## Polyphosphorus Chemistry

## Versatile Reagent Ph<sub>3</sub>As(OTf)<sub>2</sub>: One-Pot Synthesis of [P<sub>7</sub>(AsPh<sub>3</sub>)<sub>3</sub>][OTf]<sub>3</sub> from PCl<sub>3</sub>

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In memory of Professor Piero Stoppioni

**Abstract:** Compound Ph<sub>3</sub>As(OTf)<sub>2</sub> as a pentacoordinated As<sup>V</sup> Lewis acid readily forms dicationic Lewis acid/base adducts upon addition of various Lewis bases. It also represents a stronger chloride-abstracting agent than Me<sub>3</sub>SiOTf and facilitates the reductive coupling of PCl<sub>3</sub> in the presence of AsPh<sub>3</sub> to the unprecedented cation  $[P_7(AsPh_3)_3]^{3+}$  as triflate salt. This crystallographically characterized nortricyclane-type cation represents a P<sub>7</sub>R<sub>3</sub>-derivative with the most electron-withdrawing substituents, resulting in a pronounced effect on the structural parameters of the P<sub>7</sub> core.

Chloride-abstracting agents are crucial in cationic p-block chemistry and find wide application in the synthesis of highly electrophilic compounds. Their use often demands weakly coordinating anions (WCAs) to prevent detrimental nucleophilic attack of the anion followed by degradation. Often used reagents are, for example, Me<sub>3</sub>SiOTf, AgOTf, TIOTf, or the Group 13 Lewis acids, such as AlCl<sub>3</sub> and GaCl<sub>3</sub>, and they have been used in the synthesis of several phosphanylpnictonium cations.<sup>[1]</sup>

We previously reported the synthesis of the unusual butterfly-type compound  $[P_4(AsPh_3)_2][AlCl_4]_2$  (1[AlCl\_4]\_2) and  $[Ph_3AsAsPh_3][AlCl_4]_2$  (2[AlCl\_4]\_2) from a reductive-coupling reaction of PCl\_3 with AsPh\_3 in the presence of AlCl\_3 (Scheme 1).<sup>[2]</sup> In recent studies, we have realized that its follow-up chemistry is hampered by the presence of the [AlCl\_4]<sup>-</sup> anion. In solution,  $\mathbf{1}^{2+}$  slowly degrades due to nucleophilic attack of liberated Cl<sup>-</sup> ions from the [AlCl\_4]<sup>-</sup> anion.<sup>[3]</sup> This observation motivated us to search for alternative, less reactive counterions, that allow us to explore the chemistry of the [P\_4(AsPh\_3)\_2]^{2+} dication, for example, as a P\_4-transfer reagent.

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$$4 \text{ PCl}_{3} + 12 \text{ Ph}_{3}\text{As} + 12 \text{ AlCl}_{3} \longrightarrow 1 \begin{bmatrix} \text{AlCl}_{4} \end{bmatrix}_{2} \\ + 5 \begin{bmatrix} \text{Ph}_{3}\text{As}\text{-Ps} \end{bmatrix} \begin{bmatrix} \text{Ph}_{3}\text{-Ps} \end{bmatrix} \begin{bmatrix} \text{AlCl}_{4} \end{bmatrix}_{2} \\ + 5 \begin{bmatrix} \text{Ph}_{3}\text{As}\text{-Ps} \end{bmatrix} \begin{bmatrix} \text{AlCl}_{4} \end{bmatrix}_{2} \\ 2 \begin{bmatrix} \text{AlCl}_{4} \end{bmatrix}_{2} \end{bmatrix}$$

Scheme 1. Synthesis of  $1[{\sf AlCI}_4]_2$  from reductive coupling of  ${\sf PCI}_3$  with  ${\sf Ph}_3{\sf As}$  in the presence of  ${\sf AlCI}_3.$ 

