Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron Letters 47 (2006) 2687–2690
Tetrahedron Letters

Design of neutral, mono- or di-cationic water-soluble trihydrazidophosphoradamantanes

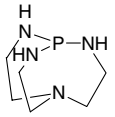
Maria Zabłocka[a,*] and Carine Duhayon[b]

[a]Centre of Molecular and Macromolecular Studies, The Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland
[b]Laboratoire de Chimie de Coordination CNRS, UPR 8241, 205 route de Narbonne, 31077 Toulouse cedex 4, France

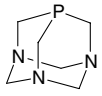
Received 19 January 2006; revised 8 February 2006; accepted 16 February 2006
Available online 6 March 2006

Abstract—The versatile behavior of a trihydrazidophosphoradamantane allowing the synthesis of a variety of neutral, mono- or di-cationic water-soluble molecules of potential interest for biphasic catalysis is reported.
© 2006 Elsevier Ltd. All rights reserved.

The success of aqueous two-phase catalysis can be explained by the fact that water is a cheap and environmentally friendly solvent and by the possibility of overcoming two basic problems encountered in homogeneous catalysis, namely, the separation and subsequent recycling of the catalyst.[1] Among the different classes of ligands used for this purpose, linear or cyclic phosphines occupy a special place because their hydrophilicity can be tuned by grafting a variety of polar groups, such as ammonium, carbohydrate, phosphonium, phosphonate, polyether, hydroxyalkyl, hydroxy, sulfonated groups, etc. In contrast, very few water soluble cage-like phosphines have been used in catalysis: the Verkade-type bases **1** are efficient ligands in a number of organic reactions[2] while 1,3,5-triaza-7-phosphoradamantane **2** (PTA) discovered in 1974[3] has received renewed interest, not only in homogeneous aqueous biphasic catalysis,[4] but also for medicinal[5] and photoluminescence uses.[6,7]



1

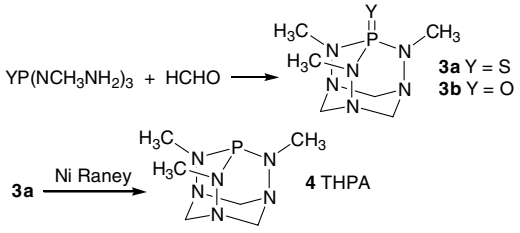


2 PTA

We were particularly interested in developing new water-soluble air-stable phosphines with a phosphoradamantane skeleton which, in principle, should present overall reactivity comparable to classical phosphines but with a higher resistance to oxidation and with enhanced possibilities to tune the solubility in water.

We herein report the synthesis of a set of neutral mono- or dicationic phosphoradamantanes derived from trimethyl-4,6,9-thio-5-hexa-1,3,4,6,7,9-phospha-5-tricyclo[3.3.1.1^{3,7}]decane **3a** as well as the X-ray structure determination of one of these phosphoradamantanes, the monocationic species **6a**.

Compound **3a**, a non-water-soluble phosphoradamantane, was prepared according to the literature procedure[8] in 80% yield from thiophosphorhydrazide $S{=}P[N(CH_3)NH_2]_3$ and formaldehyde (Scheme 1). Desulfuration of **3a** using classical methods, for example, $(Me_3Si)_3SiH$[9] or $P(NMe_2)_3$[10] did not take place. Reaction of **3a** with a large excess of tributylphosphine gave rise to the expected phosphine **4**[8] but this method, although efficient, did not afford **4** in a high enough yield since the separation of **4** from the tributylphosphine sulfide formed during the reaction and unreacted



Scheme 1. Synthesis of phosphorus(III) or (V) adamantanes **3a**,**b** and **4**.

* Corresponding author. Tel.: +48 42 680 3217; fax: +48 42 684 7126; e-mail: zabloc@bilbo.cbmm.lodz.pl

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.02.096

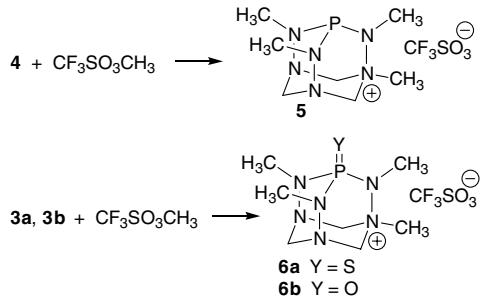
tributylphosphine is tedious. The best method we found consists of the reduction of **3a** with Raney Ni allowing the isolation of **4** in 80% yield. Remarkably **4**, for which we have proposed the acronym THPA (trihydrazidophosphoradamantane), appears to be as water soluble as its analog PTA, **2**.

