Inorg. Chem. **2004**, *43*, 2228–2230

Transformation between Diphosphinoamines and Iminobiphosphines: a Reversible P—N—P ↔ N═P–P Rearrangement Triggered by Protonation/Deprotonation†

Zhaofu Fei, Nermin Biricik, Dongbin Zhao, Rosario Scopelliti, and Paul J. Dyson*

Institut de Chimie Moléculaire et Biologique, Ecole Polytechnique Fédérale de Lausanne, EPFL-BCH, CH-1015 Lausanne, Switzerland

Received February 5, 2004

The protonation of diphosphinoamines attached to pyridine at the *ortho*-position quantitatively affords the corresponding iminobiphosphine isomers. The starting material can be recovered quantitatively by deprotonation with base. The system represents a new type of molecular switch.

Phosphorus/nitrogen and phosphorus/phosphorus bonds are among the most intriguing in main-group chemistry, and while the nature of P—N and P═N bonds has been extensively studied,[1] P—P and P═P bonds are somewhat more elusive.[2] Even rarer are compounds containing the N═P—P unit, which are isomeric with P—N—P compounds. Although a number of iminobiphosphines have been prepared by Schmidpeter in the early 1970s,[3] the chemistry related to the N═P—P is still relatively underdeveloped. For example, diphosphinoamines have been used extensively as chelating ligands in coordination chemistry for many years, whereas the coordination behavior of N═P—P toward transition metals has been investigated only very recently.[4] The formation of iminobiphosphines requires, ideally, both electron-withdrawing and sterically demanding groups, and both factors combined stabilize the N═P—P unit.[5a] We have found that anilines with electron-donating substituents give diphosphinoamines on reaction with diphenylchlorophosphine and base, whereas anilines with strongly electron-withdrawing and sterically bulky substituents give iminobiphosphines. In particular, the *ortho*-substituent plays a determining role in the formation and stabilization of the N═P—P unit.[5b]

Recently, phosphine ligand exchange at a phosphine Lewis acceptor has been reported,[6a] and the reaction has been extended to the synthesis of polymeric phosphinophosphonium salts.[6a,c] These reactions challenge the conventional Lewis acid−base chemistry associated with P—C ligands, and therefore, it is of interest to study the fundamental acid−base chemistry of P—N compounds where both the P and N centers may compete.

The diphosphinoamine **1** was prepared in near quantitative yield using a literature protocol.[7] Protonation of **1** with tetrafluoroboric acid in dichloromethane gave the highly air-sensitive salt **2**·BF_4 in quantitative yield (as evidenced by ^{31}P NMR spectroscopy, Scheme 1).[8] When the reaction is monitored by ^{31}P NMR spectroscopy, the initial signal at 59.0 ppm disappears completely with the formation of two doublets centered at 17.2 and −20.0 ppm with a $^1J_{P-P}$ value

* To whom correspondence should be addressed. E-mail: paul.dyson@epfl.ch.

† Dedicated to Professor Reinhard Schmutzler on the occasion of his 70th birthday.

(1) For leading references published recently see: (a) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Phillips, A. D.; Concolino, T. E.; Lam, K.-C.; Rheingold, A. L. *J. Am. Chem. Soc.* **2000**, *122*, 5413. (b) Burford, N.; Cameron, T. S.; Conroy, K. D.; Ellis, B.; Lumsden, M.; Macdonald, C. L. B.; McDonald, R.; Phillips, A. D.; Ragogna, P. J.; Schurko, R. W.; Walsh, D.; Wasylishen, R. E. *J. Am. Chem. Soc.* **2002**, *124*, 14012. (c) Merceron, N.; Miqueu, K.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc*. **2002**, *124*, 6806. (d) Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. J. *Chem. Commun.* **2003**, 2066.

(2) (a)Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587. (b) Yoshifuji, M.; Shibayama, K.; Inamoto, N.; Matsushita, T.; Nishimoto, K. *J. Am. Chem. Soc.* **1983**, *105*, 2495. (c) Kaukorat, T.; Neda, I.; Schmutzler, R. *Coord. Chem. Rev.* **1994**, *137*, 53. (d) Burford, N.; Cameron, T. S.; LeBlanc, D. J.; Losier, P.; Sereda, S.; Wu, G. *Organometallics* **1997**, *16*, 4712. (e) Kato, T.; Gornitzka, H.; Baceiredo, A.; Schoeller, W. W.; Bertrand, G. *Science* **2000**, *289*, 754. (f) Kato, T.; Gornitzka, H.; Baceiredo, A.; Schoeller, W. W.; Bertrand, G. *J. Am. Chem. Soc*. **2002**, *124*, 2506.

