel centre strengthens this feature.

It is interesting to compare the electronic charges on the nitrogen atoms of the side-on bonded dinitrogen and diazomethane molecules. In the dinitrogen compound both N atoms exhibit a nucleophilic character, while in the diazomethane compound only the N atom not bonded to the CH_2 group shows a nucleophilic character, which, however, is much higher due to the polarizing effect of CH_2.

Finally it is worth noting that the N_2CH_2 molecule gives rise to a stronger bond with the $Ni(PH_3)_2$ fragment than the dinitrogen, for side-on co-ordination, due to the higher π back donation, as is suggested by the Mulliken populations of Table 2 and by the π^*-orbital energies of Table 1.

Interaction between $Ni(PH_3)_2$ *and* N_2H_2.—The reduction of a dinitrogen molecule co-ordinated to a metal centre is supposed to proceed through a di-imide intermediate, sometimes.[20] It undoubtedly passes through a hydrazido(2−)-intermediate in reactions of compounds of the type $[M(N_2)_2L_4]$ (M = Mo or W; L = monotertiary phosphine).[2,51] To analyse the nature of such an intermediate, we have studied the co-ordination of *trans*-diazene and hydrazido(2−) to the $Ni(PH_3)_2$ fragment. The optimized structures of the investigated complexes are shown in Figure 1. We notice a strong lengthening of the N–N bond distance upon co-ordination in both compounds. In particular, in the *trans*-diazene ligand the N–N bond length changes from the experimental value of 1.252 Å found in the free molecule,[52] which corresponds to a double bond, to 1.421 Å which can be considered typical of a single bond. This value is even longer than the experimental ones found in some complexes of azobenzene co-ordinated to nickel(0) fragments.[38,53] The value of 1.318 Å, calculated for the N–N bond distance in the hydrazido(2−)-compound, is intermediate between a single and a double bond and is longer than the optimized value for the free molecule (1.216 Å).[37] The Ni–N distance of 1.882 Å calculated for the *trans*-diazene compound is comparable with those found in some complexes of azobenzene co-ordinated to Ni^0.[38,53] The Ni–N distance of 1.692 Å calculated for the hydrazido(2−)-compound suggests the presence of a partial double bond between the metal centre and the nitrogen atom.

The total SCF energies of the two analysed systems, Ni–η^2-N_2H_2 and Ni–σ-NNH_2, are reported in Table 1, together with estimates of the binding energies. These energies are computed to be -45.9 and -32.6 kcal mol^{-1} for the *trans*-diazene and hydrazido(2−), respectively. *trans*-Diazene gives rise to a stronger bond with the $Ni(PH_3)_2$ fragment than hydrazido(2−), even though it requires a much higher deformation energy [23.2 kcal mol^{-1} for *trans*-diazene and 2.3 kcal mol^{-1} for hydrazido(2−)]. The analysis of the molecular orbitals shows that the bonding between N_2H_2 and $Ni(PH_3)_2$ can again be explained by the Chatt–Dewar–Duncanson model,[41] although the main bonding interaction is π back donation, as already found in the case of dinitrogen and diazomethane.

The Mulliken population analysis (Table 2) suggests that the *trans*-diazene molecule exhibits both a stronger π back donation and σ donation than hydrazido(2−), in agreement with the binding energies of Table 1. Indeed, from Table 2 we can see that the decrease of the d_π orbital population upon co-ordination of N_2H_2 is 0.87 e for *trans*-diazene and 0.71 e for hydrazido(2−). Also the increase of the d_σ orbital population is larger in the case of *trans*-diazene with respect to hydrazido(2−): however, this increase is partly due to the electron-donor character of the phosphine ligands, whose population decreases upon co-ordination of the unsaturated L molecule.

The charges reported in Figure 3 show that the nitrogen atoms in both compounds are negatively charged and can support electrophilic attack, as is required in the proposed reduction mechanisms for dinitrogen. Our calculations suggest the preference for a di-imido-intermediate rather than a hydrazido(2−) one and, therefore, give some support to the mechanism which implies the presence of a di-imido-intermediate for the reduction of dinitrogen,[20] although they do not allow one to discard the other mechanism[2] since the energy difference between the two analysed intermediates is not very high and correlation effects are not included.

At this point we notice that in all the analysed systems π back donation is more important that σ donation: indeed, in all the studied $Ni(PH_3)_2L$ systems the L ligand shows an overall negative charge. This result is in agreement with the conclusions of Sakaki *et al.*[9] which suggest that the $Ni(PH_3)_2$ fragment can form only a strong back-donative interaction since it has both d_π and d_σ orbitals at a considerably higher energy with respect to other metallic fragments.