All attempts to reduce the corresponding oxide **3b** which is in marked contrast to **3a**, soluble in water, have failed up to now. One unique feature of **4** is its ability to be chemoselectively alkylated (or protonated) at nitrogen rather than at the phosphorus center. This can be achieved with a strong alkylating reagent such as $CF_3SO_3CH_3$ (Scheme 2). Further, *N*-alkylation is thermodynamically less favorable, as changes in hybridization of the nitrogen atoms, induce distortions in the adamantane backbone decreasing the overall stability. The water soluble monoalkylated phosphoradamantane **5**[11] was characterized in ^{31}P NMR by a singlet at 103.0 ppm (**4**, δ $^{31}P = 101.8$ ppm) while the desymetrization of the structure due to monoalkylation is clearly observed in the ^{1}H NMR (two types of doublets for the P–N-CH_3 groups) and in the ^{13}C NMR (two doublets for the $PNCH_3$ groups and three singlets for the CH_2 groups). Monomethylation at the nitrogen atom in the β-position relative to phosphorus was also proved by the ^{1}H NMR singlet at 2.96 ppm and the singlet at 46.16 ppm in the ^{13}C NMR spectrum.

Methylation of **3a** and **3b** with $CF_3SO_3CH_3$ also proceeds smoothly giving rise to new water-soluble phosphoradamantane monocationic species **6a** and **6b** (Scheme 2).[12,13] The structure of **6a** was fully established by X-ray diffraction studies (see the supporting information for full details[14]). An ORTEP view is shown in Figure 1. *N*-Methylation affects the bond distances associated with the phosphorus center with a significant lengthening of the P1–N1 bond (1.7211(3) Å), compared to P1–N2 (1.674(3) Å), and P1–N3 (1.648(3) Å).

The reactivity of the *N*-alkylated THPA **5** differs from that of THPA **4** itself. As an example, the Staudinger reaction between **5** and the functionalized azide $N_3P(S)(OC_6H_4CHO)_2$ does not take place even under forcing conditions while this reaction occurs readily in 2 h at room temperature with **4** leading to the iminophosphoradamantane **7** (Scheme 3).[15]

The latter compound appears to be a good model for obtaining unprecedented dicationic phosphoradaman-



Scheme 2. Selective *N*-alkylation of phosphoradamantanes **3a**,**b** and **4**.

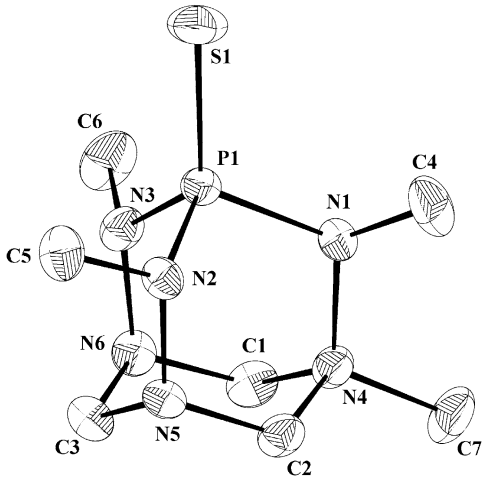
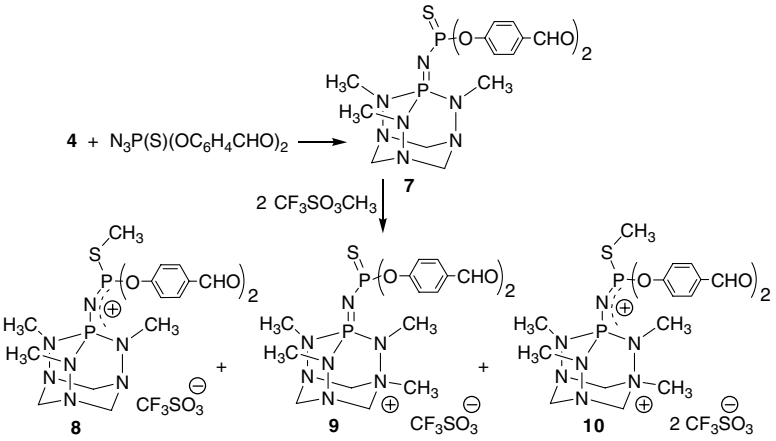