Our chemistry often involves the triflate anion, TfO<sup>-</sup>, which can be conveniently introduced by reagents, such as Me<sub>3</sub>SiOTf, AgOTf, or TIOTf.<sup>[1,4]</sup> However, their use is sometimes limited, because either Me<sub>3</sub>SiOTf is not reactive enough or the solubility of metal triflates in weakly coordinating solvents is guite low. Alternatives are chloride-abstracting agents with WCAs, such as halogenated carborane anions,<sup>[5]</sup> perfluorinated tetraphenylborate,<sup>[6]</sup> or perfluorinated tetraalkoxyaluminates.<sup>[7]</sup> However, their use is often restricted due to laborious multistep syntheses with sometimes low overall yields. Although there are cases, in which there is an essential need for those WCAs, we believe that TfO<sup>-</sup> might be a suitable counterion in many other cases, in which only a lack of an appropriate triflate transfer reagent is present. In this light, we were interested to find a triflate-based chloride-abstracting agent that overcomes the aforementioned problems.

During our literature research, we came across Verma's report on the Ph<sub>3</sub>E(OTf)<sub>2</sub> (E = Sb, Bi) derivatives, which seemed to us to be suitable chloride-abstraction reagents.<sup>[8]</sup> Very recently, Burford and co-workers used these compounds in the synthesis of interesting donor/acceptor complexes.<sup>[9]</sup> The lighter As and P derivatives were not reported. However, it is known that attempts to generate these derivatives from the reaction of Ph<sub>3</sub>PO or Ph<sub>3</sub>AsO (**3**) with Tf<sub>2</sub>O or (FSO<sub>2</sub>)<sub>2</sub>O resulted in the formation of the cationic anhydrides  $[(Ph_3P)_2O]^{2+}$  or  $[(Ph_3As)_2O]^{2+}$  (**4**<sup>2+</sup>) as  $[OTf]^-$  or  $[FSO_3]^-$  salts.<sup>[10]</sup> However, comparison of pnictogen–chlorine bond strengths (As–Cl: 107 kcal mol<sup>-1</sup>; Sb–Cl: (86±12) kcal mol<sup>-1</sup>)<sup>[11]</sup> implies that Ph<sub>3</sub>As(OTf)<sub>2</sub> (**5**) should be a very promising chloride-abstracting reagent.

We found that the reaction of Ph<sub>3</sub>AsO (**3**) with 0.5 equivalents of Tf<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> proceeds quantitatively and gives the previously reported cationic anhydride  $[(Ph_3As)_2O]^{2+}$  (**4**<sup>2+</sup>) as triflate salt. In contrast, the reaction in a 1:1 stoichiometry results in the clean formation of the unreported Ph<sub>3</sub>As(OTf)<sub>2</sub> (**5**) derivative (Scheme 2). Compound **5** was conveniently synthe-

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Scheme 2. Synthesis of  $Ph_3As(OTf)_2$  (5) from the reaction of  $Ph_3AsO$  (3) with triflic anhydride (Tf\_2O).

sized on a multigram scale (>100 g) and was obtained in high yields (91%) as a colorless, highly moisture-sensitive crystalline solid (for details, see the Supporting Information).

Single crystals of  $4[OTf]_2$  and **5** suitable for X-ray single-crystal diffraction analysis were obtained by slow diffusion of *n*-hexane into a solution of  $4[OTf]_2$  or **5** in CH<sub>2</sub>Cl<sub>2</sub> at -30 °C. The molecular structure of compound **5** revealed loosely coordinated triflate anions in the axial positions of the trigonal bipyramidal sphere of the As atom (av As–O bond lengths in  $4^{2+}$ : 1.756 vs. **5**: 2.031 Å; Figure 1).

Similarly to the related Sb and Bi derivatives,<sup>[9]</sup> **5** was expected to act as a highly reactive pentacoordinated  $As^{V}$  Lewis acid giving the corresponding donor/acceptor complexes in the reaction with appropriate Lewis bases. Thus, **5** was allowed to react with the Lewis bases AsPh<sub>3</sub>, 4-dimethylaminopyridine (DMAP) and the N-heterocyclic carbene (NHC) 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene (IDipp) to cleanly give the expected dicationic Lewis acid/base adducts **6–8**[OTf]<sub>2</sub> (Scheme 3). In all cases, the formation of the adducts proceeds through displacement of the triflate anions accompanied with the change of the coordination number at the arsenic atom from five to four (Scheme 3; for experimental details, including molecular structure, see the Supporting Information).



