A Lewis-basic, dionio-substituted phosphane

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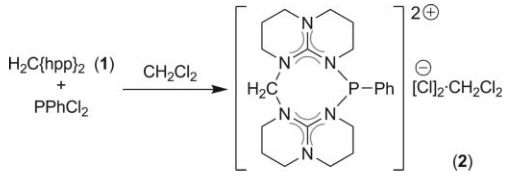
Bis{guanidine} $H_2C\{hpp\}_2$ [hppH = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine] reacts with $PPhCl_2$ to generate the dionio-substituted phosphane, $[H_2C\{hpp\}_2PPh]^{2+}[Cl]^-{}_2$ which, despite the formally dicationic phosphorus centre, forms an unprecedented coordination compound with platinum.

Formation of cationic phosphonium and phosphenium ions readily occurs *via* phosphorus–halogen bond heterolysis, and has been promoted by a range of metal and main-group reagents.[1] Over 10 years ago, Bertrand and co-workers reported an alternative protocol that exploited the nucleophilic activity of the bicyclic amidine bases, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN).[2,3] Using this approach the onio- and dionio-substituted phosphanes $[P(DBN)(N^iPr_2)_2]^+$ (**A**) and $[P(DBN)_2(NCy_2)]^{2+}$ (**B**) were isolated and structurally characterized, providing insight into the mechanism of base-induced dehydrohalogenation employing these amidine reagents.

A number of studies[4] have subsequently been presented in which the Lewis-acidic properties of cationic phosphorus centres have been investigated, using predominantly nitrogen-[5] and phosphorus-based[6] donor groups. Whilst the retention of a non-bonding electron pair has been noted,[7] and the potential for Lewis-basic behaviour of a monocationic phosphorus compound has been demonstrated,[8] this remains an underdeveloped field of study, where interest may be anticipated in the areas of coordination chemistry and catalysis with the formation of formally cationic phosphane ligands. Exploiting the ability of amidines and guanidines to disperse positive charge throughout their core, we report herein our studies to ascertain whether sufficient Lewis-basic character is retained in a novel dionio-substituted phosphane (a Weiss-type compound[9] with a formally dicationic charge at phosphorus) to enable donor ligand behaviour at a metal centre.

We have recently synthesized a series of poly{guanidyl} compounds based on the bicyclic guanidine 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH), and demonstrated coordination at neutral[10] and cationic[11] metal fragments. Reaction between the methylene linked derivative, $H_2C\{hpp\}_2$ (**1**), and $PPhCl_2$ proceeded *via* nucleophilic displacement of both chlorides to afford the heterocyclic dionio-substituted phosphane, $[H_2C\{hpp\}_2PPh][Cl]_2$ (**2**), which crystallized as the dichloromethane solvate (Scheme 1). Symmetric chelation of the formally neutral $H_2C\{hpp\}_2$ ligand to the dicationic $[PPh]^{2+}$ fragment was indicated by a single resonance for the quaternary CN_3 atoms in the ^{13}C NMR spectrum† [δ 159.8] with a $^2J_{PC}$ coupling of 13 Hz. The ^{31}P NMR spectrum†, however, indicated two phosphorus environments [δ 120.4 and 110.7; 6.6 : 1 ratio at 25 °C], resonating at slightly lower field than Bertrand's dionio-compounds of type **B** [range = 109–98 ppm]. Given the flexibility inherent in the C_3N_4P ring, (taking into account the planarity of the 'N–C–N' moiety), and the different possible orientations of the annular methylene groups, these resonances are assigned to different conformations of the heterocycle in solution.[12] The corresponding ^1H NMR spectrum† of **2** shows that for each isomer, the protons of the bridging methylene group resonate with an AB pattern (major: δ 5.67 and 4.64, $^2J_{HH}$ 15.7 Hz; minor: δ 4.88 and 4.58, $^2J_{HH}$ 24.4 Hz), consistent with inequivalent magnetic environments caused by different rigid conformations.