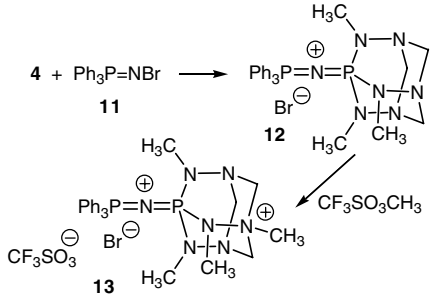
Figure 1. X-ray structure of **6a**. Selected bond distances (Å) and angles (deg): P1–S1 = 1.8999(13); P1–N1 = 1.721(3); P1–N2 = 1.674(3); P1–N3 = 1.648(3); N1–N4 = 1.482(4); N2–N5 = 1.446(4); N3–N6 = 1.449(4); N3–P1–N_2 = 104.27(15); N3–P1–N1 = 103.02(15); N2–P1–N1 = 100.20(14).

tane derivatives since alkylation can be envisaged both at the β nitrogen atom, and at the sulfur of the P=S unit. Indeed, it has already been demonstrated that methylation of a P=N–P=S linkage easily occurs on sulfur leading to $[P{=}N{-}P^{+}S(CH_3)]CF_3SO_3^{-}$ units.[16] Addition of 2 equiv of $CF_3SO_3CH_3$ to **7** allows the observation based on ^{31}P NMR of the formation of the three possible cationic species: the *S*-methylated compound **8** [δ $^{31}P = 26.10$ (d, $^{2}J_{PP} = 47.4$ Hz), and 9.32 (d, $^{2}J_{PP} = 47.4$ Hz) ppm], the *N*-methylated species **9** [δ $^{31}P = 64.02$ (d, $^{2}J_{PP} = 64$ Hz), and −4.10 (d, $^{2}J_{PP} = 64$ Hz) ppm], and the desired dicationic phosphoradamantane **10** [δ $^{31}P = 28.6$ (d, $^{2}J_{PP} = 58.3$ Hz), and 2.75 (d, $^{2}J_{PP} = 58.3$ Hz) ppm]. ^{1}H and ^{13}C NMR spectra corroborate the coexistence of these three cationic species. Unfortunately, their instability prevented their isolation and all attempts to direct such a reaction to selectivity failed. Therefore, another strategy was investigated with the aim of preparing stable and eventually water-soluble dicationic species incorporating a phosphoradamantane skeleton and a $[P{=}N{=}P]^{+}X^{-}$ unit. Phosphonioimino phosphorane cations $[P{=}N{=}P]^{+}$ have the advantageous property of forming readily isolable salts of complex anions which are soluble in organic solvents, making them widely useful in inorganic chemistry.[17] Moreover, some of these salts were recently used as promising catalysts in halogen exchange reactions (Halex reactions) where chloro- and bromoaromatics activated toward nucleophilic substitution react with a fluoride source to yield the corresponding fluoroarenes.[18,19]

Treatment of THPA **4** with $Ph_3P{=}NBr$ **11** (obtained from the addition of 2 equiv of *n*-BuLi then Br_2 to the phosphonium salt $[(Ph_3P{-}NH_2)^{+}Cl^{-}]$ overnight at room temperature) gave the unique phosphonio iminophosphorane **12** in 90% yield after workup.[20] The identity of **12** was established by NMR. ^{31}P NMR revealed the presence of two characteristic doublets at 4.45 (NPN) and 21.12 ($P(C_6H_5)_3$) ppm with $^{2}J_{PP} = 29.6$ Hz (Scheme



Scheme 3. *S*- and *N*-alkylation of the iminophosphoradamantane **7**.



Scheme 4. Synthesis of the water-soluble mono- and di-cationic [P=N=P] compounds **12** and **13**.

