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Reaction of a Cyclic Triphosphenium Ion with Triflic acid and SnX_2 ($X = Br$ or Cl): A ^{31}P NMR Study

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ABSTRACT: *The di-ium dication formed by triflic acid protonation of the cyclic triphosphenium ion derived from 1,4-bis-diphenylphosphinobutane, (dppb), and PX_3($X = Br$ or Cl) decomposes via an acyclic dication bearing a —PHX group; this intermediate is reduced by SnX_2 in the presence of HX to yield a dication with a $-PH_2$ primary phosphane terminal group, which is comparatively stable. The structure of this species has been unequivocally confirmed by ^{31}P solution-state NMR spectroscopy.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:609–612, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20302

INTRODUCTION

Protonation of the cyclic triphosphenium ions [1–6] derived from 1,2-bis-diphenylphosphinoethane (dppe) or tetraphos by a mixture of ^{t}BuCl and $AlCl_3$ was first demonstrated by Schmidpeter and coworkers [2,7]. In a recent paper, we have extended this work considerably, having protonated a wide variety of cyclic triphosphenium ions to the corresponding di-ium dications, using either a ^{t}BuCl—$AlCl_3$ mixture or triflic acid [8]. The stabilities of the dications depended on ring size, with stability decreasing in the order $5 > 6 > 7$-membered rings. We also found that decomposition of the seven-membered ring dication derived by ^{t}BuCl/$AlCl_3$ protonation of the cyclic triphosphenium ion from 1,4-bis-diphenylphosphinobutane (dppb) proceeded via ring opening to give a P—P bonded species, with the end group assigned as a —PHCl fragment. Unfortunately, we were unable to record the proton-coupled ^{31}P NMR spectrum of this intermediate, to confirm the P—H bond, before further decomposition occurred, although the final reaction products are the diprotonated diphosphane $[Ph_2PH(CH_2)_4PHPh_2]^{2+}$ and probably polymeric phosphorus [8,9]. We now present conclusive evidence from ^{31}P NMR solution-state spectroscopy, including low-temperature studies, for a further intermediate dication formed by a redox reaction in the presence of SnX_2 ($X = Br$ or Cl), with a terminal primary phosphane $-PH_2$ group; this moiety is comparatively stable, although the final decomposition products are identical to those from the ^{t}BuCl—$AlCl_3$ reaction.

RESULTS AND DISCUSSION

The cyclic triphosphenium ion **1** was formed as its hexahalogenostannate(IV) salt via

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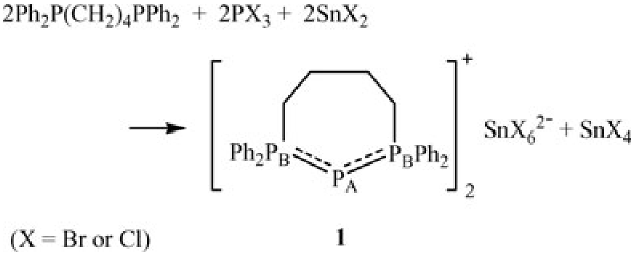


(1)

an approximately 1:1:1 reaction between dppb, PX_3, and SnX_2 (Eq. (1)) (see the Experimental section). Its formation was confirmed by ^{31}P NMR solution-state spectroscopy, e.g., for the $SnBr_6^{2-}$ salt δ P_B 34.2 (d), δ P_A −210.8 (t) ppm, $^1J_{PP}$ 453.2 Hz; lit. δ P_B 34.3 (d), δ P_A −210.9 (t) ppm, $^1J_{PP}$ 454.6 Hz for Cl^- as the counterion; δ P_B 34.1 (d), δ P_A −211.2 (t) ppm, $^1J_{PP}$ 454.3 Hz for the $SnCl_6^{2-}$ salt [4]. The solution was divided into two parts, one to act as a "blank"; excess triflic acid was added to the second portion. When the reaction was carried out using $SnBr_2$ and PBr_3 at room temperature and the ^{31}P NMR spectrum of the reaction mixture recorded after 10 min, the ring signals had disappeared and two new doublets were apparent in the $^{31}P\{^1H\}$ spectrum, at δ 24.2 and −185.8 ppm, $^1J_{PP}$ 219.0 Hz, together with a singlet at δ 10.8 ppm (Table 1). When the corresponding spectrum was recorded proton coupled, the doublet at −185.8 ppm split into a doublet of triplets, $^1J_{PP}$ 219.0 Hz, $^1J_{PH}$ 205.1 Hz, (Fig. 1), while the singlet at 10.8 ppm split into a doublet, $^1J_{PH}$ 507.4 Hz (Table 1). On the following day, a further portion of triflic acid was added to complete the decomposition; the proton-decoupled ^{31}P NMR spectrum of the resultant solution showed only a singlet at 12.6 ppm, which split into a doublet, $^1J_{PH}$ 495.6 Hz, when recorded proton coupled, ascribed to P_M in the diprotonated diphosphane **5** (Table 1 and Scheme 1). These results show conclusively that an intermediate in the decomposition process is the $[Ph_2P_LH(CH_2)_4P_KPh_2P_JH_2]^{2+}$ ion **4** (Scheme 1). A control experiment using dppb and triflic acid (1:2) in $CDCl_3$ to form **5** gave a singlet for P_M at 10.1 ppm in the proton-decoupled ^{31}P NMR spectrum, and a doublet in the same region with $^1J_{PH}$ 490.5 Hz when recorded proton coupled. The unprotonated ring in the first portion of solution remained stable throughout this period.