(3) (a) Rossknecht, H.; Schmidpeter, A. *Z. Naturforsch., B: Chem. Sci.* **1971**, *26*, 81. (b) Rossknecht, H.; Lehman, W. P.; Schmidpeter, A. *Phosphorus* **1975**, *5*, 195.

(4) In the reaction of C_6H_4(*o*-CN)N═PPh_2—PPh_2 with Pd(cod)Cl_2 and Pt(cod)Cl_2 (cod = cyclooctadiene), the N═P—P unit rearranges to the P—N—P unit, which chelates the transition metals centers. Fei, Z.; Scopelliti, R.; Dyson, P. J. *Eur. J. Inorg. Chem.* **2004**, 530.

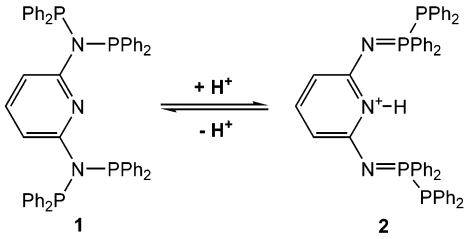
(5) C_6H_4(*o*-CN)NH_2 reacts with 2 equiv of Ph_2PCl to give C_6H_4(*o*-CN)N═PPh_2—PPh_2 in near quantitative yield, while C_6H_4(*m*-CN)NH_2 and C_6H_4(*m*-CN)NH_2 afford C_6H_4(*m*-CN)N(PPh_2)$_2$ and C_6H_4(*p*-CN)N-(PPh_2)$_2$ only. See: (a) Fei, Z.; Scopelliti, R.; Dyson, P. J. *Inorg. Chem.* **2003**, *42*, 2125. (b) Fei, Z.; Scopelliti, R.; Dyson, P. J. *Dalton Trans.* **2003**, 2772.

(6) (a) Burford, N.; Cameron, T. S.; Ragogna, P. J.; Ocando-Mavarez, E.; Gee, M.; McDonald, R.; Wasylishen, R. E. *J. Am. Chem. Soc.* **2001**, *123*, 7947. (b) Burford, N.; Ragogna, P. J. *J. Chem. Soc, Dalton Trans*. **2002**, 4307. (c) Burford, N.; Ragogna, P. J.; McDonald, R.; Ferguson, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 14404.

(7) Biricik, N.; Fei, Z.; Scopelliti, R.; Dyson, P. J. *Helv. Chim. Acta* **2003**, *86*, 3281.

10.1021/ic049850w CCC: $27.50
Published on Web 03/11/2004

Scheme 1



of 277 Hz, indicative of the iminobiphosphine structure. Similarly, reaction of **1** with trifluoromethane sulfonic acid affords **2**·SO_3CF_3. Minor differences in the ^{31}P NMR spectrum are observed, probably due to the interaction of the acidic proton with counteranion (the solid state structure of **2**·BF_4 reveals an interaction of the N—H proton with the anion, see Figure 1).

Catalytic amounts of diethylamine hydrogen chloride have previously been used to convert iminobiphosphines to diphosphinoamine systems.[9] However, in this system this reagent is ineffective; furthermore, the iminobiphosphines RN═PPh_2—PPh_2 (R = C_6H_4(*o*-CN), C_6H_4(*m*-CN), C_6H_4(*p*-CN), C_6H_4(*o*-Ph), C_6H_4(*o*-CF_3), and C_6F_5), reported recently,[5] are stable toward diethylamine hydrogen chloride and triethylamine hydrogen chloride in dry dichloromethane. In contrast, deprotonation of **2** using triethylamine or 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) results in regeneration of the diphosphinoamine **1** almost instantaneously and in quantitative yield, on the basis of in situ ^{31}P NMR spectroscopy. Recovery of **1** is straightforward, comprising removal of the solvent followed by washing with diethyl ether in order to separate the salts. Inorganic bases such as MeLi and n-BuLi can also be used to deprotonate **2**, but the yield is lower, and formation of Ph_2P—PPh_2 is observed, as indicated by a signal at −14.1 ppm in the ^{31}P NMR spectrum.