4). As expected, monoalkylation of **12** proceeded almost quantitatively leading to **13**, the first example of a dicationic species bearing a charged PNP unit and an *N*-alkylated phosphoradamantane.[21] The reaction was monitored by ^{31}P NMR with the disappearance of the two doublets due to compound **12** on behalf of two new doublets at −2.8 (NPN) and 24.8 ($P(C_6H_5)_3$) ppm ($^2J_{PP} = 35.3$ Hz). ^{1}H and ^{13}C NMR spectra corroborate the formation of **13** with the appearance of new singlets for the N–CH_3 group at 3.88 ppm in the ^{1}H NMR and 45.31 ppm in the ^{13}C NMR accompanied with multiplicity of the other signals (CH_3 and CH_2 signals) due to the desymmetrization of the molecule. Remarkably, in marked contrast with the $[P{=}N{=}P]^+$ cations reported in the literature, **12** was found to be fairly soluble in water while **13** was only slightly soluble.

In summary, we have developed new classes of neutral, monocationic, and dicationic constraint structures based on trihydrazidophosphoradamantanes, most of them being water soluble. These air-stable derivatives are convenient to prepare, store, and handle[22] and open new possibilities in homogeneous catalysis. These properties will be illustrated in forthcoming letters.

Acknowledgements

M.Z. thanks the Ministry of Science and Information Society Technologies Poland for financial support (Grant No. 3T09A 158 29).

References and notes

1. For a recent review, see: Pinault, N.; Bruce, D. W. *Coord. Chem. Rev.* **2003**, *241*, 1.
2. Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233.
3. Daigle, D. J.; Pepperman, A. B.; Vail, S. L. *J. Heterocycl. Chem.* **1974**, *11*, 407.
4. For a recent review, see: Phillips, A. D.; Gonsalvi, L.; Romerosa, A.; Vizza, F.; Peruzzini, M. *Coord. Chem. Rev.* **2004**, *248*, 955.
5. See for example: Allardyce, C. S.; Dyson, P. J.; Ellis, D. J.; Heath, S. L. *Chem. Commun.* **2001**, 1396.
6. Assefa, Z.; McBurnett, B. G.; Staples, R. J.; Fackler, J. P.; Assamann, B.; Angermaier, K.; Schmidbaur, H. *Inorg. Chem.* **1995**, *34*, 75.
7. Assefa, Z.; Omary, M. A.; McBurnett, B. G.; Mohamed, A. A.; Patterson, H. H.; Staples, R. J.; Fackler, J. P. *Inorg. Chem.* **2002**, *41*, 6274.
8. Majoral, J. P.; Kraemer, R.; Navech, J.; Mathis, F. *Tetrahedron* **1976**, *32*, 2633; Navech, J.; Kraemer, R.; Majoral, J. P. *Tetrahedron Lett.* **1980**, *21*, 1449; Majoral, J. P. *Synthesis* **1978**, *8*, 557; Jaud, J.; Benhamou, M.; Majoral, J. P.; Navech, J. *Z. Kristallogr.* **1982**, *160*, 69.
9. Romeo, R.; Wozniak, L. A.; Chatgilialoglu, C. *Tetrahedron Lett.* **2000**, *41*, 9899.
10. Omelańczuk, J.; Mikołajczyk, M. *J. Am. Chem. Soc.* **1979**, *101*, 7292.
11. Synthesis and characterization of **5**: To a solution of 0.10 g (0.5 mmol) of $(CH_2NMeN)_3P$ in CH_2Cl_2 (3 mL) at room temperature was added 0.082 g (57 μL) of $CF_3SO_3CH_3$ using a microsyringe. The reaction mixture was stirred for 4 h at rt. Evaporation of the solvent under reduced pressure afforded the expected compound as a white powder in 96% yield. $^{31}P\{^1H\}$NMR (81 MHz, $CDCl_3$) δ 103.0 (s); ^{1}H NMR (200 MHz, CD_2Cl_2) δ 2.86 (d, $^3J_{PH} = 15.0$ Hz, 6H, CH_3), 2.96 (s, 3H, CH_3), 3.08 (d, $^3J_{PH} = 15.0$ Hz, 3H, CH_3), 5.15 (d, $^2J_{HH} = 11.8$ Hz, 3H, CH_2), 5.35 (d, $^2J_{HH} = 11.8$ Hz, 3H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$) δ 35.79 (d, $^2J_{CP} = 14.9$ Hz, CH_3), 38.80 (d, $^2J_{CP} = 19.8$ Hz, CH_3), 46.16 (s, CH_3), 60.24 (s, CH_2), 66.40 (s, CH_2), 76.40 (s, CH_2), 121.25 (q, $J_{CF} = 319.8$ Hz, CF_3). Anal. Calcd for $C_8H_{18}N_6O_3PSF_3$: C, 26.23; H, 4.95; N, 22.94. Found: C, 26.16; H, 4.87; N, 22.90.
12. Synthesis and characterization of **6a**: To a solution of 0.117 g (0.5 mmol) of $(CH_2NMeN)_3P(S)$ in CH_2Cl_2 (3 mL) at room temperature (0.082 g, 57 μL) of $CF_3SO_3CH_3$ was added via microsyringe. The reaction mixture was stirred