Scheme 3. Formation of triflate salts of dicationic Lewis acid/base adducts  $6-8[OTf]_2$  between Ph<sub>3</sub>As(OTf)<sub>2</sub> (5) and neutral Lewis bases AsPh<sub>3</sub>, DMAP, and IDipp.

To test the chloride-abstracting ability of **5**, a solution of the ditriflate **5** was reacted with  $Me_3SiCl$  in various stoichiometries (Scheme 4, for detailed discussion, see the Supporting Information). The 1:1 reaction led to the clean formation of **9**[OTf] and  $Me_3SiOTf$ . In the 1:2 reaction, one equivalent of  $Me_3SiCl$  remained unreacted, indicating that **9**[OTf] was not capable of abstracting chloride ions from the chlorosilane.

OTf Ph−As <sup>…Ph</sup> Ph OTf	Me <sub>3</sub> SiCl	⊕_Ph_[O ⊕_Ph Cl−As-Ph Ph	Tf] + Me <sub>3</sub> SiOTf
5		<b>9</b> [OTf]	

Scheme 4. Chloride abstraction from  $Me_3SiCl$  by  $Ph_3As(OTf)_2$  (5) generating  $Me_3SiOTf$  and 9[OTf].

As1 01 As<sub>2</sub> a) As 0 b)

**Figure 1.** Molecular structures of a) the dication  $4^{2+}$  and b) **5**. All hydrogen atoms (a + b) and triflate anions (a) are omitted for clarity. Selected bond lengths [Å] and angles [°]: a) As1–O1 1.755(2), As2–O1 1.757(1); As1-O1-As2 149.33(8); b) As1–O1 2.038(1), As1–O4 2.023(1); O1-As1-O4 177.04(7).

Compound **5** proved to be a very strong chloride-abstracting agent, and we were interested, whether it could be used as an appropriate surrogate for  $AlCl_3$  in the synthesis of cation  $1^{2+}$  as more stable triflate salt. Thus, we reacted PCl<sub>3</sub>, AsPh<sub>3</sub>, and **5** in CH<sub>2</sub>Cl<sub>2</sub> (Scheme 5). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the



 $\label{eq:scheme 5. Idealized equation for the reductive coupling of PCI_3 with AsPh_3 and Ph_3As(OTf)_2 (5) to give [P_7(AsPh_3)_3][OTf]_3 (10[OTf]_3).$ 

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**Figure 2.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the PCl<sub>3</sub>/Ph<sub>3</sub>As(OTf)<sub>2</sub>/AsPh<sub>3</sub> reaction mixture in CH<sub>2</sub>Cl<sub>2</sub> (optimized 1:2:3 stoichiometry) after two days. Inlets  $(10^{3+})_{x'}$  ( $10^{3+})_{B'}$  and  $(10^{3+})_{A}$  show the multiplet resonances of the experimental (top) and iteratively fitted (bottom) <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 10[OTf]<sub>3</sub>.<sup>(12)</sup> Inlets  $(1^{2+})_{X}$  and  $(1^{2+})_{X}$  show the A<sub>2</sub>X<sub>2</sub> spin system of  $1^{2+}$ .

reaction mixture is depicted in Figure 2, indicating a different course of this reaction than expected.

The spectrum of this reaction mixture shows the formation of small amounts of dication  $1^{2+}$  according to the appearance of the expected  $A_2X_2$  spin system  $(\delta(1^{2+})_A = -325.4 \text{ ppm}, \delta(1^{2+})_X = -175.3 \text{ ppm}, {}^{1}J_{AX} = 162.2 \text{ Hz}).^{[2]}$  However, the main product (ca. 70%) showed three complicated multiplet resonances  $(\delta(10^{3+})_A = -139.5 \text{ ppm}, \delta(10^{3+})_B = -130.9 \text{ ppm}, \delta(10^{3+})_X = 69.6 \text{ ppm}$ ; Figure 2) that are integrating in a ratio of 3:1:3 and, according to  ${}^{31}P^{31}P^{1}H$  COSY NMR spectroscopy, belong to the same highly symmetric species  $10^{3+}$ .

