Diastereoselectivity of Borane Addition to Chiral Triquinphosphoranes. NMR, X-ray, and Molecular Modeling Studies

Caroline Marchi, Frédéric Fotiadu, and Gérard Buono*

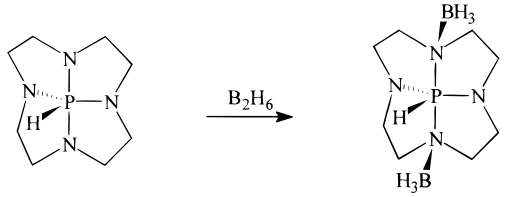
Laboratoire de Synthèse Asymétrique, UMR 6516 "Synthèse, Catalyse, et Chiralité", Ecole Nationale Supérieure de Synthèses, de Procédés et d'Ingénierie Chimiques d'Aix-Marseille, Faculté de Saint-Jérôme, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France

Received September 15, 1998

Series of new chiral tricyclic pentacoordinated phosphorus compounds, "triquinphosphoranes" (**13**−**18**, **21**, **22**, and **24**), were prepared from chiral enantiopure diamino diols that present a C_2 symmetry axis. ^{31}P and ^{13}C NMR data are consistent either with a low-energy single-step Berry pseudorotation process between the two possible diastereomeric trigonal-bipyramidal structures TBP(R_P) and TBP(S_P) or with the chiral square-pyramidal structure SP. Triquinphosphoranes reacted with borane to give two stable monoadducts with opposite configurations at the phosphorus center which do not undergo epimerization. The diastereoselectivity of this reaction depends strongly on the nature and the position of the substituents, the highest diastereomeric excesses being obtained with 4,9-diisopropyl (**28**; 90% de) and 4,9-diisobutyl (**29**; 86% de) compounds. The X-ray structure of the major diastereomer **28M** revealed that it is remarkably close to an ideal TBP, exhibiting an S_P absolute configuration. Semiempirical AM1 MO calculations predict that TBP(R_P) and TBP(S_P) ground-state species are in rapid equilibrium through a SP transition state, the activation barrier being about 5 kcal/mol. Calculations predict a marked predominance of the R_P form in all cases, except for 6,7-diPh triquinphosphorane **22**. Steric interactions between the substituents and the tricyclic phosphorane skeleton explain the prevalence of one diastereomer. The diastereoselectivity observed in borane addition on **15** is rationalized in terms of a kinetically controlled process in which the minor triquinphosphorane diastereomer reacts faster than the major one to afford (S_P)-**28M**.

Introduction

Hydridophosphoranes have been the subject of numerous studies in coordination chemistry.[1−3] Depending on the structure of the phosphorane, the action of Lewis acids leads either to a complex preserving the pentacoordinated phosphorus pattern or to a structure resulting from the opening of the hydridophosphorane and exhibiting a tricoordinated phosphorus atom. For example, Riess and co-workers have shown that the cyclenphosphorane **1** reacts with diborane to give the bis(borane) adduct **2** with a nearly ideal TBP structure in which



1 **2**

the two axial nitrogen atoms are coordinated to a BH_3 unit.[2a] Conversely, the bicyclophosphorane **3** with a single equatorial nitrogen atom, which can in principle exist in different tautomeric P^{III} and P^{V} forms, reacts with diborane at both the phosphorus and the nitrogen atoms to afford the monocyclic bis(borane) adduct **4**.[3a,b]

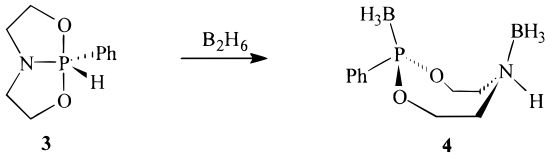
* To whom correspondence should be addressed. Tel: + 33 4 91 28 86 81. Fax: + 33 4 91 02 77 76. E-mail: buono@spi-chim.u-3mrs.fr.

(1) (a) Clardy, J. C.; Milbrath, D. S.; Verkade, J. G. *Inorg. Chem.* **1977**, *16*(8), 2135. (b) Verkade, J. G. In *Phosphorus Chemistry*; Walsh, E. N., Griffith, E. J., Parry, R. W., Quin, L. D., Eds.; ACS Symposium Series 486; American Chemical Society: Washington, DC, 1992; Chapter 5, pp 64−75.