for 2 h at rt, then the solvent was removed under reduced pressure to afford the expected compound as a white powder in 95% yield. $^{31}P\{^{1}H\}$NMR (81.015 MHz, CD_2Cl_2) δ 67.42 (s); ^{1}H NMR (200.133 MHz, CD_2Cl_2) δ 2.95 (d, $^{3}J_{PH} = 13.3$ Hz, 6H, CH_3), 3.23 (d, $^{3}J_{PH} = 13.2$ Hz, 3H, CH_3), 3.25 (d, $^{4}J_{PH} = 0.89$ Hz, 3H, CH_3), 4.61 (d, $^{2}J_{HH} = 14.6$ Hz, 1H, CH), 4.78 (d, $^{2}J_{HH} = 14.6$ Hz, 1H, CH), 5.30 (d, $^{2}J_{HH} = 11.5$ Hz, 2H, CH_2), 5.52 (d, $^{2}J_{HH} = 11.5$ Hz, 2H, CH_2); ^{13}C NMR (50.323 MHz, $CDCl_2$) δ 31.50 (s, CH_3), 35.80 (s, CH_3), 47.12 (s, CH_3), 64.90 (d, $^{3}J_{CP} = 5.9$ Hz, CH_2), 67.80 (d, $^{3}J_{CP} = 5.9$ Hz, CH_2), 76.90 (s, CH_2), 120.6 (q, $^{1}J_{CF} = 320.1$ Hz, CF_3). Anal. Calcd for $C_8H_{18}N_6O_3PS_2F_3$: C, 24.12; H, 4.55; N, 21.10. Found: C, 24.07; H, 4.48; N, 21.19.