The multiplet resonances were iteratively fitted to an AA'A"BXX'X" spin system, which is in accordance with the typical pattern of a heptaphosphanortricyclane cage and is indicative of the formation of the  $C_3$ -symmetric stereoisomer of the trication  $10^{3+}$  ( ${}^{1}J_{AX} = -355.7(4)$  Hz,  ${}^{1}J_{AA'} = -199.7(9)$  Hz,  ${}^{1}J_{BX} = -323.7(3)$  Hz,  ${}^{2}J_{AB} = 44.62(11)$  Hz,  ${}^{2}J_{AX'} = 4.77(18)$  Hz,  ${}^{2}J_{XX'} = -6.7(12)$  Hz; Figure 2, inset). Careful adjustment of the stoichiometry and the reaction conditions leads to a convenient synthesis of compound  $10[OTf]_3$ , which was comprehensively characterized. Compound  $10[OTf]_3$  forms pale yellow crystals that begin to decompose visibly only above 140 °C. Although the work-up procedure turned out to be extremely tedious, this compound can be obtained in amounts of several hundred milligrams in an overall yield of 13% based on PCl<sub>3</sub>.

Single crystals suitable for X-ray diffraction single-crystal analysis of **10**[OTf]<sub>3</sub> were obtained by slow diffusion of Et<sub>2</sub>O into a propionitrile solution of the salt at -30 °C (Figure 3). The molecular structure of the cation **10**<sup>3+</sup> revealed a heptaphosphanortricyclane cage with three triphenylarsonio substituents at the bridging phosphorus atoms. One of the three triflate anions shows close contacts between P3–O5 (2.905(2) Å), P6–O5 (2.922(2) Å), and As2–O5 (2.990(2) Å) with distances well below the sum of the van der Waals radii ( $\Sigma_{vdW}$ (As–O) 3.5 Å;  $\Sigma_{vdW}$ (P–O)=3.4 Å),<sup>[13]</sup> underlining the high electrophilicity of the cation.

The observed P–P and As–P bond lengths are in the typical range of single bonds and are comparable to those observed in cation  $1^{2+,[2]}$  There are several crystallographically characterized nortricyclane-type  $P_7R_3$  systems with varying substituents.





**Figure 3.** Molecular structure of the trication  $10^{3+}$ . a) Only the phosphorus, arsenic, and *ipso*-carbon atoms of the phenyl ring are shown for clarity. b) View illustrating the close contact between one triflate anion and the cation. Selected bond lengths [Å]: P2–As1 2.338(1), P5–P7 2.215(1), P3–P6 2.222(1), P1–P4 2.186(1), As2–O5 2.990(2), P3–O5 2.905(2), P6–O5 2.922(2).



tries 4–6 and 8–10 refer to the average bond lengths (4–6), angle sums (8 and 9), and angle differences (10).												
Entry/parameter <sup>[a]</sup>	$[P_7(AsPh_3)_3]^{3+[b]}$	$[Ph_6P_7]^{3+[c]}$	$P_7(GePh_3)_3^{[d]}$	$P_7(SiPh_3)_3^{[d]}$	$P_7(SitBu_3)_3^{[e]}$	$P_7(Si(SiMe_3)_3)_3^{[f]}$	$Li_3$ (tmeda) $_3P_7^{[g]}$	$P_7Br_3^{[h]}$	$P_7 I_3^{[h]}$			
1 $\delta^{31}$ P(P <sup>a</sup> ) [ppm]	-130.9	-157.1	-94	-105	-113	-100.6	-57	-70.7	-64.5			
2 $\delta^{31}$ P(P <sup>e</sup> ) [ppm]	69.6	112.6	12	4	-31.2	-7.3	-103	177.7	126.0			
3 δ <sup>31</sup> P(P <sup>▶</sup> ) [ppm]	-139.5	-163.7	-158	-156	-175.6	-161.6	-162	-138.8	-136.1			
4 P <sup>a</sup> —P <sup>e</sup> [Å]	2.185(5)	2.220(4)	2.184(5)	2.178(10)	2.182(10)	2.183(3)	2.204(15)	-	-			
5 P <sup>e</sup> —P <sup>b</sup> [Å]	2.224(4)	2.226(3)	2.196(5)	2.183(9)	2.186(4)	2.198(5)	2.150(16)	-	-			
6 P <sup>b</sup> —P <sup>b</sup> [Å]	2.218(7)	2.218(4)	2.215(4)	2.207(10)	2.226(4)	2.218(4)	2.255(12)	-	-			
7 Ψ(Pª) [°]	287.2(2)	274.99(12)	293.5(3)	294.8(8)	293.8(2)	292.56(17)	305.4(10)	-	-			
8 Ψ(P <sup>e</sup> ) [°]	311(3)	-	309.9(5)	313.2(16)	331.3(18)	318.1(6)	-	-	-			
9 Ψ(P <sup>ь</sup> ) [°]	263.5(12)	264.9(4)	268.3(5)	268.5(9)	267.5(7)	267.4(4)	271.5(19)	-	-			
10 $eta_2 - eta_1$ [°]	13.5(2)	3.13(16)	3.0(3)	4.5(10)	6.9(3)	6.5(3)	0.0(13)	-	-			
[a] For numbering scheme and definition of $\beta$ , see Figure 4. [b] This work. [c] Ref. [17]. [d] Ref. [14a]. [e] Ref. [14b]. [f] Ref. [14c]. [g] Refs. [14d, 17]. [h] Ref. [16]. No crystal structures were reported.												