Conclusions

The study at '*ab initio*' level of the systems $Ni(PH_3)_2L$ with L = N_2, N_2CH_2, or N_2H_2 has shown that the bonding between the fragment $Ni(PH_3)_2$ and the unsaturated molecule can be explained by the Chatt–Dewar–Duncanson model, although π back donation is much more relevant than σ donation. Dinitrogen prefers to bind to the fragment $Ni(PH_3)_2$ in a side-on fashion rather than in an end-on one, since this co-ordination mode implies an increased π back-donative interaction. This point is particularly important for its implications in the problem of nitrogen fixation. Indeed, the most efficient electron transfer can be achieved by the side-on bonding mode. This results in an efficient activation mechanism of the N_2 molecule.

Diazomethane, too, prefers to bind in a side-on mode because of the increased π back donation and this molecule gives rise to a stronger bond than dinitrogen with the fragment $Ni(PH_3)_2$ since its π^* orbital lies at lower energy.

The higher stability of the η^2-N_2H_2 complex, with respect to the σ-NNH_2 species, may account for the hydrogenation of a side-on bonded dinitrogen and gives some support to the reduction mechanism of dinitrogen, which implies the presence of a di-imido-intermediate.

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References

1 R. A. Henderson, G. J. Leigh, and C. J. Pickett, *Adv. Inorg. Chem. Radiochem.*, 1983, **27**, 197.
2 J. Chatt, J. R. Dilworth, and R. L. Richards, *Chem. Rev.*, 1978, **78**, 589.
3 P. Pelikán and R. Boca, *Coord. Chem. Rev.*, 1984, **55**, 55.
4 G. A. Ozin and A. Vander Voet, *Can. J. Chem.*, 1973, **51**, 637; *Acc. Chem. Res.*, 1973, **6**, 313.
5 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.
6 H. Veillard, *Nouv. J. Chim.*, 1978, **2**, 215.
7 K. Hori, Y. Asai, and T. Yamabe, *Inorg. Chem.*, 1983, **22**, 3218.
8 P. E. M. Siegbahn and M. R. A. Blomberg, *Chem. Phys.*, 1984, **87**, 189.
9 S. Sakaki, K. Morokuma, and K. Ohkubo, *J. Am. Chem. Soc.*, 1985, **107**, 2686.
10 A. K. Rappé, *Inorg. Chem.*, 1984, **23**, 995; 1986, **25**, 4686.
11 C. B. Powell and M. B. Hall, *Inorg. Chem.*, 1984, **23**, 4619.
12 K. I. Goldberg, D. M. Hoffman, and R. Hoffmann, *Inorg. Chem.*, 1982, **21**, 3863.
13 C. W. Bauschlicher, jun., L. G. M. Pettersson, and P. E. M. Siegbahn, *J. Chem. Phys.*, 1987, **87**, 2129.
14 S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Am. Chem. Soc.*, 1982, **104**, 1918.
15 K. D. Schramm and J. A. Ibers, *Inorg. Chem.*, 1980, **19**, 2441; A. Nakamura, T. Yoshida, M. Cowie, S. Otsuka, and J. A. Ibers, *J. Am. Chem. Soc.*, 1977, **99**, 2108.
16 M. Hidai, Y. Mizobe, M. Sato, T. Kodama, and Y. Uchida, *J. Am. Chem. Soc.*, 1978, **100**, 5740; K. D. Schramm and J. A. Ibers, *Inorg. Chem.*, 1980, **19**, 1231; 2435.
17 J. R. Dilworth and R. L. Richards, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, vol. 8, pp. 1073—1106.
18 J. Chatt, *Chemtech*, 1981, 162.
19 J. A. Baumann, G. E. Bossard, T. A. George, D. B. Howell, L. M. Koczon, R. K. Lester, and C. M. Noddings, *Inorg. Chem.*, 1985, **24**, 3568.
20 N. H. Liu, N. Strampach, J. G. Palmer, and G. N. Schrauzer, *Inorg. Chem.*, 1984, **23**, 2772; G. N. Schrauzer, N. Strampach, and L. A. Hughes, *ibid.*, 1982, **21**, 2184; G. N. Schrauzer and M. R. Palmer, *J. Am. Chem. Soc.*, 1981, **103**, 2659; S. I. Zones, M. R. Palmer, J. G. Palmer, J. M. Doemeny, and G. N. Schrauzer, *ibid.*, 1978, **100**, 2113; S. I. Zones, T. M. Vickrey, J. G. Palmer, and G. N. Schrauzer, *ibid.*, 1976, **98**, 7289.
