Dinitrogen Species

Dinitrogen as Double Lewis Acid: Structure and Bonding of Triphenylphosphinazine N₂(PPh₃)₂**

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Much progress has been made in recent years in the synthesis and isolation of small lowvalent, low oxidation state main-group molecules M which are stabilized by N-heterocyclic carbene ligands (NHC) in donor-acceptor complexes $(NHC \rightarrow)_n M.^{[1]}$ In particular, diatomic species E₂ of Group 13-15 elements E which cannot be isolated as free molecules have been synthesized as $NHC \rightarrow E_2 \leftarrow NHC$ species. Robinson et al. reported in 2008 the isolation of the silicon complex Si₂(NHC)₂ which has a trans-planar arrangement of the CSiSiC moiety featuring a Si=Si double bond.^[2] A similar structure was found by us for the heavier homologues $Ge_2(NHC)_2^{[3]}$ and Sn₂(NHC)₂.^[4] Theoretical studies suggest that the NHC \rightarrow E₂ \leftarrow NHC donation in both these compexes is into the vacant in-plane $1\pi_{\mu}$ and $1\pi_{\sigma}$ valence orbitals of E₂ in the excited $(1)^{1}\Delta_{\sigma}$ state which yields two lone-pairs at the |E| = E | moiety (Figure 1 a).^[2-4] An even more dramatic stabilization is found in the recently synthesized boron complex NHC \rightarrow B₂ \leftarrow NHC by Braunschweig et al.^[5] which has a boronboron triple bond and a linear CBBC arrange-

ment. The charge donation of the NHC ligands occurs into the vacant $1\sigma_u$ and $2\sigma_g$ valence orbitals of the highly (double) excited $(3)^1\Sigma_g^+$ state of B₂ which leads to an electron configuration that is similar to the ground-state configuration of N₂ (Figure 1b).^[6] Theoretical studies predict that the heavier Group 13 homologues NHC \rightarrow E₂ \leftarrow NHC where E = Al–In have an anti-periplanar structure.^[6a] The Al–In complexes could not become synthesized to date.

Complexes NHC \rightarrow E₂ \leftarrow NHC have also been isolated for the Group 15 elements E = P, As.^[7] Depending on the size of the substituents at nitrogen, the equilibrium structures have either an anti-periplanar arrangement of the NHC ligands

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Figure 1. Schematic representation of the electronic reference states of some diatomic species E_2 in the complexes $L \rightarrow E_2 \leftarrow L$. a) $(1)^1 \Delta_g$ state of Ge_2 , Sn_2 . b) $(3)^1 \Sigma_g^+$ state of B_2 . c) $(1)^1 \Gamma_g$ state of N_2 , P_2 , As_2 . d) Donation of the plus and minus combination of the lone-pair donor orbitals of L into the vacant in-plane π and π^* orbitals of N_2 . The orbital numbering refers to the valence orbitals of E_2 .

where the C-E-E-C torsion angle is 180° or a *gauche* conformation where the torsion angle is between 99°–134°.^[1,7] The donation of the NHC ligands takes place into the vacant in-plane $1\pi_{u'}$ (bonding) and $1\pi_{g'}$ (antibonding) orbitals of E_2 in the doubly excited (1)¹ Γ_g state (Figure 1c) which has four lone-pairs at the $|\overline{E} - \underline{E}|$ acceptor fragment. Two of them have π symmetry $(1\pi_u/1\pi_g)$ while two have σ -symmetry $(1\sigma_u/2\sigma_g)$.