Scheme 1

The molecular structure of **2** has been solved by single-crystal X-ray diffraction‡, confirming the formation of the cyclic $[H_2C\{hpp\}_2PPh]^{2+}$ dication (Fig. 1a). The chloride counter ions are integrated into a hydrogen-bonded $[Cl\cdots H–C(Cl)_2–H\cdots Cl]^{2-}$ dianion, which is positioned with the chlorides located above the central CN_3 regions of the guanidyl groups (Fig. 1b). The dication itself is monomeric, with the P-atom incorporated into an unusual eight-membered C_3N_4P heterocycle, with a degree of pyramidalization[13] at phosphorus of 51.7%, suggesting retention of a

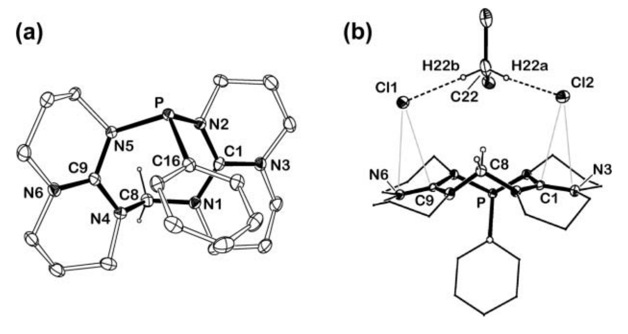


Fig. 1 (a) Molecular structure of the dicationic component of **2** (ORTEP, ellipsoids at 30%, hydrogens except on the bridging methylene omitted). Selected bond lengths (Å) and angles (°): P–N2 1.7326(17), P–N5 1.7351(16), P–C16 1.825(2), C1–N1 1.346(3), C1–N2 1.375(2), C1–N3 1.319(2), C9–N4 1.344(2), C9–N5 1.379(2), C9–N6 1.312(2); N2–P–N5 107.63(8), N2–P–C16 103.71(8), N5–P–C16 102.09(9). (b) Arrangement of the ion-pair in **2**: H22a···Cl2 2.45, H22b···Cl1 2.46, Cl1···N6 3.46, Cl1···C9 3.33, Cl2···N3 3.43, Cl1···C1 3.37.

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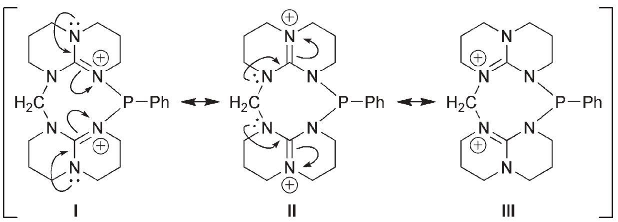


Scheme 2 Key resonance forms of dionio-substituted phosphane, **2**.

non-bonded electron pair. The bridging methylene and PPh groups are located on opposite sides of the approximate C_2N_4 plane generated by the guanidine rings, giving a *pseudo*-chair conformation that accounts for the inequivalent proton environments in the NMR spectrum of the major isomer. The P–N bonding is essentially symmetrical [1.7326(17) Å and 1.7351(16) Å], being considerably shorter than in the dicationic DBN adduct **B** [$P–N_{amidine}$ = 1.766(5) Å and 1.752(4) Å].[2]

The carbon–nitrogen bond distances within the CN_3 core of the guanidyl groups suggest delocalization of the positive charge into the bicyclic system. Significantly shorter bonds to N3/N6 (ave. 1.32 Å) and N1/N4 (ave. 1.34 Å) compared with those to the phosphorus bound nitrogen (ave. 1.38 Å), are consistent with a large contribution from resonance forms **II** and **III** (Scheme 2). This contrasts with the observed trend in the aluminocenium ion $[H_2C\{hpp\}_2AlMe_2][BPh_4]$, in which it is suggested that **I** and **II** are the major contributors to the overall bonding.[11]

The isolated dication has been examined using the B3LYP density functional theory and the 6-31g(d) basis set, implemented by Gaussian 03.[14] The NBO charges (Fig. 2) are consistent with the phosphorus atom retaining cationic character (+1.286), with the remaining positive charge delocalized into the guanidyl fragments. The relative charges at nitrogen are in agreement with resonance forms **II** and **III** dominating the bonding, as described above. Interestingly, the HOMO is representative of considerable non-bonding electron density at phosphorus, with several lower energy MOs indicative of delocalized electron density within π-symmetry orbitals across the CN_3 component of the guanidyl rings.

