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Evidence for Nondissociative Ligand Exchange within [4+2]-Coordinate Phosphorus Species in Solution

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[4+2]-Coordinate phosphorus compounds, [bis(8-(dimethylamino)-1-naphthyl)]phenylphosphane, [bis(8-(dimethylamino)-1-naphthyl)]phenylphosphane sulfide, [bis(8-(dimethylamino)-1-naphthyl)]phenylphosphonium bromide, [bis(8-(dimethylamino)-1-naphthyl)]methylphosphane, and [bis(8-(dimethylamino)-1-naphthyl)]phosphane oxide, with two identical bidentate (8-(dimethylamino)-1-naphthyl) ligands have asymmetrical geometries in solution and undergo intramolecular nondissociative ligand exchange as shown by dynamic ^{1}H NMR studies. The $\Delta G^\ddagger$ values for this process were found to lie in the range 56.2−61.7 kJ mol^{-1}. The ^{1}H NMR study for bis[(8-(dimethylamino)-1-naphthyl)]phenylphosphane sulfide has revealed that two hexacoordinate isomers coexist in solution in a solvent dependent ratio. Their interconversion in solution is consistent with an intramolecular 1,2-shift of adjacent ligands.

Introduction

Phosphorus, like silicon, is able to expand its coordination number by intramolecular coordination of a strategically placed donor group, leading to the formation of stable hypercoordinate phosphorus species. However, though numerous examples of neutral hexacoordinate phosphorus compounds have been reported in the literature, most of them are derived from pentavalent phosphorus.[1,2] For some years, we have been investigating [4+2]-coordinate phosphorus compounds made from tri- or tetravalent phosphorus. Thus, the X-ray crystal analyses of phosphane **1**,[3] phosphane sulfide **2**,[3] and phosphonium salt **3**,[4] containing two 8-(dimethylamino)-1-naphthyl ligands, have revealed pseudo-[4+2] coordination at the phosphorus center for **1** (taking into account the lone pair) and [4+2] coordination at phosphorus for **2** and **3** owing to the coordination of both NMe$_2$ groups to the central phosphorus with N−P distances of 2.78−2.79 Å for **1**, 3.01 Å for **3**, and 2.70−2.74 Å for **3**. The geometry of **1**, **2**, and **3** corresponds to bicapped tetrahedrons which is the geometry observed for the neutral [4+2]-coordinate silicon compounds **4a** and **4b**.[5] Furthermore, a dynamic ^{1}H NMR study carried out on these silanes has clearly shown that the hexacoordination of the silicon atom is maintained in solution with the same dissymmetric geometry. A nondissociative permutational isomerization process was proposed to explain the dynamic ^{1}H NMR results.[6] The similar structures for compounds **1**, **2**, and **3** on the one hand and **4a** and **4b** on the other prompted us to investigate the solution behavior of phosphorus compounds in which hexacoordination at phosphorus could be achieved by intramolecular coordination of two NMe$_2$ groups.

In this paper, the intramolecular nondissociative ligand exchange of [4+2]-coordinate phosphorus compounds **1**−**3**, **5**, and **6** is described. An analysis of the ligand exchange is made by dynamic ^{1}H NMR studies and a mechanistic pathway is proposed and compared to that obtained for the analogous silicon compounds.

Experimental Section

NMR spectra were recorded on Bruker 200-SY, 250-AC, and DRX-400 spectrophotometers. ^{1}H and ^{13}C spectra were referenced relative to SR of the internal TMS signal measured in pure solvents. The same method was used for ^{31}P spectra with external H_3PO_4. 2 D spectra were acquired using standard Bruker microprograms with 16 scans, 2048 points in t_2 and 1024 points and zero-filling in t_1. The NOESY experiment was performed with a relaxation delay D1 of 10 s, a 900 ms mixing time, and the COSY-LR with a D1 of 2 s and an 80 ms delay D2 to emphasize correlations through long-range coupling constants.