(2) (a) Dupart, J.-M.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 1051. (b) Dupart, J.-M.; Grand, A.; Pace, S.; Riess, J. G. *Inorg. Chem.* **1984**, *23*, 3776. (c) Dupart, J.-M.; Le Borgne, G.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1985**, *107*, 1202. (d) Bondoux, D.; Houalla, D.; Pradat, C.; Riess, J. G.; Tkachenko, I.; Wolf, R. In *Fundamental Research in Homogeneous Catalysis*; Tsutui, M., Ed.; Pergamon Press: New York, 1979; Vol. 3, pp 969−981. (e) Rauchfuss, T. B. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; Chapter 7, pp 244−247. (f) Riess, J. G. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis of Organic Compounds and Metal Complexes*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; Chapter 20, pp 695−712. (g) Lattman, M.; Olmstead, M. M.; Power, P. P.; Rankin, D. W. H.; Roberston, H. E. *Inorg. Chem.* **1988**, *22*, 3012. (h) Lattman, M.; Chopra, S. K.; Cowley, A. H.; Arif, A. M. *Organometallics* **1986**, *5*, 677. (i) Khasnis, D. V.; Lattman, M.; Siriwardane, U. *Inorg. Chem.* **1989**, *28*, 681. (j) Moon, C. D; Chopra, S. K; Martin, J. C. In *Phosphorus Chemistry*; Walsh, E. N., Griffith, E. J., Parry, R. W., Quin, L. D., Eds.; ACS Symposium Series 486; American Chemical Society: Washington, DC, 1992; Chapter 10, pp 128−136. (k) For a review on the use of phosphoranides as ligands for transition metals see: Dillon, K. B. *Chem. Rev.* **1994**, *94*, 1441.

(3) (a) Contreras, R. *Main Group Chem. News* **1994**, *2*(1), 22. (b) Contreras, R. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *87*, 49. (c) For a review on spirophosphoranes and polycyclic phosphoranes with a PH bond see: Burgada, R.; Setton, R. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1994; Vol. 3, pp 185−272.

10.1021/om980774c CCC: $18.00
Publication on Web 02/10/1999



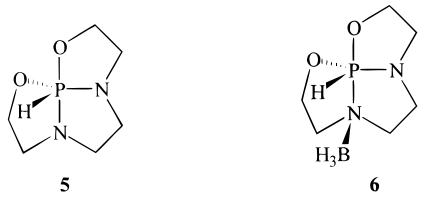
3 4

The difference in behavior of **1** and **3** can be assigned both to a strong macrocyclic effect in **1** which favors the closed form and to the presence in **1** of two axial nitrogen atoms that are much more basic than the equatorial one in **3**.

Several chiral hydridophosphoranes have been prepared from optically active amino alcohols.[3c,4,5] The presence of the chirality on the ligands in addition to that on the asymmetric pentacoordinate phophorus atom produces diastereomers which can be monitored by spectroscopy methods such as NMR.[4a−h] Some phosphoranes have been successfully isolated as enantiopure diastereomers by crystallization, and the absolute configuration of the phosphorus atom in the TBP structure was determined by X-ray diffraction.[4i] Recently, Akiba *et al*. synthesized the first stable optically phosphoranes with asymmetry only at the pentacoordinate phosphorus atom from diastereomeric phosphoranes.[4l,m] By this synthetic method an optically active pair of enantiomeric P−H phosphoranes, including Martin's ligand[6] (*o*-$(OCF_3)_2C_6H_4)_2$P*H, could be obtained.

Although hydridophosphoranes offer great potential in coordination chemistry due to their remarkable ability for complexation with transition metals[1−3] and in organic synthesis,[3c,7] few applications of chiral hydridophosphoranes have been reported.[3c] We previously reported the synthesis of new tricyclic chiral P−H-bonded phosphorane "triquinphosphoranes" from chiral enantiopure diamino diols having a C_2 symmetry axis to reduce the number of diastereomers.[8] In this paper we demonstrate that such chiral triquinphosphoranes may exist as two diastereomeric TBP structures in fast equilibrium by a Berry pseudorotation process. Structural factors governing the equilibrium are studied by molecular modeling.