Table 1. Selected <sup>31</sup>P NMR shifts, bond lengths, and angles of selected  $C_{3}$ - and  $C_{3}$ -symmetric stereoisomers of heptaphosphanortricyclane derivatives. En-

Interestingly, the observed P–P bond lengths in those compounds are comparable, indicating only a minor influence of the substituents (Table 1, compare entries 4–6).<sup>[14]</sup> The P–P bond lengths of  $10^{3+}$  (P<sup>b</sup>–P<sup>b</sup> (av) 2.218(7) Å) within the basal P<sub>3</sub> ring (Table 1, entry 6) are slightly longer than between the apical and the equatorial P atoms (P<sup>a</sup>–P<sup>e</sup>(av) 2.185(5) Å; Table 1, entry 4).

This is in line with the P–P bond lengths of the neutral, isoelectronic derivative P<sub>7</sub>(GePh<sub>3</sub>)<sub>3</sub>.<sup>[14a]</sup> However, the P–P bonds of **10**<sup>3+</sup> between the basal and equatorial phosphorus atoms (P<sup>b</sup>–P<sup>e</sup> (av) 2.224(1) Å) are significantly longer than in P<sub>7</sub>(GePh<sub>3</sub>)<sub>3</sub> (P<sup>b</sup>–P<sup>e</sup> (av) 2.195(2) Å), which is most likely due to electronic effects (Table 1, entry 5). The inner angles  $\alpha$ ,  $\gamma$ , and  $\delta$  have very similar values compared to known P<sub>7</sub>R<sub>3</sub> derivatives, whereas for the angles  $\beta_1$  and  $\beta_2$ , large deviations were found (Figure 4).<sup>[14]</sup> With the difference between these angles the twisting of the cage around the threefold axis can be quantified. The trication **10**<sup>3+</sup> ( $\mathcal{O}(\beta_2 - \beta_1) = 13.5(2)^\circ$ ) shows a measured value, which is four times as high as was found for its isoelectronic derivative P<sub>7</sub>(GePh<sub>3</sub>)<sub>3</sub> ( $\mathcal{O}(\beta_2 - \beta_1) = 3.0(3)^\circ$ ; Table 1,



**Figure 4.** Denotations of the chemically different phosphorus atoms and the most important bond angles in heptaphosphanortricyclane systems.