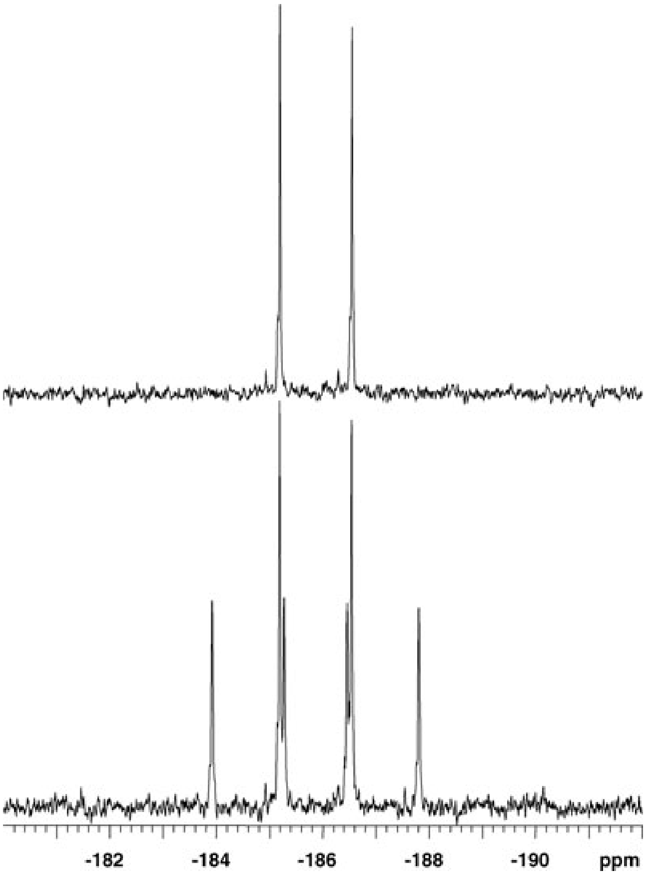


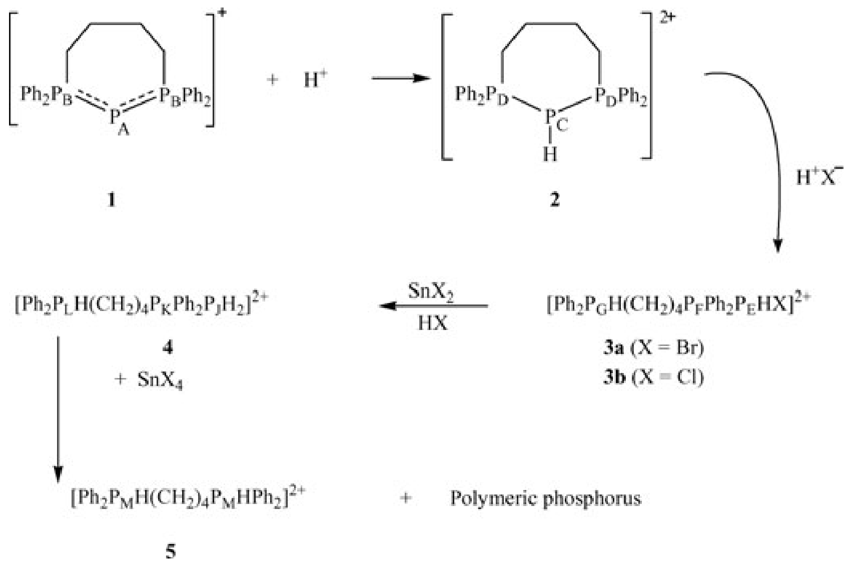
FIGURE 1 ^{31}P NMR spectrum of the $-PH_2$ group in **4** (upper part) proton decoupled and (lower part) proton coupled. Recorded in $CDCl_3$ at 161.9 MHz; 96 transients in each case.