The donor–acceptor interaction NHC \rightarrow E₂ \leftarrow NHC in the complexes of the Group 13-15 atoms E are strong enough to overcompensate the excitation energies of E_2 into the electronic reference state which leads to thermodynamically stable species $E_2(NHC)_2$. The situation looks less favorable for dinitrogen species N₂(NHC)₂. A recent computational study of Group 14 and 15 complexes NHC \rightarrow E₂ \leftarrow NHC by Wilson et al. showed that all the complexes are stable toward dissociation of the NHC ligands except for E = N.^[8] Depending on the substituents R at nitrogen of the NHC ligand, the dissociation reaction $N_2(NHC)_2 \rightarrow N_2 + 2 NHC$ was calculated to be exergonic by between $21.9 \text{ kcalmol}^{-1}$ (R = H) and 33.5 kcal mol⁻¹ (R = methyl). Even lower thermodynamic stabilities were predicted for the phosphine complexes $R_3P \rightarrow N_2 \leftarrow PR_3$ for which the calculated dissociation reaction $N_2(PR_3)_2 \rightarrow N_2 + 2PR_3$ is exergonic by between 87.8 kcal mol⁻¹ (R = phenyl) and 129.9 kcal mol⁻¹ (R = H).^[8]

The calculated thermodynamic instabilities of N₂(NHC)₂ and $N_2(PR_3)_2$ are in striking contrast to experimental studies. Himmel and co-workers reported in 2011 that N₂(NHC)₂ in which the NHC ligand has methyl groups at nitrogen is thermally stable and can be purified by sublimation at 90°.^[9] The X-ray structure of the compound showed an antiperiplanar arrangement of the NHC ligands and a N-N bond length of 1.415 Å which is in good agreement with the calculated structure of Wilson et al.^[8] Even more surprising is the experimental study by Appel and Schöllhorn who reported in 1964 that triphenylphosphinazine which was sketched with the formula Ph₃P=N-N=PPh₃ is a thermally stable diamagnetic species that has a melting point of 184°.^[10] However, no structural information about the compound was given in the work. In the light of the theoretically predicted free reaction energy of $N_2(PPh_3)_2$ for decomposition into N_2 and two PPh₃ molecules of $-87.8 \text{ kcal mol}^{-1[\hat{8}]}$ we decided to reinvestigate the experimental work and to determine the geometry of the compound.

The triphenylphosphinazine, N₂(PPh₃)₂, was prepared according to the method of Appel and co-workers,^[10] that is, by deprotonation of [Ph₃PN(H)N(H)PPh₃]Cl₂ with KOtBu. It is a deep red crystalline solid that quantitatively decomposes in the melt to PPh₃ and N₂ above 215°C (m.p. 184–186°C). When exposed to the air it is rapidly and quantitatively oxidized to O=PPh₃, presumably also generating N₂. In their original publication, Appel and co-workers did not report NMR spectroscopic data for $N_2(PPh_3)_2$. In the current study we obtained these data, most notable of which is the ³¹P{¹H} NMR chemical shift of the compound at $\delta =$ 9.16 ppm. Moreover, the X-ray crystal structure of the compound was obtained (Figure 2). This structure shows it to be dimeric with a planar PN₂P fragment with PNN angles of 107.10(11)°. The N-N separation in the compound (1.497(2) Å) is extremely long for a single bond, and in fact lies within the longest 0.1% of such interactions in compounds bearing XN–NX fragments (X = any atom, N is twocoordinate).^[11] Conversely, the P–N bonds in $N_2(PPh_3)_2$ (1.5819(12) Å), while short, are close in length to the mean value (1.579 Å) for all reported $Ph_3P-N_{(two-coordinate)}$ separations.^[11]