21 R. Roos, A. Veillard, and G. Vinot, *Theor. Chim. Acta*, 1971, **20**, 1.
22 D. M. Hood, R. M. Pitzer, and H. F. Schaefer III, *J. Chem. Phys.*, 1979, **71**, 705.
23 A. K. Rappe, T. A. Smedley, and W. A. Goddard III, *J. Phys. Chem.*, 1981, **85**, 2607.
24 Y. Sakai, H. Tatewaki, and S. Huzinaga, *J. Comput. Chem.*, 1981, **2**, 100.
25 T. H. Dunning, jun., *J. Chem. Phys.*, 1970, **53**, 2823.
26 V. R. Saunders and J. H. Van Lenthe, *Mol. Phys.*, 1983, **48**, 923.
27 E. R. Davidson, in 'The World of Quantum Chemistry,' eds. R. Daudel and B. Pullman, Reidel, Dordrecht, 1974.
28 M. R. A. Blomberg and P. E. M. Siegbahn, *J. Chem. Phys.*, 1983, **78**, 5682.
29 M. Dupuis, D. Spangler, and J. Wendolowski, NRCC Software Catalog, National Resource for Computation in Chemistry, Lawrence Berkeley Laboratory, University of California, Berkeley, CA, 1980, vol. 1, Program No. QG01 (GAMESS); M. F. Guest and J. Kendrick, GAMESS User Manual, Daresbury Technical Memorandum, Daresbury Laboratory, 1985.
30 S. Sakaki, K. Kitaura, and K. Morokuma, *Inorg. Chem.*, 1982, **21**, 760.
31 P. O. Widmark, B. O. Roos, and P. E. M. Siegbahn, *J. Phys. Chem.*, 1985, **89**, 2180.
32 A. B. Rives and R. F. Fenske, *J. Chem. Phys.*, 1981, **75**, 1293.
33 M. R. A. Blomberg, U. B. Brandemark, P. E. M. Siegbahn, K. B. Mathisen, and G. Karlström, *J. Phys. Chem.*, 1985, **89**, 2171.
34 K. P. Huber and G. Herzberg, 'Constants of Diatomic Molecules,' Van Nostrand, New York, 1979.
35 G. Herzberg, 'Electronic Spectra and Electronic Structure of Polyatomic Molecules,' Van Nostrand, Princeton, 1966.
36 C. Willis and R. A. Back, *Can. J. Chem.*, 1973, **51**, 3605.
37 J. H. Davis and W. A. Goddard III, *J. Am. Chem. Soc.*, 1977, **99**, 7111.
38 S. D. Ittel and J. A. Ibers, *J. Organomet. Chem.*, 1973, **57**, 389.
39 E. Sutton, 'Tables of Interatomic Distances and Configuration in Molecules and Ions,' The Chemical Society, London, 1958.
40 U. Brandemark and P. E. M. Siegbahn, *Theor. Chim. Acta*, 1984, **66**, 217.
41 M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, 1951, **18c**, 71; J. Chatt and J. A. Duncanson, *J. Chem. Soc.*, 1953, 2939.
42 F. Finn and W. L. Jolly, *Inorg. Chem.*, 1972, **11**, 1434; H. Binder and D. Sellmann, *Angew. Chem., Int. Ed. Engl.*, 1973, **12**, 1017; J. Chatt, C. M. Elson, N. E. Hooper, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 1975, 2392.
43 G. J. Leigh, J. N. Murrell, W. Bremser, and W. G. Proctor, *Chem. Commun.*, 1970, 1661.
44 R. Hoffmann, M. M. L. Chen, and D. L. Thorn, *Inorg. Chem.*, 1977, **16**, 503; D. L. DuBois and R. Hoffmann, *Nouv. J. Chim.*, 1977, **1**, 479.
45 J. Chatt, J. R. Dilworth, G. J. Leigh, and R. L. Richards, *Chem. Commun.*, 1970, 955.
46 S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1982, 1015; *J. Am. Chem. Soc.*, 1983, **105**, 7295; *Inorg. Chem.*, 1983, **22**, 2029.
47 C. Floriani and F. Corazza, unpublished work.
48 H. Itoh, G. Ertl, and A. B. Kunz, *Chem. Phys.*, 1981, **59**, 149.
49 P. W. Jolly, K. Jonas, C. Krüger, and Y-H. Tsay, *J. Organomet. Chem.*, 1971, **33**, 109; M. Aresta, C. F. Nobile, and A. Sacco, *Inorg. Chim. Acta*, 1975, **12**, 167.
50 C. A. Tolman, D. H. Gerlach, J. P. Jesson, and R. A. Schunn, *J. Organomet. Chem.*, 1974, **65**, C23.
51 J. Chatt, A. J. Pearman, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1977, 1852.
52 M. Carlotti, J. W. C. Johns, and A. Trombetti, *Can. J. Phys.*, 1974, **52**, 340.
53 R. S. Dickson and J. A. Ibers, *J. Am. Chem. Soc.*, 1972, **94**, 2988.

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