Preparation of [Bis(8-(dimethylamino)-1-naphthyl)]phosphane Oxide 6. A 1.25 g (8.57 mmol) amount of dichloro *N*-dimethylaminophosphane was added dropwise, at −80 °C, to 3 g (16.95 mmol) of 8-(dimethylamino)-1-naphthyllithium in 80 mL of THF. The reaction mixture was stirred at room temperature for 15 h and then hydrolyzed with 10 mL of distilled water. After removal of the THF, 40 mL of ether was added to extract the product. The insoluble impurities were eliminated by filtration, and the ethereal solution was dried on MgSO$_4$. The solvent was removed in vacuo to afford 1.26 g of **6** (38% yield) as a white powder. ^{31}P NMR (CDCl$_3$): 16.5 (d, J = 597 Hz). ^{1}H NMR (toluene-d_8): 1.98 (broad signal, 12 H, Me), 7.0−8.1 (m, 11 H,

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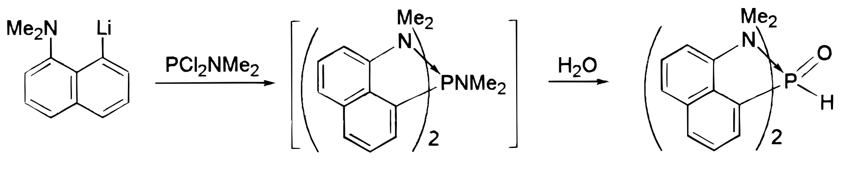
Scheme 1

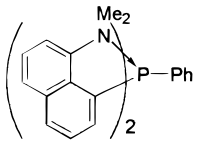


7 **6**

naphthyl H), 9.2 (d, $J = 597$ Hz, 1 H, PH). Anal. Calcd for $C_{24}H_{25}N_2OP$: C, 74.22; H, 6.44; N, 7.21. Found: C, 73.96; H, 6.27; N, 7.24.

Results and Discussion

A. Fluxional Behavior in Solution for Compounds 1, 3, 5, and 6. The synthesis of compounds **1**−**3** and **5** has been



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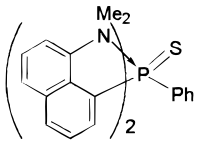

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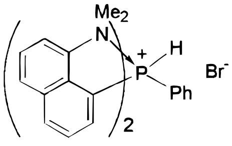

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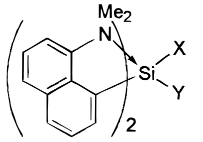
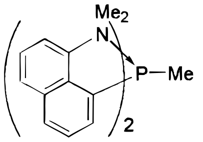


4 a : X = Y = H
4 b : X = H, Y = F



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previously reported.[3,4] Compound **6** was obtained in 38% yield by the hydrolysis of aminophosphane **7** which was not isolated (Scheme 1).

The ^{1}H NMR spectra of compounds **1**, **3**, **5**, and **6** in solution are temperature dependent as are those of silanes **4a** and **4b**.[6] At low temperature, the ^{1}H NMR spectra of these compounds display four sharp signals for the *N*-methyl hydrogens and two distinct sets of signals for the naphthyl hydrogens. This shows that compounds **1**, **3**, **5**, and **6** are [4+2]-coordinated in solution with asymmetrical geometries as has been observed in the solid state for **1**[3] and **3**.[4] Long-range homonuclear COSY experiments allowed assignment of the methyl groups attached to the same nitrogen atom, whereas NOESY experiments as well as saturation transfer by selective irradiation permitted identification of the exchange signals. For example, if we label the two methyl groups of one NMe$_2$ unit as A and B and the methyl groups of the other NMe$_2$ unit as A′ and B′, by detecting long-range couplings between A and B and between A′ and B′, respectively, we ascertain that A is exchanging with A′ and B with B′, as indicated in Table 1.

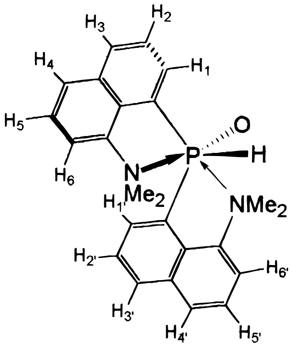
It is to be noted that, at low temperature, each nitrogen atom bears one methyl group the resonance of which occurs around 3 ppm while the resonance of the other methyl occurs 0.8−2.4 ppm upfield, the upper value being observed for compound **6** at 233 K (Table 1). Furthermore, there is no correlation between the presence or absence of a phenyl group at the phosphorus atom and the upfield shifts (compare **1** and **5** in Table 1).