We analyzed the electronic structure of $N_2(PPh_3)_2$ with quantum chemical methods^[12] to understand the surprising thermal stability of the compound. The geometry optimization at RI-BP86/def2-TZVPP gave an anti-periplanar arrangement of the phosphine ligands as it is found in the solid state. Figure 2 shows that the calculated bond lengths and angles at RI-BP86/def2-TZVPP are in reasonable agreement with the experimental values. The theoretical N-N bond length (1.441 Å) is shorter than the experimental value (1.497 Å) while the calculated P-N bonds are a bit longer (1.606 Å) than the measured value (1.582 Å). The calculated N-N distance at B3LYP/TZVP which was reported by Wilson et al. $(1.457 \text{ Å})^{[8]}$ is also shorter than the experimental data. The theoretically predicted reaction energy for the dissociation $N_2(PPh_3)_2 \rightarrow N_2 + 2PPh_3$ at RI-BP86/def2-TZVPP is -47.5 kcalmol⁻¹. After correcting for thermal and entropic contributions we calculate a Gibbs free energy of -74.5 kcal mol⁻¹. This value is a bit smaller than the MP2/TZVP// B3LYP/TZVP value of -87.8 kcalmol⁻¹ which was reported by Wilson et al.^[8] but there is agreement that triphenylphosphinazine is a thermodynamically unstable species.

Figure 3 shows the most important occupied orbitals of $N_2(PPh_3)_2$ which are relevant for the bonding interactions between dinitrogen and the phosphine ligands. The HOMO is the out-of-plane^[13] π^* orbital of N_2 ($1\pi_g$ in Figure 1 c) which has only small contributions at PPh₃. The shape of the HOMO and the anti-periplanar arrangement of the PPh₃ ligands indicate that the electronic reference state of N_2 is the highly excited (1)¹ Γ_g state which has the valence configuration $(1\sigma_g)^2(1\sigma_u)^2(1\pi_u)^2(2\sigma_g)^2(1\pi_g)^2$ where the $1\pi_u'$ and $1\pi_g'$ are vacant (Figure 1 c). The $1\pi_u'$ and $1\pi_g'$ MOs serve as in-plane^[13] acceptor orbitals for the plus and minus combinations of the PPh₃ σ lone-pair orbitals. Figure 3 shows that the HOMO–1 displays the features of the Ph₃P \rightarrow N₂ \leftarrow PPh₃ σ donation from the plus combination of the phosphorus lone-pairs while the



Figure 2. X-ray crystal structure of N_2 (PPh₃)₂. Selected bond lengths [Å] and angles [°]. Calculated values at RI-BP86/def2-TZVPP are given in brackets: N1–N1 1.497(2) [1.441], P1–N1 1.5819(12) [1.606], P1-N1-N1' 107.10(11) [112.6], P1-N1-N1'-P1' 180.0 [180.0].



Figure 3. Plot of the relevant occupied orbitals of $N_2(PPh_3)_2$.

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HOMO-15 can be identified as the minus combination of the $Ph_3P \rightarrow N_2 \leftarrow PPh_3 \sigma$ donation. The HOMO-15 orbital is much lower in energy than the HOMO-1, because the donation takes place into the bonding $1\pi_u'$ orbital of N_2 while the $1\pi_g'$ acceptor orbital of N_2 is N-N antibonding. The shape of the $1\pi_g'$ MO suggests that there is some mixing with the $2\sigma_g$ orbital of N_2 which has lone-pair character (Figure 1). The HOMO-14 is the occupied $1\pi_u$ orbital of N_2 which exhibits some mixing with the π orbitals of the phenyl rings.

The bonding situation in $N_2(PPh_3)_2$ was further analyzed with the EDA-NOCV method.^[14] Table 1 gives the numerical

Table 1: EDA-NOCV results of N₂(PPh₃)₂ using the fragments N₂ in the (1)¹ Γ_{g} reference state and 2 PPh₃. Energy values in kcal mol⁻¹.

() g	5 87
ΔE_{int}	-300.1
ΔE_{Pauli}	853.4
$\Delta E_{\text{elstat}}^{[a]}$	-377.4 (32.7%)
$\Delta E_{ m orb}^{[a]}$	-776.1 (67.3%)
$\Delta E_{\sigma 1}^{[b,c]}$	-357.9 (46.1%)
$\Delta E_{\sigma 2}^{[b,c]}$	-289.8 (37.3%)
$\Delta E_{\pi 1}^{[b,c]}$	-46.9 (6.0%)
$\Delta E_{\rm resr}^{[b]}$	-81.5 (10.6%)