Given the lone-pair characteristics calculated for the HOMO of **2**, we wished to ascertain whether the phosphorus atom would exhibit Lewis-basic properties, despite its formally positive charge. No reaction was detected by NMR spectroscopy upon mixing a sample of **2** with elemental selenium, despite prolonged heating and sonication. This is attributed to the heterogeneity of the system as the reaction with $[PtCl(PEt_3)(\mu\text{-}Cl)]_2$, indicated rapid formation of $[PtCl_2(H_2C\{hpp\}_2PPh\text{-}\kappa P)(PEt_3)][Cl]_2$ (**3**) (∼50% conversion), in which the dionio-phosphane was coordinated to platinum. New resonances in the ^{31}P NMR spectrum† at δ 101.8 ($^1J_{PtP}$ 2950 Hz, $H_2C\{hpp\}_2PPh$) and δ 15.9 ($^1J_{PtP}$ 2530 Hz, PEt_3) with a $^2J_{PP}$ of 570 Hz are consistent with the formation of the *trans*-product. Gentle heating of the sample (50 °C, 24 h) led to the formation of a new product (**4**), indicated by a single phosphorus resonance at δ 72.5 ($^1J_{PtP}$ 4877 Hz), significantly shifted from that of the *trans*-diphosphane, **3**. The ^1H NMR spectrum of **4** contained a widely spaced AB pattern for the bridging methylene protons (δ 7.05 and 4.66, $^2J_{HH}$ 15.7 Hz), confirming the presence of the cationic phosphane and the lack of resonances for the ethyl groups led us to conclude that PEt_3 had been displaced from the metal coordination sphere. In agreement with the NMR data, crystals of **4** were analyzed by X-ray crystallography and shown to correspond to the monocationic platinum compound, $[PtCl_3(H_2C\{hpp\}_2PPh\text{-}\kappa P)][Cl]$ (Fig. 3), generated by the phosphane displacement from platinum by chloride (Scheme 3).

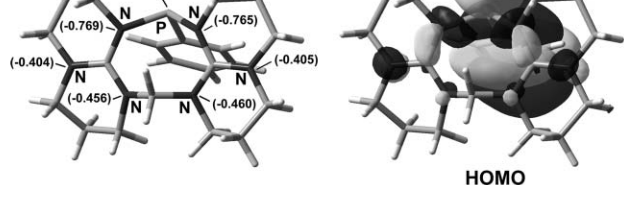


Fig. 2 Calculated NBO charges and HOMO of the isolated dionio-substituted phosphane, **2**.

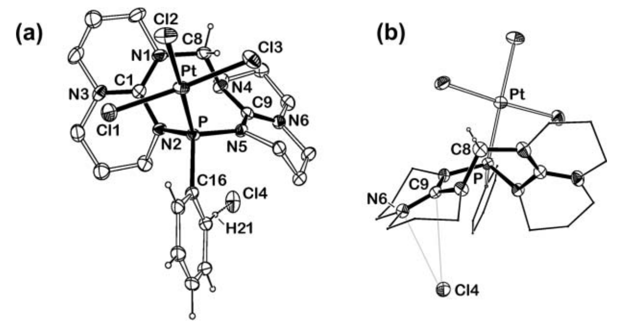
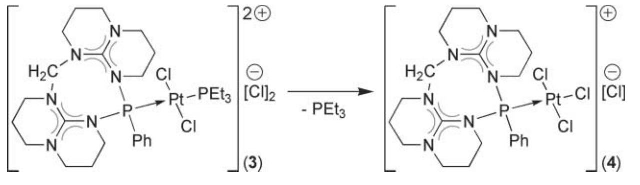