TABLE 1 ^{31}P NMR Data

		$\delta^{31}P$ (ppm)	*$^1J_{PP}$ (Hz)*	*$^1J_{PH}$ (Hz)*
1[a]	P_A	−210.8 t	453.2	
1[a]	P_B	34.2 d	453.2	
2	P_C	−132.7 dt	251.8	235.7
2	P_D	29.0 d	251.8	
3a	P_E	−50.0 dd	279.3	186.8
3b	P_E	−16.2 dd	279.9	197.9
3a	P_F	23.8 dm	278.5	
3b	P_F	28.3 dm	279.9	
3a	P_G	10.5 d		495.1
3b	P_G	10.5 d		506.6
4	P_J	−185.8 dt	219.0	205.1
4	P_K	24.2 d	219.0	
4	P_L	10.8 d		507.4
5	P_M	12.6 d		495.6

[a] $^{31}P\{^1H\}$ NMR spectrum.

In an attempt to clarify the earlier stages of reaction, this was repeated using $SnBr_2$, PBr_3, and dppb at −78°C; as at room temperature, formation of the ring was first confirmed, the solution was divided into two parts, and excess triflic acid was added to one of these at −78°C. The sample was taken rapidly to the spectrometer while still at low temperature, and the proton-decoupled and proton-coupled ^{31}P NMR spectra were obtained. The signals for the protonated triphosphenium ion **2** (Scheme 1) were



SCHEME 1

clearly evident: $^{31}P\{^1H\}$ NMR data δ P_C−132.7 (t), δ P_D 29.0 (d) ppm, $^1J_{PP}$ 251.8 Hz; ^{31}P NMR data: δ P_C −132.7 (dt) ppm, $^1J_{PP}$ 251.8 Hz, $^1J_{PH}$ 235.7 Hz, δ P_D 29.0 (d) ppm. These values compare well with δ P_C −134.4 (dt) ppm, $^1J_{PP}$ 255.0 Hz, $^1J_{PH}$ 236.0 Hz, δ P_D 28.6 (d) ppm from using $AlCl_3/^tBuCl$ [8]. Two doublets in the ^1H-decoupled spectrum, at 23.8 and −50.0 ppm, $^1J_{PP}$ 278.9 Hz, and a singlet at 10.6 ppm were also present. The lower frequency doublet split into a doublet of doublets when recorded proton coupled, with δ P −50.0 ppm, $^1J_{PP}$ 278.5 Hz, $^1J_{PH}$ 186.8 Hz, and the singlet at 10.6 ppm split into a doublet, $^1J_{PH}$ 495.1 Hz. These signals are therefore assigned to the acyclic intermediate **3a**, with structure $Ph_2P^+_GH(CH_2)_4P^+_FPh_2P_EHX$, where X is probably Br (Table 1). The value of $^1J_{PH}$ is comparable with those reported for $Tms_3CP(H)Cl$ (160.6 Hz) and 2,4,6-$^tBu_3C_6H_2P(H)Cl$ (215.0 Hz) [10].

Weak signals were also observed for the dication with a primary phosphane terminal group, $Ph_2P^+H(CH_2)_4P^+Ph_2PH_2$ **4** (Scheme 1). Over time, the signals for **4** grew at the expense of those for the intermediate **3a**. The primary phosphane species **4** was comparatively stable and could be observed in solution for several days, even after the sample was allowed to warm up to room temperature. Addition of further triflic acid, or leaving the solution for a long time, led to **5** and (probably) polymeric phosphorus as the final decomposition products. The formation of **4** from **3** necessarily involves a redox reaction, with SnX_2 as the reducing agent in the presence of HX, as shown in Scheme 1. This rationalizes the nonappearance of **4** in the $^tBuCl/AlCl_3$ reaction, where there was no comparable reducing agent present [8].