We have already shown that the parent triquinphosphorane **5**, derived from achiral *N*,*N*′-bis(2-hydroxyethyl)ethylenediamine, reacted with borane to afford the single stable mono(borane) adduct **6**. We now report that



5 6

the addition of borane to chiral triquinphosphoranes leads to two diastereomeric TBP borane complexes that do not undergo epimerization at the phosphorus atom. We show that the observed diastereoselectivity results from the relative rates of borane addition to each TBP triquinphosphorane. Therefore, we illustrate for the first time a diastereoselective reaction of chiral phosphoranes under kinetic control.

Results

Synthesis of Chiral Triquinphosphoranes. According to the synthesis procedure previously described, compounds **13**−**18** were easily prepared in 80−90% chemical yield by a stoichiometric exchange reaction between diamino diols[9] **7**−**12** and hexamethylphosphorustriamide (1 equiv) in refluxing toluene under a nitrogen atmosphere for $^1/_2$ h (Scheme 1).

Two new classes of triquinphosphoranes derived from chiral diamino diols coming respectively from chiral diamines[10] and chiral α-hydroxy acids[11] were prepared. Diamino diols **19** and **20** were synthesized in two steps from (*R*,*R*)-cyclohexanediamine and (*S*,*S*)-1,2-diphenylethylene-1,2-diamine, respectively. These compounds were prepared by condensation of chiral diamine and ethyloxalyl chloride in the molar ratio 1/2 followed by reduction of the diamide diester compound by $AlLiH_4$. Diamino diol **23** was obtained in four steps from (*R*)-mandelic acid: (i) protection of the α-hydroxy group by acetylation, (ii) synthesis of (*R*)-α-acetoxybenzeneacetyl chloride, (iii) condensation with ethylenediamine, and (iv) reduction of the diamide diester compound with $AlLiH_4$.

The ^{31}P NMR spectra in benzene-d_6 of all these hydridophosphoranes exhibit a single high-field signal (δ ∼−36.7 ppm), characteristic of pentacoordinated phosphorus compounds (10-P-5),[12] and a large P−H coupling constant ($^1J_{P-H} \approx 716$ Hz) revealing a pronounced s character for this bond.[13] No signal was detected for the tricoordinated bicyclic alkoxyoxaza-

(4) (a) Burgada, R.; Bon, M.; Mathis, F. *C. R. Acad. Sci., Ser. C* **1967**, *265*, 1499. (b) Ferekh, J.; Brazier, J. F.; Muñoz, A.; Wolf, R. *C. R. Acad. Sci., Ser. C* **1970**, *270*, 865. (c) Contreras, R.; Brazier, J. F.; Klaebe, A.; Wolf, R. *Phosphorus Relat. Group V Elem.* **1972**, *2*, 67. (d) Contreras, R.; Wolf, R. *Synth. Inorg. Met.-Org. Chem.* **1973**, *3*(1), 37. (e) Brazier, J. F.; Ferekh, J.; Muñoz, A.; Wolf, R. *C. R. Acad. Sci., Ser. C* **1971**, *272*, 1521. (f) Klaebe, A.; Brazier, J. F.; Mathis, F.; Wolf, R. *Tetrahedron Lett.* **1972**, *42*, 4367. (g) Houalla, D.; Sanchez, M.; Wolf, R. *Org. Magn. Reson.* **1973**, *5*, 451. (h) Klaebe, A.; Cachapuz-Carrelhas, Brazier, J. F.; Marre, M. R.; Wolf. R. *Tetrahedron Lett.* **1974**, 3971. (i) Newton, M. G.; Collier, J. E.; Wolf, R. *J. Am. Chem. Soc.* **1974**, *96*, 6888. (j) Klaebe, A.; Cachapuz-Carrelas, X.; Brazier, J. F.; Houalla, D.; Wolf, R. *Phosphorus Sulfur Relat. Elem.* **1979**, *5*, 291. (k) Kojima, S.; Nakamoto, M.; Kajiyama, K.; Akiba, K. Y. *Tetrahedron Lett.* **1995**, *36*(13), 2261−2264. (l) Kojima, S.; Kajiyama, K.; Akiba, K. Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1785−1797. (m) It is worth noting that Hellwinkel isolated the first optically active pentaarylphosphorane. However, it undergoes stereoisomerization with low conversion energy barriers: Hellwinkel, D. *Chem. Ber.* **1966**, *99*, 3642.