Fig. 3 (a) Molecular structure of **4** (ORTEP, ellipsoids at 30%, hydrogens except on the bridging methylene and phenyl group, and MeCN solvate omitted). Selected bond lengths (Å) and angles (°): P–Pt 2.2006(17), P–N2 1.684(6), P–N5 1.738(5), P–C16 1.813(6), Pt–Cl1 2.3068(19), Pt–Cl2 2.3524(18), Pt–Cl3 2.2961(19), C1–N1 1.321(8), C1–N2 1.388(8), C1–N3 1.314(9), C9–N4 1.349(8), C9–N5 1.358(8), C9–N6 1.301(8), H21···Cl4 2.65; N2–P–N5 104.7(3), N2–P–Pt 113.62(19), N5–P–Pt 115.5(2), C16–P–Pt 114.8(2), N2–P–C16 105.5(3), N5–P–C16 101.3(3). (b) View emphasizing the twisted heterocycle and anion interactions: Cl4···N6 3.31, Cl4···C9 3.52.

The molecular structure is comprised of the metallated C_3N_4P heterocycle in which a $PtCl_3$ unit occupies the fourth vertex of a distorted tetrahedral phosphorus atom [angles in the range 101.3(3)°–115.5(2)°]. Similar to the ion-packing arrangement in **2**, the chloride is located with closest contacts to the relatively short C9–N6 bond [1.301(8) Å], with additional hydrogen bonding to an *ortho*-proton (H21) of the phenyl substituent in this instance. Upon coordination of the platinum trichloride fragment, the heterocycle distorts from the symmetrical chair-like conformation in **2**, to what is best described as a *pseudo*-twist-boat (Fig. 3b). A significant difference in the P–N distances is noted (Δ_{PN} = 0.054 Å), reflected in different C–N bond lengths within each guanidyl component, indicated by $|\Delta_{CN}|$ values of 0.067 Å (N1–C1–N2) and



Scheme 3

0.009 Å (N4–C9–N5). These metrical parameters demonstrate the high degree of flexibility within the dionio-substituted phosphane **2**, regarding both conformational changes within the eight-membered heterocycle and, perhaps more importantly, with respect to the distribution of electron density within the guanidyl units.

Further studies on the coordinating ability of this and other related onio- and dionio-substituted phosphanes are underway in our laboratory. We wish to acknowledge the University of Sussex for financial support and Prof. J. F. Nixon for helpful discussion and the loan of $[\mathrm{PtCl(PEt_3)(\mu\text{-}Cl)}]_2$.