A similar low-temperature reaction between PCl_3, $SnCl_2$, and dppb with triflic acid (see the Experimental section) produced parallel results; in this case, a larger excess of $SnCl_2$ was deliberately added, to ensure that there was plenty of reducing agent present. The main difference was that the two doublets in the proton-decoupled spectrum for the acyclic intermediate **3b** were now at δ ^{31}P 28.3 and −16.2 ppm, $^1J_{PP}$ 279.9 Hz. This species was very short lived, and two separate experiments were required to obtain the proton-coupled spectrum, which gave $^1J_{PH} = 197.9$ Hz. The results may be compared with those previously reported by us for the decomposition product $Ph_2P^+H(CH_2)_4P^+Ph_2PHCl$ from the $^tBuCl/AlCl_3$reaction, with δ P 27.6 (d), −16.9 (d) ppm, $^1J_{PP}$277.6 Hz, and δ P 10.5 (s) ppm [8]; in this case, the spectrum was not recorded proton coupled in the time available before decomposition occurred at room temperature. The large low-frequency shift on replacing Cl by a probable Br (33.1 ppm) is similar to the behavior observed in series such as $POCl_nBr_{3-n}$ [11] or $PCl_nBr^+_{4-n}$ [12], where shifts to lower frequency of between 35 and 40 ppm have been observed for replacing a Cl by a Br. The possibility of the triflate group being attached to P_E in **3a** cannot be entirely discounted, however, although this is clearly not the case in **3b**, in view of the close agreement between the results from the $AlCl_3/^tBuCl$ reaction and the triflic acid reaction.

We thus conclude that a dication with a primary phosphane ($-PH_2$) terminal group **4**, as clearly established by solution-state ^{31}P NMR spectroscopy, may be formed by reduction of **3**, which is an intermediate on the decomposition path of the protonated triphosphenium ion **2** to the diprotonated diphosphane **5**. This reduction requires the presence of a strong reducing agent such as SnX_2, as well as an acidic medium to provide the extra proton required, so is not observed in the decomposition when the protonating agent is $^tBuCl/AlCl_3$.

EXPERIMENTAL

All manipulations, including NMR sample preparation, were carried out either under an inert atmosphere of dry nitrogen or in vacuo, using standard Schlenk line or glovebox techniques. Chemicals of the best available commercial grade were used without further purification. The ^{31}P NMR spectra of all phosphorus-containing starting materials were recorded, to check that no major impurities were present. ^{31}P NMR spectra were recorded on a Varian Unity 300 or Varian VXR 400 Fourier-transform spectrometer at 121.40 or 161.91 MHz, respectively; chemical shifts are referenced to external 85% H_3PO_4, with the high-frequency direction taken as positive.

Typical Preparation of the Cyclic Triphosphenium Ion **1** *(As Its Hexabromostannate)*

Tin(II) bromide (0.162 g, 0.58 mmol) was weighed out into a small Schlenk tube and placed in the glovebox. A small quantity of $CDCl_3$ was added, to dissolve it and provide a deuterium lock for the spectrometer. The tube was attached to the Schlenk line, and PBr_3 (0.043 mL, 0.59 mmol) was added by syringe. The mixture was stirred for 30 min. A solution of dppb (0.216 g, 0.51 mmol) dissolved in dichloromethane was added, causing a bright yellow precipitate to appear. The solution-state ^{31}P NMR spectrum confirmed that the ion **1** had been formed (see the Results and Discussion section). A similar procedure was followed for the preparation of **1** as its hexachlorostannate, using 0.0938 g (0.49 mmol) tin(II) chloride, 0.02 mL (0.22 mmol) PCl_3 and 0.0936 g (0.25 mmol) dppb.

Protonation of **1** *and Decomposition of the Protonated Ring*

The reaction vessel was placed in the glovebox, and triflic acid (0.13 mL, 1.46 mmol) was added by syringe. The experiment was subsequently repeated on a larger scale, and after formation of the cyclic triphosphenium ion had been confirmed by ^{31}P NMR spectroscopy the solution was divided into two parts. Excess triflic acid (as above) was added by syringe to one portion, and the other portion was retained as a "blank." For the low-temperature experiments, the reaction vessel containing the portion of the solution to which triflic acid was to be added was cooled in an acetone–cardice slush bath before addition of the acid.

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