13. Synthesis and characterization of **6b**: To a solution of 0.10 g (0.5 mmol) of $(CH_2NMeN)_3P(O)$ in CH_2Cl_2 (3 mL) at room temperature was added 0.082 g (57 μL) of $CF_3SO_3CH_3$ by microsyringe. The reaction mixture was stirred for 2 h at rt. Removal of the solvent afforded the expected compound as a white powder in 94% yield. $^{31}P\{^{1}H\}$NMR (101 MHz, CD_3CN) δ 2.94 (s); ^{1}H NMR (250 MHz, CD_3CN) δ 2.86 (d, $^{3}J_{PH} = 10.7$ Hz, 6H, CH_3), 3.04 (d, $^{3}J_{PH} = 10.1$ Hz, 3H, CH_3), 3.13 (d, $^{4}J_{PH} = 1.5$ Hz, 3H, CH_3), 4.34 (d, $^{2}J_{HH} = 14.2$ Hz, 1H, CH), 4.69 (d, $^{2}J_{HH} = 14.2$ Hz, 1H, CH), 5.11 (d, $^{2}J_{HH} = 12.1$ Hz, 2H, CH_2), 5.27 (d, $^{2}J_{HH} = 12.1$ Hz, 2H, CH_2); ^{13}C NMR (63 MHz, CD_3CN) δ 29.10 (d, $^{2}J_{CP} = 2.5$ Hz, CH_3), 33.31 (s, CH_3), 45.52 (s, CH_3), 63.54 (s, CH_2), 63.60 (s, CH_2), 76.02 (s, CH_2), 120.8 (*q*, $^{1}J_{CF} = 319.2$ Hz, CF_3). Anal. Calcd for $C_8H_{18}N_6O_4PSF_3$: C, 25.13; H, 4.75; N, 21.98. Found: C, 25.16; H, 4.67; N, 21.82.
14. Crystallographic data (excluding structure factors) for the structure in this letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC294642.
15. Synthesis and characterization of **7**: To a solution of 0.10 g (0.5 mmol) of $(CH_2NMeN)_3P$ in 4 mL THF was added $N_3P(S)(OC_6H_4CHO)_2$ (0.174 g, 0.5 mmol) in 3 mL THF via cannula at room temperature. The reaction mixture was stirred at rt for 2 h. After solvent removal under reduced pressure, the product was obtained as a white powder in 95% yield. $^{31}P\{^{1}H\}$NMR (101 MHz, $CDCl_3$) δ 3.83 (d, $^{2}J_{PP} = 58.15$ Hz, P═N), 48.10 (d, $^{2}J_{PP} = 58.15$ Hz, P═S), ^{1}H NMR (200 MHz, CD_2Cl_2) δ 2.81 (d, $^{3}J_{PH} = 12.7$ Hz, 9H, CH_3), 4.24 (d, $^{2}J_{HH} = 13.1$ Hz, 3H, CH_2), 4.80 (d, $^{2}J_{HH} = 13.1$ Hz, 3H, CH_2), 7.45 (d, $^{3}J_{HH} = 8.2$ Hz, 4H, C_6H_4), 7.92 (d, $^{3}J_{HH} = 8.2$ Hz, 4H, C_6H_4), 9.99 (s, 2H, CHO); ^{13}C NMR (63 MHz, CD_2Cl_2) δ 34.98 (s, CH_3), 66.41 (s, CH_2), 122.0 (s, CH, C_6H_4), 131.17 (s, CH, C_6H_4), 133.24 (s, C, C_6H_4), 156.31 (d, $J_{CP} = 8.8$ Hz, C, C_6H_4), 190.80 (s, CHO). Anal. Calcd for $C_{20}H_{25}N_7O_4P_2S$: C, 46.07; H, 4.83; N, 18.80. Found: C, 46.12; H, 4.79; N, 18.72.
16. Galliot, C.; Larre, C.; Caminade, A. M.; Majoral, J. P. *Science* **1997**, *277*, 1981; Larre, C.; Caminade, A. M.; Majoral, J. P. *Angew. Chem., Int. Ed.* **1997**, *36*, 596.
17. *Ylides and Imines of Phosphorus*; Johnson, A. N., Ed.; John Wiley Sons, 1993; p 452.
18. Schanen, V.; Cristau, H. J.; Taillefer, M. WO Patent, 2002, 092226. *Chem. Abstr. 137*, 386310.
19. Pleschke, A.; Marhold, A.; Schneider, M.; Kolomeitsev, A.; Röschenthaler, G. V. *J. Fluorine Chem.* **2004**, *125*, 1031.