(5) (a) Klaebe, A.; Brazier, J. F.; Guarrigues, B.; Wolf, R.; Stefanovsky, Y. *Phosphorus Sulfur Relat. Elem.* **1981**, *10*, 53. (b) Jeanneaux, F.; Riess, J. G.; Wachter, J. *Inorg. Chem.* **1984**, *23*, 3036.

(6) (a) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 7434. (b) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4623. (c) Ross, M. R.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 1234.

(7) Spirophosphoranes have been recently applied with success in Wittig type reactions. These spirophosphoranes were prepared from the corresponding P−H spirophosphoranes by alkylation: (a) Bojin, M. L.; Barkallha, S.; Evans, S. A., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 1549. (b) Kojima, S.; Takagi, R. Akiba, K.-y. *J. Am. Chem. Soc.* **1997**, *119*, 5970. (c) Burger, K. Pentacoordinated Phosphorus in Synthesis. In *Organophosphorus Reagents in Organic Synthesis*; Cadogan, J. I. G., Ed.; Academic Press: New York, 1979; pp 467−510. (d) For the free radical alkylthiylation of hydridophosphorane **5**, see: Bentrude, W. G.; Kawashima, T.; Keys, B. A.; Garroussian, M.; Heide, W.; Wedegaertner, D. A. *J. Am. Chem. Soc.* **1987**, *109*, 1227. (e) Chiral triquinphosphoranes were shown to undergo UV-light-induced alkylthiylation reactions by a series of alkyl disulfides to give the corresponding isolable thia chiral triquinphosphoranes: Unpublished results.

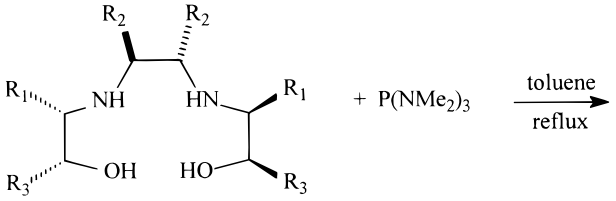
(8) Vannoorenberghe, Y.; Buono, G. *J. Am. Chem. Soc.* **1990**, *112*, 6142.

(9) *N*,*N*′-Bis(1-alkyl-2-hydroxyethyl)ethylenediamine: diamino diols **7**−**12**.

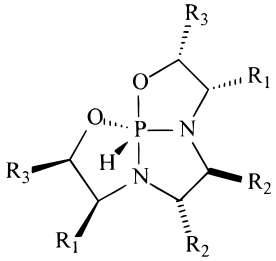
(10) *N*,*N*′-Bis(2-hydroxyethyl)-1,2-dialkylethylene-1,2-diamine: diamino diols **19** and **20**.

(11) *N*,*N*′-Bis(2-alkyl-2-hydroxyethyl)ethylenediamine: diamino diol **23**.

Scheme 1[a]



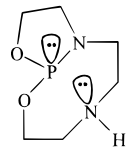
$R_2 = R_3 = H$ **7-12**
$R_1 = R_3 = H$ **19-20**
$R_1 = R_2 = H$ **23**



13-18
21-22
24

[a] Legend: **7** and **13**, R_1 = Me; **8** and **14**, R_1 = Et; **9** and **15**, R_1 = ^{i}Pr; **10** and **16**, R_1 = ^{i}Bu; **11** and **17**, R_1 = Ph; **12** and **18**, R_1 = Bn; **19** and **21**, R_2 = $-(CH_2)_4-$; **20** and **22,** R_2 = Ph; **23** and **24,** R_3 = Ph.

phospholane **25** (8-P-3),[12] even at a higher temperature

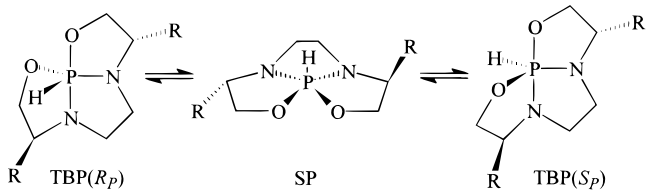


25

(80 °C) or in a more polar solvent such as DMSO-d_6 at room temperature.[14]

