Coordination Modes

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A Stable Structurally Characterized Phosphorus-Bound Isocyanide and Its Thermal and Catalyzed Isomerization to the Corresponding Cyanide**

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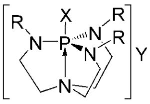
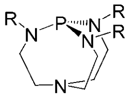
Although the chemistry and structural characteristics of carbon-bound isocyanides and cyanides have been well documented,[1] the relatively few examples of isocyanides that possess CN–heteroatom bonds are largely restricted to sulfur, nitrogen, oxygen, and phosphorus heteroatoms.[2–6] Isocyanides that are bound to heteroatoms are chemically reactive, thermally unstable, and, thus, are readily isomerizable to the corresponding cyanides, which are more stable. Indeed, these properties were reported for the first and only time 30 years ago by Stec et al. for a phosphorus-bound isocyanide.[7] The cationic halogen-bearing azaphosphatranes **1a** and **1b** are robust species stabilized by relatively short $N_{ax}\rightarrow P$ transannular bonds (ax = axial).[8] It occurred to us that the pseudo-halogen character of the CN group might allow the formation of similarly stabilized isocyano analogues, which might isomerize to the cyano-bound species sufficiently slowly to be monitored by spectroscopic means. Herein, we report the facile synthesis of such analogues that were sufficiently stable to permit the structural parameters of a phosphorus-bound isocyano group and its cyano isomer to be determined for the first time and the thermal and Lewis acid catalyzed transformations of the P–NC species into the



	X	Y	R		X	Y	R
1a:	Cl	Cl	Me	**1g**:	–CN	Br	Me
1b:	F	Cl	Me	**1h**:	–CN	Br	*i*Bu
1c:	Br	Br	Me	**1i**:	Br	$AlCl_3Br$	*i*Bu
1d:	Br	Br	*i*Bu	**1j**:	–NC	$AlCl_3Br$	*i*Bu
1e:	–NC	Br	Me	**1k**:	–CN	$AlCl_3Br$	*i*Bu
1f:	–NC	Br	*i*Bu	**1l**:	Cl	Br	*i*Bu



2a: R = Me
2b: R = *i*Bu

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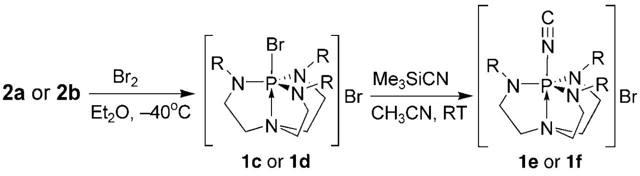
isomeric P–CN species to be followed by ^{31}P NMR spectroscopic analysis.

The reaction of proazaphosphatranes **2a** and **2b** with bromine at room temperature resulted in the formation of **1c** and **1d**, respectively, in near quantitative yield (Scheme 1) as pale yellow solids that are soluble in polar solvents. Trimethylsilyl cyanide reacted quickly with **1c** and **1d** at room temperature in dry acetonitrile (Scheme 1), and immediate removal of all volatiles at room temperature resulted in the formation of off-white solids. Characterization of the product from **2b** revealed the first example of a stable species **1f** that possesses a P–NC linkage, and the product from **2a** was found to be a mixture of **1e** and **1g**. The ^{31}P NMR spectrum of **1f** in solution showed a signal at $\delta = -40.3$ ppm (-40.8 ppm, solid-state ^{31}P MAS NMR spectroscopy). A strong isocyanide stretching vibration at 2088 cm^{-1} that is comparable with the N–C stretching frequencies reported for other known examples of heteroatom-bound isocyanides[6] was observed in the IR spectrum. The ^{13}C NMR spectrum of **1f** showed a doublet at $\delta = 173$ ppm with ^{2}J(P-C) = 26.4 Hz that is assignable to the isocyanide carbon atom. Compound **1f** is stable in the solid state and can be stored in an inert atmosphere at room temperature without observable decomposition or isomerization for at least one month. A single crystal of **1f**[9] suitable for X-ray crystallographic study was obtained by recrystallization from a cooled solution of acetonitrile/diethyl ether. Its molecular structure revealed a trigonal-bipyramidal geometry about the phosphorus center with a P–N$_{ax}$ bond length of 1.9178(13) Å and an apical isocyano group with P–N and N–C bond lengths of 1.7814(14) and 1.154(2) Å, respectively (Figure 1; see also the Supporting Information). The stability of **1f** may, at least in part, be attributed to a linear delocalized four-center six-electron σ-bonding framework along the pseudo-threefold axis of the cation. Interestingly, when the reaction of trimethylsilyl cyanide was attempted with the acyclic trisaminophosphine analogue (namely, [(Me$_2$N)$_3$PBr]Br),[10] no product formation was observed at room temperature over 16 h. At 80 °C, however, the cyanophosphonium salt [(Me$_2$N)$_3$PCN]Br formed quantitatively in 48 h.