Notes and references

† Selected analytical data: **2**, elemental analysis calcd (%) for $C_{22}H_{33}Cl_4N_6P$: C 47.67, H 6.00, N 15.16; found: C 47.90, H 6.30, N 14.86. ^{31}P NMR (CD_3CN, 121.4 MHz, 298 K): δ 120.4 (major), 110.7 (minor). ^{1}H NMR (CD_3CN, 300.1 MHz, 298 K, coupling constants in Hz): δ 7.65 (m, 2H, o-C_6H_5), 7.54 (m, 2H, m-C_6H_5), 7.17 (t, $^3J_{\mathrm{HH}}$ 6.8, 1H, p-C_6H_5), 5.67 (d, $^2J_{\mathrm{HH}}$ 15.7, 1H, $H_2\mathrm{C}\{\mathrm{hpp}\}_2$ major), 5.46 (s, 2H, $\mathrm{C}H_2\mathrm{Cl}_2$), 4.88 (d, $^2J_{\mathrm{HH}}$ 24.5, $H_2\mathrm{C}\{\mathrm{hpp}\}_2$ minor), 4.64 (d, $^2J_{\mathrm{HH}}$ 15.7, 1H, $H_2\mathrm{C}\{\mathrm{hpp}\}_2$ major), 4.58 (d, $^2J_{\mathrm{HH}}$ 24.3, $H_2\mathrm{C}\{\mathrm{hpp}\}_2$ minor), 3.94 (m, 6H, hpp-$\mathrm{C}H_2$), 3.47 (m, 8H, hpp-$\mathrm{C}H_2$), 2.74 (m, 2H, hpp-$\mathrm{C}H_2$), 2.23–1.77 (m, 8H, hpp-$\mathrm{C}H_2$). ^{13}C NMR (CD_3CN, 75.5 MHz, 298 K, coupling constants in Hz): δ 159.8 (d, $^2J_{\mathrm{PC}}$ 13, $C\mathrm{N}_3$), 133.9 (d, J_{PC} 14, $C_6\mathrm{H}_5$), 131.6 (d, J_{PC} 2, $C_6\mathrm{H}_5$), 130.9 (d, J_{PC} 3, $C_6\mathrm{H}_5$), 128.9 (d, J_{PC} 18, $C_6\mathrm{H}_5$), 72.5 ($\mathrm{H_2}C\{\mathrm{hpp}\}_2$), 55.2 ($C\mathrm{H_2Cl_2}$), 50.5 (d, J_{PC} 47, hpp-$C\mathrm{H}_2$), 49.2, 48.8, 47.5 (hpp-$C\mathrm{H}_2$), 23.7 (d, J_{PC} 3, hpp-$C\mathrm{H}_2$), 21.7 (hpp-$C\mathrm{H}_2$). **3**, ^{31}P NMR (CD_3CN, 121.4 MHz, 298 K, coupling constants in Hz): δ 101.8 (d, $^2J_{\mathrm{PP}} = 570$, $^1J_{\mathrm{PtP}} = 2950$, $P\{\mathrm{hpp}\}_2\mathrm{Ph}$), 15.9 (d, $^2J_{\mathrm{PP}} = 570$, $^1J_{\mathrm{PtP}} = 2530$) $P\mathrm{Et}_3$. **4**, ^{31}P NMR (CD_3CN, 121.4 MHz, 298 K, coupling constants in Hz): δ 72.5 ($^1J_{\mathrm{PtP}} = 4877$, $P\{\mathrm{hpp}\}_2\mathrm{Ph}$). ^{1}H NMR ($CD_3CN$, 300.1 MHz, 298 K, coupling constants in Hz): δ 8.61 (dd, $^3J_{\mathrm{PH}} = 14.7$, $^3J_{\mathrm{HH}} = 7.4$, 2H, o-C_6H_5), 7.83 (m, 1H, p-C_6H_5), 7.73 (m, 2H, m-C_6H_5), 7.05 (d, $^2J_{\mathrm{HH}}$ 15.7, 1H, $H_2\mathrm{C}\{\mathrm{hpp}\}_2$), 4.66 (d, $^2J_{\mathrm{HH}}$ 15.7, 1H, $H_2\mathrm{C}\{\mathrm{hpp}\}_2$), 3.70–3.27 (m, 14H, hpp-$\mathrm{C}H_2$), 2.21–1.91 (m, 10H, hpp-$\mathrm{C}H_2$).

‡ Crystallographic data: **2**, $C_{21}H_{31}Cl_2N_6P\cdot CH_2Cl_2$, $M_r = 554.31$, crystal dimensions 0.40 × 0.40 × 0.40 mm, orthorhombic, space group $Pna2_1$ (No. 33), $a = 13.5675(3)$, $b = 15.3805(2)$, $c = 12.3987(3)$ Å, $V = 2587.30(9)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.42$ Mg m^{-3}, $\mu = 0.54$ mm^{-1}; of 25557 reflections collected ($3.42 < \theta < 26.01°$), 5042 were independent ($R_{\mathrm{int}} = 0.047$), $R1 = 0.028$, w$R2 = 0.080$ (data for 4845 reflections with $I > 2\sigma(I)$), $R1 = 0.030$, w$R2 = 0.082$ (all data). **4**, $C_{21}H_{31}Cl_4N_6PPt\cdot C_2H_3N$, $M_r = 776.43$, crystal dimensions 0.15 × 0.10 × 0.10 mm, monoclinic, space group $P2_1/c$ (No. 14), $a = 14.0180(5)$, $b = 14.4145(4)$, $c = 15.2158(5)$ Å, $V = 2811.39(16)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.83$ Mg m^{-3}, $\mu = 5.46$ mm^{-1}; of 38517 reflections collected ($3.48 < \theta < 26.04°$), 5528 were independent ($R_{\mathrm{int}} = 0.077$), $R1 = 0.044$, w$R2 = 0.107$ (data for 4763 reflections with $I > 2\sigma(I)$), $R1 = 0.055$, w$R2 = 0.112$ (all data). CCDC 644406 and 644407. For crystallographic data in CIF format, see DOI: 10.1039/b710923g