The solid state structure of **2**·BF_4 is shown in Figure 1. The cation and the disordered anion lie both on a 2-fold axis and are bound by N—H···F hydrogen bond [N2···F2B, 2.902(6) Å; N2—H2A···F2B, 164.2°]. Within the cation, the P—P and the P═N bond lengths are very similar to those of already reported compounds (showing a light shortening of the P—P and a consequent lengthening of the P═N).[5]

In order to probe if this rearrangement can be transferred into other systems, diphosphinoamines **3**−**7** (see Chart 1) were prepared using a standard aminolysis reaction. The pyridine N-atom in the precursors does not affect the phosphylation of the NH_2 group, and in all reactions, the diphosphinoamine is the only product formed, contrary to other observations.[10] The formation of iminobiphosphines

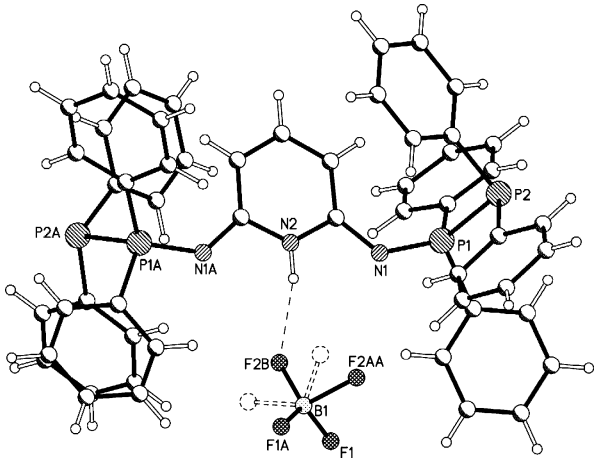
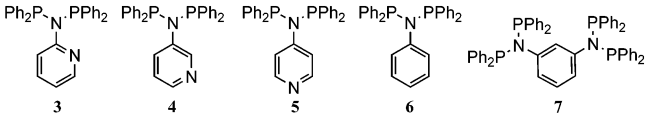
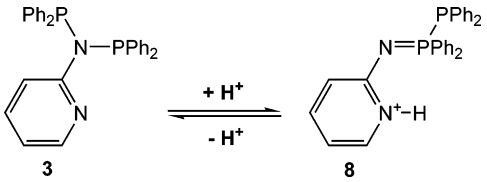


Figure 1. The molecular structure of **2** in the solid state. Key bond distances (Å) and angles (deg): P1—N1, 1.591(2); P1—P2, 2.2253(12); N1—C1, 1.356(4); N2—C1, 1.366(3); N1—P1—P2, 120.27(11); C1—N1—P1, 126.2(4).

Chart 1



Scheme 2



was not observed, which is not the case for nitrile-substituted anilines,[5] and the lack of the additional steric hindrance may account for the exclusive formation of the P—N—P products.

Treatment of **3** with HBF_4·Et_2O or CF_3SO_3H under the same conditions as those described for **1** also gave the N═P—P products **8**·BF_4 and **8**·SO_3CF_3 in near-quantitative yield, respectively (Scheme 2). The frequency and the $^1J_{P-P}$ value for **8**·BF_4 [18.9, −20.3 ppm, 280 Hz] and **8**·SO_3CF_3 [19.0, −20.0 ppm, 283 Hz] are very close to those for **2**. Similarly, deprotonation of **8** results in regeneration of **3**. (The structure of **8**·BF_4 is closely related to that of **2**·BF_4 and is given in the Supporting Information.)

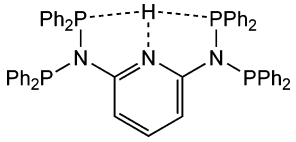
The reaction of **4** and **5** with HBF_4 under analogous conditions is somewhat more complicated giving several products, as evidenced by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of a 1:1 reaction mixture of **4** and HBF_4·Et_2O displays seven signals between 165.0 and −19.0 ppm. Two of the signals are doublets, 21.0 and −19.5 ppm ($^1J_{P-P}$ = 285 Hz), which could be assigned to the expected iminobiphosphine cation, but the total yield is less than 20% on the basis of relative intensities. We were unable to isolate any single product from the reaction mixture. Protonation of **6** and **7** does not afford N═P—P systems, although protonation of similar compounds has been reported, and in a few cases phosphinophosphinium salts with P—P bonds could be isolated.[2c]

(8) HBF_4·Et_2O (0.320 g, 2.0 mmol) was added slowly to a solution of **1** (1.710 g, 2.02 mmol) in CH_2C1_2 (50 mL) at 0 °C. The reaction mixture was stirred at RT for 1 h, and the solvent was removed under reduced pressure. The solid was washed with diethyl ether (3 × 15 mL), and the solid was collected by filtration dried in a vacuum. (Full details are given in the Supporting Information.)