Scheme 1. Synthesis of isocyano azaphosphatranes **1e** and **1f**.

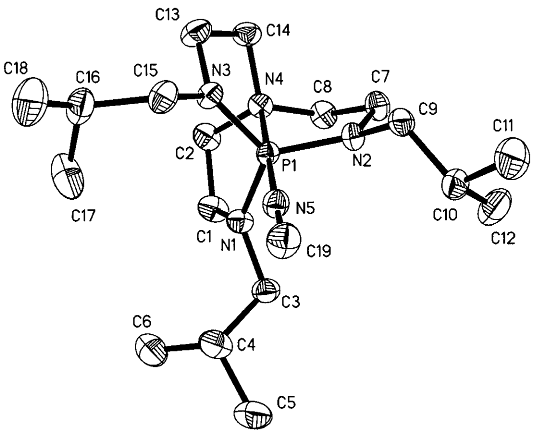
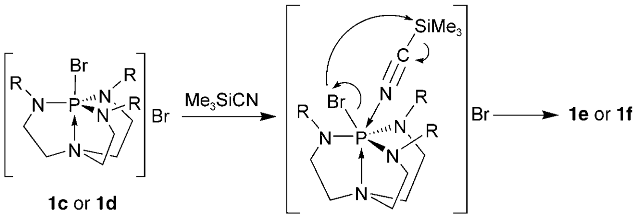


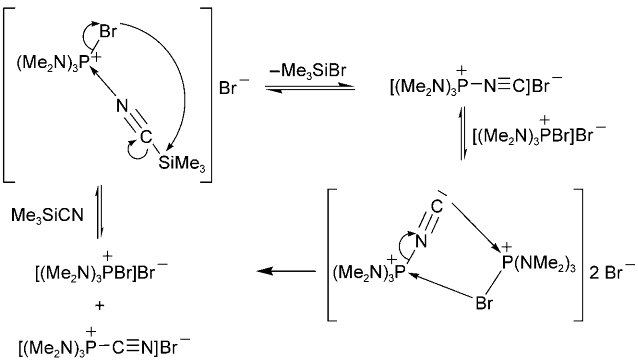
Figure 1. Molecular structure of isocyano azaphosphatrane **1f**.[9]

The initial formation of isocyanides **1e** and **1f** in the reaction of trimethylsilyl cyanide with **1c** and **1d**, respectively, is intriguing. Useful speculation on a reasonable pathway from **1c** and **1d** to **1e** and **1f**, respectively, is somewhat complicated by the assertion that Me$_3$SiCN exists in equilibrium with its more reactive isocyanide isomer.[11] However, the formation of Me$_3$SiNC is rather slow in solution (albeit in 1-chloronaphthalene rather than MeCN), thus taking approximately 10 minutes at 225 °C to reach an approximate concentration of 0.15 % relative to that of the cyano isomer.[12] It is therefore reasonable to conclude that this equilibrium would be reached even more slowly at room temperature, thus suggesting that the provenance of the isocyano isomers **1e** and **1f** and, through their isomerization, the cyano isomers **1g** and **1h**, respectively, is Me$_3$SiCN and not Me$_3$SiNC because of the almost instantaneous formation of **1e** and **1f** at room temperature.