[a] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{\text{elstat}} + \Delta E_{\text{orb}}$. [b] The percentage values in parentheses give the contribution to the total orbital interactions ΔE_{orb} . [c] The notation σ_1 , σ_2 , π_1 refers to the orbital pairs which are associated with the deformation densities $\Delta \rho_1$, $\Delta \rho_2$, $\Delta \rho_3$ that are shown in Figure 4.

results. The intrinsic interaction energy ΔE_{int} between the fragments N₂ in the $(1)^1 \Gamma_g$ reference state and PPh₃ in the frozen geometry of N₂(PPh₃)₂ is very large [Eq. (1)]

$$N_2(1^1\Gamma_g)_{fr} + 2\,(PPh_3)_{fr} \to N_2(PPh_3)_2 \qquad -300.1\,\,kcal\,mol^{-1} \qquad (1)$$

The EDA-NOCV data suggest that one third of the attraction between $N_2({}^1\Gamma_{e})$ and the two PPh₃ molecules comes from electrostatic interactions ΔE_{elstat} while two thirds comes from orbital interactions $\Delta E_{\rm orb}$. Inspection of the pair contributions to the $\Delta E_{\rm orb}$ terms reveals that the dominant interactions come from the plus and minus combinations of $Ph_3P \rightarrow N_2 \leftarrow PPh_3 \sigma$ donation. Figure 4 shows the deformation densities $\Delta \rho$ which are associated with the most important orbital interactions. Note that the color coding indicates the direction of the charge flow donor \rightarrow acceptor (red \rightarrow blue). The deformation density $\Delta \rho_1$ can be identified with the charge donation $Ph_3P \rightarrow N_2 \leftarrow PPh_3$ into the vacant in-plane^[13] π orbital of $N_2({}^1\Gamma_g)$ while $\Delta\rho_2$ illustrates the charge flow of the phosphorus lone-pair electrons into the vacant π^* orbital of $N_2({}^1\Gamma_g)$. The sum of the two interactions provides 83.4% of ΔE_{orb} (Table 1). The π back-donation Ph₃P \leftarrow N₂ \rightarrow PPh₃ which is associated with the deformation

density $\Delta \rho_3$ contributes only 6.0%. The EDA-NOCV results and

the shape of the valence orbitals suggest that the bonding between dinitrogen and the phosphine ligands comes from strong $Ph_3P \rightarrow N_2 \leftarrow PPh_3 \sigma$ donation and less



Figure 4. Plot of the deformation densities $\Delta\rho$ which are associated with most relevant orbital interactions in N₂(PPh₃)₂. a) Deformation density $\Delta\rho_1$ arising from donation Ph₃P \rightarrow N₂ \leftarrow PPh₃ into the vacant inplane π orbital of N₂($^{1}\Gamma_{g}$). b) Deformation density $\Delta\rho_2$ arising from donation Ph₃P \rightarrow N₂ \leftarrow PPh₃ into the vacant inplane π^* orbital of N₂-($^{1}\Gamma_{g}$). c) Deformation density $\Delta\rho_3$ arising from π back-donation Ph₃P \leftarrow N₂ \leftarrow PPh₃ from the occupied out-of-plane π orbital of N₂($^{1}\Gamma_{g}$).

Ph₃P ← N₂ → PPh₃ π back-donation. This picture is also supported by an NBO analysis of N₂(PPh₃)₂. The calculated partial charge of the N₂ moiety in the complex is -1.73 e. The NBO calculations give a N–N single bond which has nearly perfect sp³ hybridization (Table 2). There are two lone-pair orbitals at each nitrogen, one with σ symmetry that has 48% s contribution and one π lone-pair. The NBO results give two P–N single bonds which are clearly localized toward the nitrogen end (66%). The resulting extended Lewis structure for triphenylphosphinazine which uses arrows for donor–acceptor bonds reads as:

P٢

The bonding situation may be expressed as double ylid $Ph_3P^+-N^--P^+Ph_3$ as it was done in a later paper by Appel et al.^[15] We prefer the notation with arrows because it directly reveals the electronic reference state of N_2 and the nature of the phosphorus–nitrogen bonds.