1 A. H. Cowley and R. A. Kemp, *Chem. Rev.*, 1985, **85**, 367.

2 R. Reed, R. Réau, F. Dahan and G. Bertrand, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 399.

3 G. Bouhadir, R. W. Reed, R. Réau and G. Bertrand, *Heteroat. Chem.*, 1995, **6**, 371.

4 N. Burford and P. J. Ragogna, *J. Chem. Soc., Dalton Trans.*, 2002, 4307; B. D. Ellis and C. L. B. Macdonald, *Coord. Chem. Rev.*, 2007, **251**, 936.

5 N. Burford, P. Losier, A. D. Phillips, P. J. Ragogna and T. S. Cameron, *Inorg. Chem.*, 2003, **42**, 1087; N. Burford, H. A. Spinney, M. J. Ferguson and R. McDonald, *Chem. Commun.*, 2004, 2696; E. Rivard, K. Huynh, A. J. Lough and I. Manners, *J. Am. Chem. Soc.*, 2004, **126**, 2286; N. Burford, A. D. Phillips, H. A. Spinney, M. Lumsden, U. Werner-Zwanziger, M. J. Ferguson and R. McDonald, *J. Am. Chem. Soc.*, 2005, **127**, 3921.

6 C. A. Dyker, N. Burford, M. D. Lumsden and A. Decken, *J. Am. Chem. Soc.*, 2006, **128**, 9632; N. Burford, T. S. Cameron, J. A. C. Clyburne, K. Eichele, K. N. Robertson, S. Sereda, R. E. Wasylishen and W. A. Whitla, *Inorg. Chem.*, 1996, **35**, 5460; K. Huynh, A. J. Lough and I. Manners, *J. Am. Chem. Soc.*, 2006, **128**, 14002; N. Burford, P. J. Ragogna, R. McDonald and M. J. Ferguson, *J. Am. Chem. Soc.*, 2003, **125**, 14404.

7 D. Gudat, *Coord. Chem. Rev.*, 1997, **163**, 71.

8 N. Burford, P. Losier, S. V. Sereda, T. S. Cameron and G. Wu, *J. Am. Chem. Soc.*, 1994, **116**, 6474.

9 R. Weiss and S. Engel, *Synthesis*, 1991, 1077; R. Weiss and S. Engel, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 216.

10 S. H. Oakley, M. P. Coles and P. B. Hitchcock, *Inorg. Chem.*, 2004, **43**, 7564; S. H. Oakley, M. P. Coles and P. B. Hitchcock, *Dalton Trans.*, 2004, 1113; M. P. Coles, *Dalton Trans.*, 2006, 985.

11 P. J. Aragón Sáez, S. H. Oakley, M. P. Coles and P. B. Hitchcock, *Chem. Commun.*, 2007, 816.

12 Analysis of the dicationic component $[\mathrm{H_2C\{hpp\}_2PPh}]^{2+}$ computationally, by means of geometry optimizations at a B3LYP/6-31+G** level of theory, have identified several minima in the potential hypersurface. Two stable conformations have been identified as corresponding to approximate 'chair' and 'twist-boat': M. P. Coles and G. Estiu, unpublished results. Furthermore, variable temperature NMR studies indicate a shift in the relative integrals of the two species upon heating [25 °C, major : minor = 6.6 : 1; 50 °C, major : minor = 4.2 : 1] consistent with a shift in the position of the equilibrium between the two conformations.

13 Z. B. Maksić and B. Kovaĉević, *J. Chem. Soc., Perkin Trans. 2*, 1999, 2623.

14 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, 2004. The input coordinates were taken from the X-ray data and the true energy minimum was confirmed by the absence of any imaginary frequencies.