It has also been reported that the ability of Me$_3$SiCN to act as a source of either cyanide or isocyanide in reactions with ketones and epoxides is greatly affected by the presence of hard or soft Lewis acids that favor the formation of C–CN and C–NC linkages, respectively.[13] Compounds **1c** and **1d** could possess soft Lewis acid character, thus leading to the creation of the corresponding isocyanide isomers as the kinetically favored stable species **1e** and **1f** (Scheme 2). It is interesting in this regard that acyclic [(Me$_2$N)$_3$PBr]Br does not form detectable amounts of [(Me$_2$N)$_3$PNC]Br with Me$_3$SiCN but rather gives [(Me$_2$N)$_3$PCN]Br (albeit only on heating). The preferential formation of the cyano isomer in the latter reaction may be associated with the harder Lewis acidity of the phosphorus center in the cation of [(Me$_2$N)$_3$PBr]Br as a result of the greater concentration of positive charge at the phosphorus center than in **1d**, which delocalizes this charge more extensively over the nitrogen atoms. Therefore, it is possible that [(Me$_2$N)$_3$PNC]Br is formed kinetically followed by rapid isomerization (Scheme 3). As the reaction proceeds, the Lewis acid catalyst, the [(Me$_2$N)$_3$PBr]$^+$ ion, in Scheme 3 would be replaced by Me$_3$SiBr (see later) or by the [(Me$_2$N)$_3$PCN]$^+$ ion as a Lewis



Scheme 2. Possible mechanism for the formation of isocyanides **1e** and **1f**.



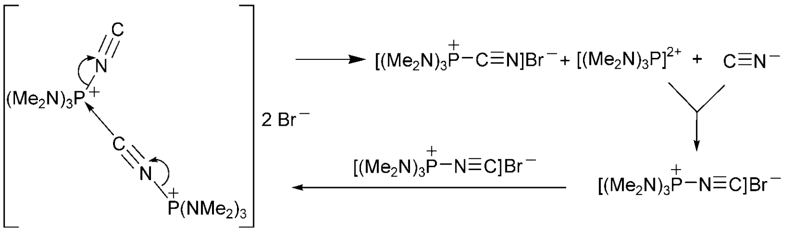
Scheme 3. Possible mechanism for the preferential formation of cyanide in the reaction of $[(Me_2N)_3PBr]Br$ with Me_3SiCN.

Table 1: Factors affecting the rate of isomerization of isocyanide **1f** to cyanide **1h**.

Entry	Solvent	Lewis acid	T [°C]	t	Isomerization [%]
1	MeCN		80	96 h	90
2	benzene		80	96 h	<2
3	MeCN	Me_3SiCl	80	24 h	80
4	MeCN	Me_3SiBr[a]	80	30 min	98
5	MeCN	Me_3SiBr[a]	60	1 h	97
6	MeCN	Me_3SiBr[a]	25	16 h	97
7	MeCN	Me_3SiOTf	25	5 min	99
8	MeCN	$AlCl_3$	25	5 min	99

[a] One equivalent of Me_3SiBr was generated in situ by the reaction of **1d** with Me_3SiCN, as shown by ^1H NMR spectroscopic analysis. Tf = trifluoromethanesulfonyl.