Table 1. ^{1}H NMR Chemical Shifts of the *N*-Methyl Protons for Compounds **1**, **3**, **5**, and **6** at Low and at High Temperature

	Me			
compound	A	A′	B	B′
1[a] at 258 K	2.84	1.547	1.70	2.60
1[a] at 398 K	2.26[d,e]		2.22[d,e]	
1[b] at 283 K	3.18	1.94	2.06	2.93
1[b] at 373 K	2.56[f]		2.56[f]	
3[b] at 283 K	3.20	1.67	1.88	3.02
3[b] at 395 K[g]	2.44[d]		2.49[d]	
5[c] at 233 K	2.84	1.63	2.43	2.69
5[c] at 373 K	2.22		2.54	
6[c] at 233 K	3.06	1.92	0.82	2.71
6[c] at 373 K	2.52		1.92	

[a] In *o*-dichlorobenzene-d_4. [b] In $CDBr_3$. [c] In toluene-d_8. [d] Assignments may be reversed. [e] These two signals coalesce at 418 K. [f] Unresolved doublet. [g] The compound decomposes at this temperature.

Scheme 2



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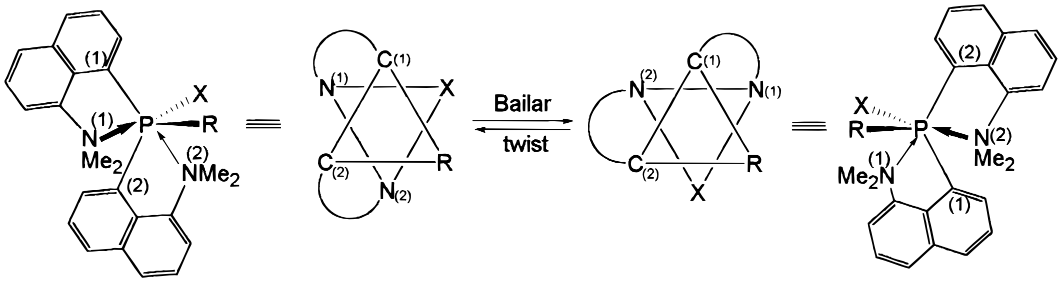
Therefore, the upfield shifts of some methyl groups are probably due to the geometry of the corresponding compound in which the two methyl groups of an NMe$_2$ unit are unequally affected by the shielding zone of the naphthyl rings as can be seen in the ORTEP representations of the molecular structures of **1**[3] and **3**.[4]

On raising the temperature, coalescence of the *N*-methyl signals is observed. As indicated in Table 1, signal A coalesces with signal A′ and signal B coalesces with signal B′ giving rise to two signals AA′ and BB′ (Table 1) which are poorly separated for **1** ($\Delta\delta = 0.038$ in *o*-dichlorobenzene-d_4) and **3** ($\Delta\delta = 0.044$ ppm in $CDBr_3$), whereas the separation is more evident for **5** ($\Delta\delta = 0.3$ ppm in toluene-d_8) and **6** ($\Delta\delta = 0.6$ ppm in toluene-d_8). The observation of the coalescence of a methyl group of one NMe$_2$ unit with a methyl group of the other NMe$_2$ unit excludes a process involving N→P coordinative bond breaking. Such a dissociation would result in the coalescence of methyl resonances of the same NMe$_2$ unit through inversion at the nitrogen atom. Thus a nondissociative intramolecular isomerization process must occur.

On raising the temperature, coalescence of the naphthyl proton resonances also occurs thus showing the equivalence of both

Scheme 3



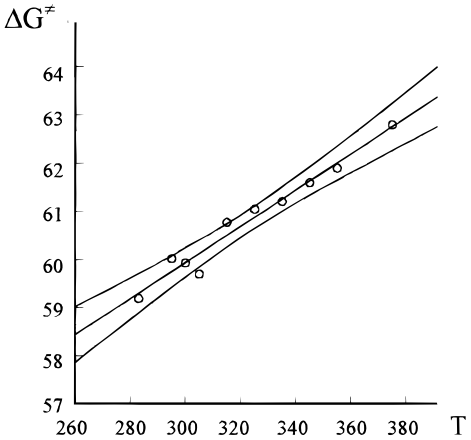


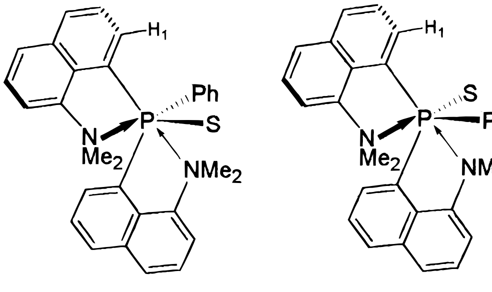
Figure 1. Plot of $\Delta G^{\ddagger}$ (kJ mol^{-1}) versus temperature T (K) for compound **3**.