entry 10). A comparison to other  $C_3$ -symmetric  $P_7R_3$  nortriclyclane derivatives<sup>[14]</sup> shows that the cage twist is usually much lower within a narrow range up to  $\mathcal{O}(\beta_2 - \beta_1) = 6.9(3)^\circ$  for  $R = tBu_3Si^{[14b]}$  The angle sum at the equatorial phosphorus atoms (Table 1, entry 8) in  $\mathbf{10}^{3+}$  ( $\Psi(\mathsf{P}^{\mathsf{e}}) = 311(3)^{\circ}$ ) is comparable to those of  $P_7(GePh_3)_3 \Psi(P^e) = 309.9(5)^\circ)$  and  $P_7(SiPh_3)_3 (\Psi(P^e) =$  $313.2(16)^{\circ}$ ,<sup>[14a]</sup> but smaller than those found for P<sub>7</sub>R<sub>3</sub> derivatives with sterically more demanding substituents (R=SitBu<sub>3</sub>:  $\Psi(P^{e}) = 331.3(18)^{\circ}; R = Si(SiMe_{3})_{3}; \Psi(P^{e}) = 318.1(6)^{\circ}).^{[14b,c]}$  This leads us to the assumption that the cage twist angle is more influenced by the electronic properties of the substituent than by its steric demand. The angle sum at the basal phosphorus atoms  $\Psi(P^b)$  (Table 1, entry 9) instead decreases with the decrease of electron density inside the P<sub>7</sub> cage from  $\Psi(P^b) =$ 271.5(19)° (R = Li(tmeda))<sup>[14d]</sup> to  $\Psi(P^b) = 263.5(12)^\circ$  (R =  $(AsPh_3)^+$ ). The angle sum at the apical phosphorus atom  $\Psi(P^b)$ (Table 1, entry 7) follows the same trend from  $\Psi(P^a) =$ 305.4(10)° (R = Li(tmeda)) to  $\Psi(P^a) = 287.2(2)^\circ$  (R = (AsPh<sub>3</sub>)<sup>+</sup>).<sup>[14]</sup> Both of the observed, relatively small angle sums  $\Psi(P^b)$  and  $\Psi(P^a)$  are reflected in the <sup>31</sup>P NMR shifts of the basal and apical phosphorus atoms ( $\delta(P^b) = -139.5 \text{ ppm}, \delta(P^a) = -130.9 \text{ ppm}$ ) of 10<sup>3+</sup>, which appear at relatively low and high field, respectively.

If the angle sum  $\Psi(P^{b})$  decreases (Table 1, compare entries 3 and 9) the s character of the lone pair of electrons decreases resulting in a deshielding of the phosphorus nucleus and thus in a downfield shift.<sup>[15]</sup> The same effect can be observed for the apical phosphorus atom P<sup>a</sup> (Table 1, compare entries 1 and 7). Herein, the decrease of the angle sum  $\Psi(P^a)$  towards 270° results in the increase of the s character of the lone pair of electrons. Therefore, the phosphorus nucleus is more shielded, which causes a highfield shift. The resonance for the equatorial phosphorus atoms P<sup>e</sup> appears at relatively low field ( $\delta =$ 69.6 ppm). Similar <sup>31</sup>P NMR shifts are usually observed for  $C_{3}$ symmetric P<sub>7</sub>R<sub>3</sub> cage compounds with electronegative substituents (R=Br, I; Table 1, entry 2).<sup>[16]</sup> Due to the lack of crystal structures of P<sub>7</sub>Br<sub>3</sub> and P<sub>7</sub>I<sub>3</sub>, **10**[OTf]<sub>3</sub> represents the heptaphosphanortricyclane derivative with the most electron-withdrawing substituents, in which these effects could be observed to date.

Chem. Eur. J. 2014, 20, 17306 - 17310

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In summary, we presented the synthesis of Ph<sub>3</sub>As(OTf)<sub>2</sub> through the facile one-pot reaction of Ph<sub>3</sub>AsO with Tf<sub>2</sub>O. Compound Ph<sub>3</sub>As(OTf)<sub>2</sub> readily forms dicationic Lewis acid/base adducts upon addition of Lewis bases under displacement of the triflate anions. We could demonstrate its great potential as a strong chloride-abstracting agent with a high solubility in weakly coordinating solvents. Initial application of Ph<sub>3</sub>As(OTf)<sub>2</sub> as chloride-abstracting Lewis acid could be demonstrated in the synthesis of the first  $C_3$  symmetric P<sub>7</sub>R<sub>3</sub> tri-arsonium trication [P<sub>7</sub>(AsPh<sub>3</sub>)<sub>3</sub>]<sup>3+</sup> (**10**<sup>3+</sup>) with a nortricyclane type structure of the P<sub>7</sub> core.

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