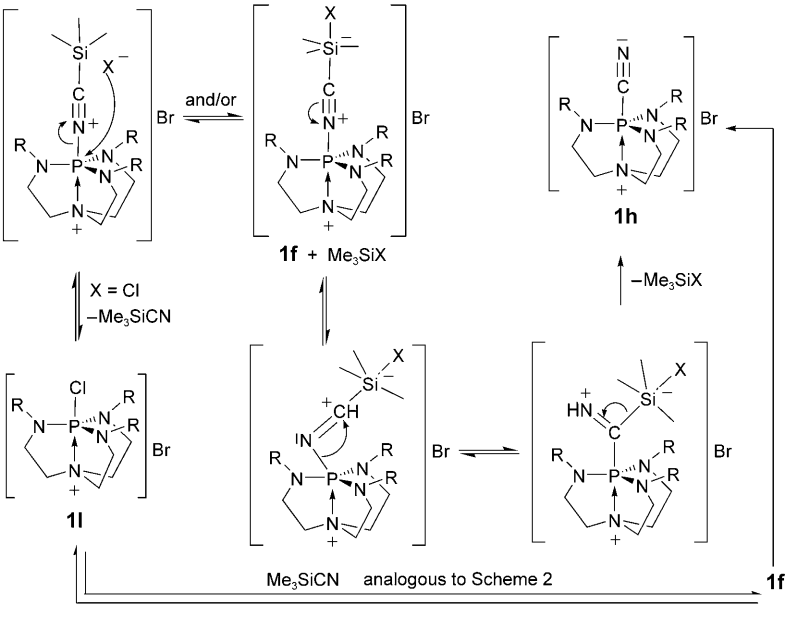
acid isomerization catalyst (Scheme 4). However, the $[(Me_2N)_3PCN]^+$ ion in this role would form an unlikely dicationic intermediate. Such a mechanism might be contemplated, however, for the thermal isomerization of **1e** and **1f** because the analogous intermediate $^{+}\overline{P(RNCH_2CH_2)_3N}^{+}$ is isoelectronic with boratrane ($\overline{B(OCH_2CH_2)_3N}$) (**4**), the structure of which has been determined by X-ray crystallographic studies.[14] Dipositive heterocyclic cations with charges on adjacent atoms are known, as in the cases of $^{+}\overline{S[(CH_2)_x]_2S}^{+}$ in which $x = 2$ or 3[15ab] and $^{+}\overline{P[(CH_2)_x]_3P}^{+}$ in which $x = 3$ or 4.[15c]



Scheme 4. Possible mechanism for the self-catalyzed isomerization of $[(Me_2N)_3PNC]Br$ to $[(Me_2N)_3PCN]Br$.

Heating a solution of **1f** in acetonitrile at 80 °C resulted in quantitative isomerization to **1h** in 120 h, as shown by ^{31}P NMR spectroscopic analysis. The rate of isomerization of **1f** was found to be dramatically influenced by the solvent polarity (Table 1, entries 1 and 2) and the presence of one equivalent of a Lewis acid (see Schemes 3–5 and the Supporting Information). Almost instantaneous isomerization occurred with the addition of one equivalent of $AlCl_3$ or Me_3SiOTf at room temperature. The trend $Me_3SiOTf > Me_3SiBr > Me_3SiCl$ in Table 1 parallels their decreasing Lewis acidity.[11] Interestingly, when the isomerization of **1f** promoted by Me_3SiCl was followed by ^{31}P NMR spectroscopic analysis, a transient signal at $\delta = -1.7$ ppm corresponding to **1l**, perhaps from an intermediate in a competing pathway, was observed (Scheme 5). It was expected that the addition of one equivalent of a Lewis acid (e.g., $AlCl_3$ or Me_3SiX) to the isomerization reaction of **1f** to **1h** would establish an equilibrium that involves the formation of the $[AlCl_3Br]^-$ ion or the pentavalent silicate $[Me_3Si(X)Br]^-$ ion (formed from $AlCl_3$ and Me_3SiX as the Lewis acids, respectively), which are both complex anions that would result from the addition of the bromide anion in **1f**. The presence of these anions containing coordinatively saturated central atoms was found to suppress the concentration of $[Me_3SiX]/[AlCl_3]$; consequently, the Lewis acid catalyzed izomerization of P–NC linkages to P–CN in **1f** was inhibited. It was interesting in this regard to observe that the conversion of **1i** into **1j** followed by the addition of a catalytic amount of $AlCl_3$ (10 mol %) resulted in the complete isomerization of **1j** to **1k** in CH_3CN in five minutes at room temperature.