(9) (a) Foss, V. L.; Veits, Y. A.; Tretyakova, T. E.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1977**, *47*, 954. (b) Foss, V. L.; Veits, Y. A.; Ghernykh, T. E.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1984**, *54*, 2670. (c) Veits, Y. A.; Neganova, E. G.; Borisenko, A. A.; Foss, V. L.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1989**, *59*, 1733.

(10) Rasala, D. *Bull. Soc. Chim. Fr.* **1992**, *129*, 79.

In general, protonation of P—N compounds with Brönsted acids is believed to take place initially at the P-center[11] (evidenced by large J_{P-H} values); subsequently, the proton is transferred to the neighboring N-center with, in some cases, concomitant formation of a P—P bond to yield phosphinophosphonium salts. The basicity of the N- and the P-centers in **1** has not been quantified, although the pK_a's of some P—N compounds have been determined in aqueous solution.[12] Reaction of **1** with HBF_4 in a 1:2 ratio does not lead to compounds containing P—P bonds according to ^{31}P NMR spectroscopy: the initially formed N═P—P product reacts further with another equivalent of HBF_4, so that no compounds containing P—P bonds remain. The reaction of **1** with catalytic amounts of HBF_4 results in a partial transformation to the N═P—P product, demonstrating the reaction is stoichiometric, with 1 equiv of HBF_4 converting the two P—N—P units in the starting material to N═P—P moieties. The analogous reaction of **3** also requires a stoichiometry of 1:1. On the basis of these observations, we postulate that the initial protonated intermediate involves an interaction of the proton over several sites as shown, and not too dissimilar from that present in proton sponge.[14]



Although we are not aware of any structural analogues of the proposed intermediate in the literature, there are many transition metal complexes with this kind of topology.[13] Such an intermediate could rearrange rapidly to yield the iminobiphosphine (after addition of the acid the ^1H-coupled ^{31}P NMR spectra immediately show the two doublets for the final product, even at −20 °C, and no $^1H-^{31}P$ coupling could be observed). The formation of **8** should follow a related mechanism with the protonated pyridine N-center assisting the rearrangement of the P—N—P group. In **4** and **5**, the proton-acceptor is not in the ideally suited *ortho*-position, which presumably leads to the lower selectivity, and in **6** and **7**, it is not surprising that in the absence of any proton-acceptor no reaction takes place.

In conclusion, we have demonstrated, for the first time, a reversible transformation between diphosphinoamines and iminobiphosphines. It is not unreasonable to envisage that this type of transformation can be expanded to many other diphosphinoamine systems allowing the synthesis of otherwise inaccessible cationic iminobiphosphines and polyiminobiphosphines. Moreover, the two N═P—P units in compound **2** offer opportunities for both polynuclear and supramolecular organophosphorus chemistry.

Acknowledgment. We thank the Swiss National Science Foundation and the EPFL for financial support.

Supporting Information Available: Experimental details, including synthesis and characterization of starting materials, and a figure of **8**·BF_4. Crystallographic data in CIF format for structures **2**·BF_4 and **8**·BF_4. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049850W

(11) (a) Dahl, O. *Tetrahedron Lett.* **1982**, 1493. (b) Cowley, A. H.; Lattman, M.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 2916.
(12) Kaljurand, I.; Rodima, T.; Leito, I.; Koppel, I. A.; Schwesinger R. *J. Org. Chem.* **2002**, *65*, 6202.
(13) (a) Schirmer, W.; Floerke, U.; Haupt, H. J. *Z. Anorg. Allg. Chem.* **1987**, *545*, 83. (b) Schirmer, W.; Floerke, U.; Haupt, H. J. *Z. Anorg. Allg. Chem.* **1989**, *574*, 239.
(14) (a) Brzezinski, B.; Grech, E.; Malarski, Z.; Sobczyk, L. *J. Chem. Soc., Perkin Trans. 2* **1991**, 857. (b) Pozharskii, A.; Ozeryanskii, V. A.; Starikova, Z. A. *J. Chem. Soc., Perkin Trans. 2* **2002**, 318.