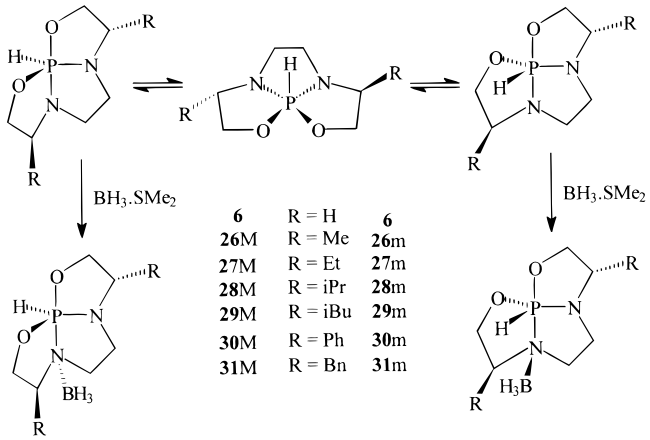
The ^{13}C NMR spectrum of these new triquinphosphoranes showed that the carbon atoms which are symmetric with respect to the C_2 axis in the starting diamino diols are anisochronous. Taken together, ^{31}P and ^{13}C NMR data for **13**−**18**, **21**, **22**, and **24** are consistent with either a time-averaged spectrum characteristic of a low-energy single-step Berry pseudorotation process[15] with the hydrogen atom as the pivot between the two possible diastereomeric trigonal-bipyramidal structures (TBP(R_P), TBP(S_P)),[16] with epimerization at the phosphorus atom and interchange of anisochronous carbon atoms of the tricyclic structure, or, alternatively, a chiral square-pyramidal structure (SP) (Scheme 2). Dynamic ^{31}P NMR spectroscopy showed only one upfield signal to a temperature of −100 °C in toluene-d_8 at 161.9 MHz.[17]

Scheme 2[a]



[a] A similar scheme could be depicted for compounds **21**, **22**, and **24**.

Scheme 3[a]



[a] A similar scheme could be depicted for compounds **32**−**34**.

Reactivity toward BH_3.SMe_2. The parent triquinphosphorane **5** (R = H, Scheme 3) reacted with BH_3 to give both enantiomers of the monoborane adduct. In an analogous way, compounds **13**−**18**, **21**, **22**, and **24** reacted rapidly with BH_3·SMe_2 in toluene under a nitrogen atmosphere to afford two diastereomeric stable

(12) The *N*-X-*L* nomenclature system has been previously described: *N* valence electrons about an atomic center X with *L* ligands: Perkins, C. W.; Martin, J. C.; Arduengo, A. J., III; Lau, W.; Algeria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

(13) (a) Tebby, J. C. In *Methods in Stereochemical Analysis: Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, D. L., Eds.; VCH: Deerfield Beach, FL, 1987; Vol. 8, p 40. (b) Tebby, J. C. *Handbook of Phosphorus 31 Nuclear Magnetic Resonance Data*; CRC Press: Boca Raton, FL, 1991. (c) Gallagher, M. J. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, D. L., Verkade, J. G., Eds.; VCH: New York, 1994; Chapter 29, pp 385−393.

(14) Several 10-P-5 hydridophosphoranes are in equilibrium with a 8-P-3 tautomeric structure. It has been found that factors such as temperature, solvent basicity, basicity of the heteroatoms at the binding site, ring size, the presence of an unsaturation in the rings, and the size of the substituents on the ring affect the ratio between the 10-P-5 and the 8-P-3 species: (a) Burgada, R. *Bull. Soc. Chim. Fr.* **1975**, 407. (b) Muños, A. *Bull. Soc. Chim. Fr.* **1977**, 728. (c) Burgada, R.; Laurenço, C. *J. Organomet. Chem.* **1974**, *66*, 255. (d) Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* **1978**, 4333. (e) Atkins, T. J.; Richman, J. E. *Tetrahedron Lett.* **1978**, 5149. (f) Houalla, D.; Sanchez, M.; Gonbeau, D.; Pfister-Guillouzo, G. *Nouv. J. Chem.* **1979**, *8*−*9*, 507. (g) Houalla, D.; Brazier, J. F.; Sanchez, M.; Wolf, R. *Tetrahedron Lett.* **1972**, 2969.