Evidence to support an equilibrium process for the Lewis acid catalyzed isomerization of the phosphorus-bound isocyanides **1e** or **1f** was obtained as follows: Treatment of **1c** with one equivalent of Me_3SiCN at room temperature led to a



Scheme 5. Lewis acid promoted isomerization of isocyanide **1f** to cyanide **1h** by Me_3SiX.

mixture of **1e** and **1g** in a ratio of 10:90 being obtained within five minutes. This ratio became 50:50 on addition of two equivalents of Me_3SiCN and 90:10 on addition of five equivalents of Me_3SiCN within the same time period. This observation suggests that a silicon-based Lewis acid catalyst does interact with the isocyano compound **1e** (or **1f**), perhaps as shown in Scheme 5, because in the presence of five equivalents of Me_3SiCN, which is a very weak Lewis acid relative to Me_3SiBr, it is more probable that Me_3SiCN will interact with **1e**, thus inhibiting the isomerization process.

Although an isomerization of tertiary alkyl isocyanides catalyzed by $BF_3 \cdot Et_2O$ has been described,[16] neither $AlCl_3$ nor silicon-based Lewis acids have been reported to isomerize isocyanides of any type. Moreover, it is interesting that $AlCl_3$ and Me_3SiX ($X = Cl$, Br, OTf) are capable of converting **1f** into **1h**, even though **1f** bears a positive charge and might be expected to behave poorly as a Lewis base.

Although uni- and bimolecular mechanisms for the isomerization of carbon-bound isocyanide have been proposed, the available experimental and theoretical results suggest a unimolecular pathway that involves a three-membered-ring transition state.[17] Initial kinetic studies of the isomerization of **1f** to **1h** suggest that the mechanism for the uncatalyzed thermal isomerization involves a pathway more complicated than the uni- or bimolecular mechanisms.

A white solid was isolated after complete isomerization of **1f** in acetonitrile. The ^{31}P NMR spectrum of this compound showed a single resonance at $\delta = -35.3$ ppm with $^{1}J(\text{P-C}) = 122.4$ Hz consistent with **1h**, and the ^{13}C NMR spectrum revealed a doublet for the carbon atom of the cyano group at $\delta = 123$ ppm with $^{1}J(\text{P-C}) = 122.3$ Hz. IR spectroscopic analysis revealed a rather weak C–N stretching vibration at 2197 cm^{-1}, which is comparable with frequencies of other known examples of phosphorus-bound cyanides.[18] A single-crystal X-ray structural analysis of **1h**[9] supports its formation from the isomerization of **1f** (P–C: 1.854(2) Å; C–N: 1.148(3) Å) because the P–C bond is longer than the P–N bond in **1f**, which is as expected (see Figure 2 and the Supporting Information).

A detailed kinetic analysis of the isomerization of **1f** to **1h**, for example, and theoretical calculations aimed at a deeper understanding of the bonding and the isomerization pathways of these systems will be reported in due course.

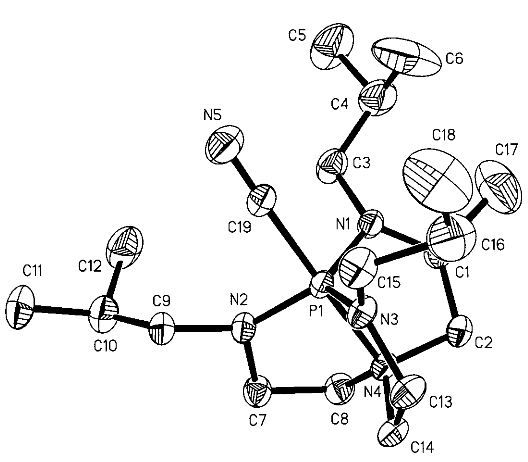


Figure 2. Molecular structure of cyano azaphosphatrane **1h**.[9]

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