20. Synthesis and characterization of **12**: To a suspension containing 0.157 g (0.5 mmol) of $(C_6H_5)_3PNH_2Cl$ in THF (6 mL) at −50 °C was added dropwise a solution of 0.625 mL (1 mmol) of *n*-BuLi (1.6 M solution in hexane). The reaction mixture was allowed to reach room temperature and 0.257 mL (0.5 mmol) of Br_2 was added. After 1 h, a solution of 0.101 g (0.5 mmol) of $(CH_2NMeN)_3P$ in 3 mL THF was added via cannula. The reaction mixture was stirred overnight at room temperature and the resulting white precipitate was filtered. The white solid was washed with a 1:1 ether/THF solution. Compound **12** was obtained as a white powder in 90% yield. $^{31}P\{^{1}H\}$NMR (101 MHz, $CDCl_3$) δ 4.45 (d, $^{2}J_{PP} = 29.6$ Hz, NPN), 21.12 (d, $^{2}J_{PP} = 29.6$ Hz, $P(C_6H_5)_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.65 (d, $^{3}J_{PH} = 13.05$ Hz, 9H, CH_3), 4.61 (d, $^{2}J_{HH} = 12.6$ Hz, 3H, CH_2), 4.82 (d, $^{2}J_{HH} = 12.6$ Hz, 3H, CH_2), 7.67 (m, 15H, CH, C_6H_5); ^{13}C NMR (63 MHz, $CDCl_3$) δ 35.04 (s, CH_3), 66.72 (d, $^{3}J_{CP} = 5.66$ Hz, CH_2), 123.10 (d, $^{1}J_{CP} = 103.8$ Hz, C, *i*-C_6H_5), 125.50 (d, $^{1}J_{CP} = 108.2$ Hz, C, *i*-C_6H_5), 129.51 (d, $J_{CP} = 13.2$ Hz, CH, C_6H_5), 130.12 (d, $J_{CP} = 13.8$ Hz, CH, C_6H_5), 131.90 (d, $J_{CP} = 11.9$ Hz, CH, C_6H_5), 133.25 (d, $J_{CP} = 11.9$ Hz, CH, C_6H_5), 134.31 (d, $^{4}J_{CP} = 3.1$ Hz, CH, *p*-C_6H_5), 134.75 (d, $^{4}J_{CP} = 2.5$ Hz, CH, *p*-C_6H_5). Anal. Calcd for $C_{24}H_{30}N_7P_2Br$: C, 51.62; H, 5.42; N, 17.56. Found: C, 51.58; H, 5.38; N, 17.60.
21. Synthesis and characterization of **13**: To a solution of 0.28 g (0.5 mmol) of **12** in CH_2Cl_2 (3 mL) at room temperature was added 0.82 g (56.6 μL) of $CF_3SO_3CH_3$ using a microsyringe. The reaction mixture was stirred overnight at rt. Evaporation of the solvent under reduced pressure afforded the expected compound as a white powder in 95% yield. $^{31}P\{^{1}H\}$NMR (101 MHz, $CDCl_3$) δ −2.8 (d, $^{2}J_{PP} = 35.3$ Hz, NPN), 24.8 (d, $^{2}J_{PP} = 35.3$ Hz, $P(C_6H_5)_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.75 (d, $^{3}J_{PH} = 12.4$ Hz, 6H, CH_3), 3.04 (d, $^{3}J_{PH} = 12.4$ Hz, 3H, CH_3), 3.88 (s, 3H, CH_3), 4.59 (d, $^{2}J_{HH} = 12.5$ Hz, 1H, CH), 4.78 (d, $^{2}J_{HH} = 12.5$ Hz, 1H, CH), 5.43 (d, $^{2}J_{HH} = 12.6$ Hz, 2H, CH_2), 5.68 (d, $^{2}J_{HH} = 12.6$ Hz, 2H, CH_2), 7.71 (m, 15H, CH, C_6H_5); ^{13}C NMR (63 MHz, $CDCl_3$) δ 30.64 (d, $^{2}J_{CP} = 3.8$ Hz, CH_3), 35.09 (s, CH_3), 45.31 (s, CH_3), 64.26 (s, CH_2), 76.34 (s, CH_2), 120.4 (q, $^{1}J_{CF} = 320.1$ Hz, CF_3), 122.42 (d, $^{1}J_{CP} = 86.8$ Hz, C, *i*-C_6H_5), 124.5 (d, $^{1}J_{CP} = 91.8$ Hz, C, *i*-C_6H_5), 129.7 (d, $J_{CP} = 14.4$ Hz, CH, C_6H_5), 130.40 (d, $J_{CP} = 13.8$ Hz, CH, C_6H_5), 132.20 (d, $J_{CP} = 11.9$ Hz, CH, C_6H_5), 132.92 (d, $J_{CP} = 11.3$ Hz, CH, C_6H_5), 134.82 (d, $J_{CP} = 2.5$ Hz, CH, *p*-C_6H_5), 135.21 (d, $J_{CP} = 3.1$ Hz, CH, *p*-C_6H_5). Anal. Calcd for $C_{26}H_{33}N_7O_3P_2SBrF_3$: C, 43.22; H, 4.60; N, 13.57. Found: C, 43.14; H, 4.52; N, 13.48.
22. No cleavage of the P–N bond was detected in all these experiments confirming the rigidity brought about by the adamantane skeleton.