Table 2. Calculated Energies Barriers for the Fluxional Processes for Compounds **1**, **3**, **5**, and **6**

compound	$\Delta G^{\ddagger}$ (kJ mol^{-1}) at 300 K	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
1^{a}	61.7	53 ± 1	−28 ± 3
1^{b}	62.3	52.3 ± 0.8	−33 ± 3
3^{b}	59.9	48.7 ± 0.8	−38 ± 3
5^{c}	57.5	58.5 ± 0.5	+4 ± 2
6^{c}	56.2	52 ± 1	−13 ± 4

^{a} In *o*-dichlorobenzene-d_4. ^{b} In CDBr$_3$. ^{c} In toluene-d_8.

Scheme 4



2a **2b**

naphthyl rings. This phenomenon has been analyzed in detail for compound **6** using a 400 MHz spectrometer. It was found that, at 233 K, the signals of the hydrogens of the two naphthyl rings present very different chemical shifts for the three spin systems. A downfield signal was observed at 9.78 ppm and was assigned to the H_1 located in the deshielding zone of the P=O bond, which means that **6** is in the conformation indicated in Scheme 2. Two upfield signals at 6.88 and 6.36 ppm have been attributed respectively to protons $H_{1'}$ and $H_{2'}$ (Scheme 2). When the temperature is increased, the signals first broaden and then coalesce leading at 373 K to a single naphthyl system. Raising the further temperature resulted in decomposition of **3** and **6** above 400 K, thus preventing the observation of a possible coalescence of the two methyl signals. However, coalescence of two methyl signals for **1** was observed on raising the temperature to 418 K.

The results presented above are in agreement with an intramolecular nondissiociative mechanism involving ligands exchanges without N→P coordinative bond cleavage. In order to determine the rate constants of this permutational isomerization process at various temperatures, a simulation of all the dynamic NMR spectra line shapes of methyl group signals was made with either gNMR[7] or DNMR4.[8] The values of the free energies of activation $\Delta G^{\ddagger}$ of these permutational site exchanges were obtained from the Eyring equation,[9] and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated by use of Eyring plots. A linear relationship was found (see one example in Figure 1) which could indicate that a single mechanism is operative throughout the temperature range studied. The results obtained are shown in Table 2. In the case of phosphane **1**, the broad signal corresponding to two poorly resolved signals at 398 K becomes sharper as the temperature increases, but this could be due either to a coalescence or to slight changes in chemical shifts with the temperature. For these reasons, the simulations have been made assuming that the process involving N→P coordinative bond cleavage is insignificant in the temperature range in which the exchange process of A with A′ and B with B′ takes place. The coalescence of these two signals at 418 K may indicate the cleavage of the N→P coordinative bond. The free energy of activation for this cleavage was estimated to be 90 kJ mol^{-1}.

The equivalence of the naphthyl rings as well as that of the methyl groups by pairs is consistent with a Bailar twist type mechanism[10] (Scheme 3) or a Ray−Dutt twist type mechanism[11] in which one enantiomer interconverts to the other, the intermediate in both processes being similar.[12]

B. Fluxional Behavior of Phosphane Sulfide 2. The X-ray structure determination of the phosphane sulfide **2** reveals that the latter exists as one isomer in which one N→P coordinative bond is trans to the P−Ph bond[3] (Scheme 4). The solid state ^{31}P NMR spectrum shows one signal at $\delta = 50.9$ ppm. In contrast, the ^{1}H NMR study of the phosphane sulfide **2** in solution indicates the presence of two isomers, the ratio of which depends on the nature of the solvent. Indeed, the ^{1}H NMR spectrum of **2** displays at room temperature eight sharp signals attributed to the *N*-methyl hydrogens in a 60/40 ratio in CDCl$_3$ or CDBr$_3$ and in an 80/20 ratio in toluene-d_8.