Table 2: NBO results at BP86/def2-TZVPP for the PNNP moiety of N2(PPh3)2.

Orbital	Bond order	Occupancy.	% (N)	% s(N)	% p(N)	% (P)	% s(P)	% p(P)
N-N	1.056	1.97	50.0	23.7	76.1	_	_	_
P-N	1.184	1.97	66.4	28.3	71.2	33.6	29.4	70.0
N (lone pair)	_	1.90	-	47.7	52.1	-	-	-
N (lone pair)	-	1.63	-	0.4	99.3	-	-	-

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The description of $N_2(PPh_3)_2$ with two lone-pairs at each nitrogen atom suggests that the compound should be a strong proton acceptor and that even the second proton affinity, where the same nitrogen atom is protonated, should be rather high. This idea is verified by the calculated proton affinities (PAs). The first PA of $N_2(PPh_3)_2$ is 245.2 kcalmol⁻¹ which is larger than the PA of most amines.^[16] The second PA yielding Ph₃PN(H⁺)₂NPPh₃ is 170.5 kcalmol⁻¹ which is only a bit smaller than the second PA yielding Ph₃PN(H⁺)N(H⁺)PPh₃ (195.6 kcalmol⁻¹). It has been shown that the second PA is a sensitive probe for the occurrence of two lone pairs in carbon bases.^[17] The calculated second PA for one nitrogen atom is a further evidence for the existence of two lone-pair orbitals at nitrogen.^[18]

Why is triphenylphosphinazine an amazingly stable compound although the dissociation reaction into $N_2 + 2PPh_3$ is strongly exergonic? As shown above, the intrinsic interaction energy ΔE_{int} between the fragments N₂ in the (1)¹ Γ_{g} reference state and PPh₃ in the frozen geometry of N₂(PPh₃)₂ is very large (-300.1 kcal mol⁻¹). Thus, dinitrogen in the $(1)^{1}\Gamma_{g}$ state is a very powerful Lewis acid which is due to two reasons. One reason is the rather high electronegativity of nitrogen while the other reason is that the nitrogen atoms in $\overline{|N - N|}$ have only an electron sextet. However, the large interaction energy does not compensate for the relaxation of the fragments into the equilibrium geometries and electronic ground states which are calculated to be 8.3 kcalmol⁻¹ for both phosphine ligands and 341.0 kcal mol⁻¹ for the process N₂ $(1^{1}\Gamma_{e})_{\rm fr} \rightarrow$ $N_2(X^1\Sigma_{\rho}^+)$. High-level ab initio calculations predict that the $(1)^{1}\Gamma_{g}$ state of N₂ has an equilibrium separation of 1.608 Å and is 294.3 kcalmol⁻¹ above the $X^{1}\Sigma_{g}^{+}$ ground state.^[19] The RI-BP86/def2-TZVPP calculations for N₂ (1)¹ Γ_g give a N-N separation of 1.661 Å and an excitation energy of 328.6 kcal mol⁻¹. This is a remarkably good agreement with the ab initio result in light of the approximations of the DFT method. The N-N separation becomes shorter in N₂(PPh₃)₂ because the donation into the N–N bonding orbital $1\pi_{u'}$ is likely to affect the N-N distance more strongly than the donation into the antibonding $1\pi_{g}'$ acceptor orbital (See Figure 1d and Figure 3). The $1\pi_{e'}$ orbital mixes with the $2\sigma_{e}$ orbital of N₂ (Figure 1) which decreases the N-N antibonding character.