(15) (a) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933. (b) Mislow, K. *Acc. Chem. Res.* **1970**, *3*, 321. (c) The turnstile mechanism is sometimes alternatively invoked, but for the triquinphosphoranes the pseudorotation according to Berry is by far the most appropriated in the sense of symmetrical factors and is due to the structural dependence of five-membered rings: Ugi, I.; Marquarding, D.; Klusacek, H.; Gillespie, P.; Ramirez, F. *Acc. Chem. Res.* **1971**, *4*, 288. (d) The topological equivalence between Berry and turnstile pseudorotations has been addressed: Russeger, P.; Brickmann, J. *Chem. Phys. Lett.* **1975**, *30*, 276.

(16) For the nomenclature of chiral pentacoordinate compounds see: Martin, J. C.; Balthazor, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 152. "The sense of chirality can be specified by viewing the idealized TBP structure along its axial axis in the orientation which places nearer the viewer that axial substituent which has the higher priority rank in the CIP nomenclature scheme. The priority ranking of the equatorial ligands using the CIP conventions results in order of decreasing priority which can be recognized by the viewer as being clockwise (*R*) or counterclockwise (*S*)."

(17) According to Holmes' empirical calculations the energy difference between the TBP and the SP structures should be 2.0 ± 1.5 kcal/mol in favor of the former, supporting a fast pseudorotation process at room temperature: Holmes, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 433.

Table 1. Diastereomeric Excesses (de) of Triquinphosphorane−Borane Complexes

entry no.	triquinphosphorane	adduct	de[a] (%)
1	**5**	**6**	*b*
2	**13**	**26**	54
3	**14**	**27**	63
4	**15**	**28**	90
5	**16**	**29**	86
6	**17**	**30**	64
7	**18**	**31**	64
8	**21**	**32**	10
9	**22**	**33**	60
10	**24**	**34**	28

[a] Determined by integration of the ^{31}P NMR signals of both adducts, Conditions: C_6D_6, 100 MHz, 298 K. [b] A single ^{31}P signal was observed.

monoadducts in different proportions (Scheme 3). The diastereomeric excesses were determined by integration of the ^{31}P NMR signals of both adducts (Table 1).

The diastereoselectivity of this reaction depends strongly on the nature and the position of the substituents on the tricyclic structure. In the case of the compound **28** (R = ^{i}Pr), the major diastereomer **28M** was crystallized. The X-ray diffraction structure revealed that borane coordinated to the axial nitrogen of the TBP structure is in a *syn* position with respect to the P−H bond and in an *anti* position with respect to the adjacent pseudoaxial isopropyl substituent (*vide infra*). Thus, borane must preferentially attack the phosphorane diastereomer featuring the least hindered axial nitrogen atom.

The addition of BH_3·SMe_2 to triquinphosphoranes is fast, and no variation of the diastereomeric excess with temperatures ranging from −50 to 100 °C was found. At lower temperature, a small decrease of the diastereoselectivity (from 85% at −50 °C to 79% at −75 °C for adduct **28**) was observed. The diastereoselectivity should result from the relative rates of addition of borane on the two diastereomeric TBP structures in equilibrium by a fast pseudorotation process. It is therefore difficult to relate the observed diastereoselectivity to simple structural factors.

Dynamic ^{31}P NMR experiments at temperatures up to 100 °C in toluene-d_8 showed that there is no interconversion between the two diastereomeric triquinphosphorane−BH_3 complexes. Such a process should have resulted from either (1) dissociation of the borane complex, fast epimerization of the free phosphorane, and reassociation or (2) a Berry pseudorotation from one diastereomeric borane complex together with a borane exchange between the two nitrogens *via* a direct transfer of the BH_3 unit between the two basal nitrogen atoms in the SP structure. However, complexation by borane should hinder the phosphorane epimerization *via* pseudorotation. Indeed, the borane contributes to enhance the apicophilicity of the nitrogen atom that bears it and stabilizes the TBP structure with respect to the free phosphorane, in which the apicophilicity rule[18−20] is contravened.