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Table 3. NOESY[a] and COSYLR[b] Connectivity Matrix for *N*-Methyl Protons[c] for Compound **2** in $CDCl_3$

	isomer **a** Me (A)	isomer **b** Me (A)	isomer **a** Me (B′)	isomer **b** Me (B′)	isomer **b** Me (A′)	isomer **a** Me (A′)	isomer **a** Me (B)	isomer **b** Me (B)
isomer **a**, Me (A)	2.736			E		E	LR	E
isomer **b**, Me (A)		2.631	E		E		E	LR
isomer **a,** Me (B′)		E	2.241		E	LR	E	
isomer **b**, Me (B′)	E			2.108	LR	E		E
isomer **b**, Me (A′)		E	E	LR	1.253		E	
isomer **a**, Me (A′)	E		LR	E		1.088		E
isomer **a**, Me (B)	LR	E	E		E		1.073	
isomer **b**, Me (B)	E	LR		E		E		1.043

[a] E, signals belonging to exchangeable nucleii. [b] LR, signals belonging to nucleii connected by long-range coupling constants. [c] Chemical shifts (ppm) are called back in the diagonal.

Thus, it can be concluded that both isomers are [4+2]-coordinated in solution with an asymmetrical geometry. Furthermore, the ^{31}P NMR spectrum for **2** in benzene exhibits two signals, one at $\delta = 63.9$ (minor) and the other at $\delta = 53.5$ (major), this latter signal having a chemical shift very close to that observed in the solid state (50.9 in solid state ^{31}P NMR spectroscopy). Thus, the major isomer **2a** should presumably have the same geometry as **2** in the solid state.[3] The geometry of the minor isomer (**2b**) was inferred from the ^1H NMR study of the naphthyl protons. Indeed, at low temperature in toluene-d_8, the ^1H NMR spectrum of the minor isomer exhibits a signal at 9.8 ppm. Hence, one proton of a naphthyl ring is very deshielded, in a similar manner to that previously observed for compound **6**. This downfield signal was attributed to proton H_1 in close proximity to the sulfur atom. Thus the minor isomer should have a geometry similar to that of **6** with one N→P coordinative bond trans to the P═S bond (Scheme 4). Assignments of the eight methyl signals have been made by using long-range homonuclear COSY and NOESY experiments. Their scalar coupling and exchange relationships are summarized in Table 3. These experiments show that the two isomers interconvert in solution. On raising the temperature, the methyl signals finally coalesce into a very broad signal at 373 K. Further heating at 405 K caused decomposition of **2** and, for this reason, there is no evidence of the existence of the equilibrium between **2a** and **2b** on the NMR time scale. The ^1H NMR spectrum of the mixture of phosphane sulfide isomers **2a** and **2b** is too complicated to allow the determination of $\Delta G^\ddagger$ values for the permutational site-exchange process by line-shape studies as above. However by deconvolution studies, we found that when the temperature increases, the signals of isomer **2a** are always broader than those of the isomer **2b**. Simulations at 295, 305, 315, and 325 K showed that in order to account for the experimental half-height widths, the $\Delta G^\ddagger$ value for **2a** must be 2 kJ lower than the $\Delta G^\ddagger$ value for **2b**. However, whereas both isomers **2a** and **2b** should undergo intramolecular ligand exchange processes of the Bailar or Ray−Dutt type, the interconvertion of isomers **2a** and **2b**, detected by COSY and NOESY experiments, is consistent with a 1,2-shift mechanism[13] consisting of a direct intramolecular 1,2-shift of adjacent ligands in the bicapped tetrahedral phosphane sulfide **2**. Thus, in solution, each of the two isomers of phosphane sulfide **2** undergoes a permutational isomerization process, the $\Delta G^\ddagger$ value of which could not be determinated. However, this value must be lower than that for the interconvertion of the isomers.

Conclusion

In this paper, we describe a further example of analogy existing between hypercoordinate silicon and phosphorus compounds. Similar structures for [4+2]-coordinate silicon derivatives **4a** and **4b**[5] and [4+2]-coordinate phosphorus derivatives **1**−**3**[3,4] were already established in the solid state. Dynamic ^1H NMR studies in solution of phosphorus derivatives **1**−**3**, **5**, and **6** show that these compounds undergo intramolecular ligand exchanges which are of the same nature as those already found for the silicon compounds **4a** and **4b**.[6] Another isomerization process consisting in the 1,2 adjacent ligand shift[13] was observed with the phosphane sulfide **2**.

Supporting Information Available: ^1H NMR chemical shifts and coupling constants of the naphthalene protons for **6** in toluene-d_8; ^1H NMR chemical shifts of the *N*-methyl protons for compound **2** in different solvents; long-range ^1H homonuclear COSY of compound **2** (zone of the *N*-methyl signals); NOESY of compound **2** (zone of the *N*-methyl signals). This material is available free of charge via the Internet at http://pubs.acs.org.

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