The calculations thus suggest that the very strong $Ph_3P \rightarrow$ $N_2(1)^1\Gamma_e \leftarrow PPh_3$ attraction makes triphenylphosphinazine a kinetically stable compound, because the activation energy for breaking the donor-acceptor bonds is very high. We carried out preliminary calculations to estimate the activation barrier for dissociation of the phosphine ligands but we experienced severe convergence problems. The transition state for the dissociation reaction $N_2(PPh_3)_2 \rightarrow$ N_2 +2PPh₃ which involves a change in the configuration of the N₂ moiety from the $(1)^{1}\Gamma_{g}$ excited state to the X¹ Σ_{g}^{+} ground state can be optimized only at a multi-reference level. This is a formidable task which requires substantial computational resources, because a size reduction of the molecule to a model system such as $N_2(PH_3)_2$ is not feasible because hydrogen migration may take place during the geometry optimization. A calculation of the transition state for the molecule which has C_1 symmetry involves the optimization of 3N-6=214 geometry variables at

a RASSCF level which is not possible for us. However, our calculations do provide information about the dissociation pathway. We calculated N₂(PPh₃)₂ at RI-BP86/def2-TZVPP where one P-N separation was fixed at longer distances than the equilibrium values with intervals of 0.1 Å. The second P-N bond becomes longer while the N-N bond becomes clearly shorter up to a value of 2.0 Å for the frozen P-N bond. At this point, the second P-N bond length was 1.606 Å, the N-N separation was 1.379 Å, and the energy was $25.1 \text{ kcalmol}^{-1}$ higher than the optimized structure. When the P-N frozen separation was further elongated to 2.1 Å, the second P-N bond broke and the associated PPh3 ligand dissociated. A geometry optimization of a possible intermediate N₂(PPh₃) did not give an equilibrium structure. The calculations suggest that the reaction $N_2(PPh_3)_2 \rightarrow N_2 + 2PPh_3$ which proceeds as concerted but not necessarily synchronous rupture of the P-N bonds with a rather high barrier. The DFT calculations suggest that the activation barrier for the concerted but not necessarily synchronous reaction is higher than 25.1 kcal mol⁻¹ but lower than 67.6 kcalmol⁻¹ which is the bond dissociation energy for the N-N bond of N₂(PPh₃)₂ yielding NPPh₃ in the electronic doublet ground state [Eq. (2)].

$$\mathbf{N}_2(\mathbf{PPh}_3)_2 \rightarrow 2\,\mathbf{NPPh}_3 \qquad +\,67.6\,\mathbf{kcal}\,\mathbf{mol}^{-1} \tag{2}$$

The above results suggest that donor-acceptor interactions^[20] in main-group compounds of atoms of the first octalrow may be more important than hitherto realized. In 2006 it was recognized by one of us^[21] that carbodiphosphoranes $C(PR_3)_2$ which were synthesized as early as $1961^{[22]}$ are examples for the compound class of carbones CL₂ which have donor-acceptor bonds $L \rightarrow C \leftarrow L$ to a naked carbon atom in the singlet ¹D state that has two lone pairs, and is thus a double Lewis base. This was the starting point for intensive studies which led to the synthesis of new carbones and carbone complexes.^[23] Herein we show that triphenylphosphinazine which was isolated in 1964^[10] is a donoracceptor complex of dinitrogen $Ph_3P \rightarrow N_2 \leftarrow PPh_3$ which can be considered as an example of dinitrogen complexes $L \rightarrow$ $N_2 \leftarrow L$. We think that triphenylphosphinazine is an exceptional compound, because it melts at 184° and it decomposes into N₂ and PPh₃ only above 215° although the associated bond breaking reaction is calculated to be exergonic by 74.5-87.7 kcal mol⁻¹. Further studies might lead to the synthesis of complexes $N_2(L)_2$ with other ligands L and to transition-metal complexes in which the nitrogen atoms of N₂(L)₂ serve as double donors to the metal. Also, it has not escaped our attention that the direct synthesis of $N_2(PPh_3)_2$ from N_2 and PPh₃ would be a significant contribution to the topics of nitrogen activation and chemical energy storage. The results which are reported herein are a challenge for experiment.

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