The best diastereoselectivity was obtained with the isopropyl substituents in 4- and 9-positions of the triquinphosphorane (Table 1, entry 4). For the triquinphosphoranes with the substituents in 4- and 9-positions (entries 2−7) the diastereoselectivity depends on the steric effects and we observe the best distereoselectivities with the isopropyl (90%, entry 4) and isobutyl substituents (86%, entry 5). In the case of the phenyl-disubstituted triquinphosphoranes **17**, **22**, and **24** (entries 6, 9, and 10) the diastereoselectivity depends on the relative position of the substituents with respect to the axial nitrogen atom. When the substituents are connected to the carbon bound to the axial nitrogen (carbons 6,7 or 4,9), similar diastereoselectivities are obtained. On the other hand, when the substituents are in β-positions with respect to the axial nitrogen (3,10-substituted compounds) the diastereoselectivity strongly decreases.

Table 2. X-ray Data for Triquinphosphorane−Borane Complex 28M

$C_{12}H_{28}N_2O_2BP$	d(calcd) = 1.19 g cm^{-3}
fw = 274.15	recording temp: 18 °C
space group: $P2_1$	Mo Kα radiation: λ = 0.710 69
a = 9.513(2) Å	θ range: $5 \le 2\theta \le 35°$
b = 6.134(1) Å	data collected: 2778
c = 13.313(3) Å	no. of data with $I \ge 2.5\sigma(I)$: 2531
β = 98.99(2)°	cryst size: 0.12 × 0.18 × 0.47 mm
V = 767.3(3) Å^3	R = 0.030
Z = 2	R_w = 0.032
μ(Mo Kα) = 1.81 cm^{-1}	

Addition of excess BH_3·SMe_2 did not lead to bis(borane) adducts. This result is in accordance with those obtained by Riess *et al*. concerning the lack of reactivity of the equatorial nitrogen atom of the TBP toward Lewis acids.[2a] The strong basic character exhibited by the axial nitrogen atom should be due to its sp^3 type hybridization, whereas the equatorial nitrogen adopts an sp^2 type hybridization that considerably decreases its basic character.[21] It is worth noting that the $^1J_{P-H}$ coupling constant increases upon complexation, indicating an enhanced s character in the equatorial plane. The complexation by borane of the triquinphosphoranes resulted in a lower ^{31}P chemical shift that can be assigned to an increased positive charge on the phosphorus atom.

X-ray Structure. Selected bond lengths and angles are shown in Table 3. The molecular structure and atom labeling are shown in Figure 1. Despite the presence in **28** of three five-membered rings, all in axial−equatorial positions, the arrangement of the five bonds around phosphorus is remarkably close to that of a regular TBP. The minute structural distortion from TBP is reflected in the values of the axial and equatorial N−P−O angles of 176.7(1) and 122.6(1)°, respectively. By the use of the dihedral angle method and the unit bond lengths, it was estimated that the structure is displaced by only 5.9% along the Berry coordinate[15] from the ideal TBP (0%)

(18) It is well-known that a phosphorane bearing oxygen and nitrogen substituents preferentially has oxygen atoms in the axial positions as the most stable stereoisomer according to the apicophilicity of the elements: Trippett, S. *Phosphorus Sulfur Relat. Elem.* **1976**, *1*, 89.

(19) Holmes, R. R. *Pentacoordinated Phosphorus*; ACS Monograph Series 175 and 176; American Chemical Society: Washington, DC, 1980; Vols. 1 and 2.

(20) (a) McDowell, S.; Streitwieser, A. *J. Am. Chem. Soc.* **1985**, *107*, 5849. (b) Thatcher, G. R. J.; Kluger, R. In *Advances in Physical Organic Chemistry*; Bethell, D., Ed.; Academic Press: New York, 1989; Vol. 25. (c) Buono, G.; Llinas, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 4532. (d) Wang, P.; Zhang, Y.; Glaser, R.; Reed, A. E.; Schleyer, P. v. R.; Streitwieser, A. *J. Am. Chem. Soc.* **1991**, *113*, 55. (e) Thatcher, G. R. J.; Campbell, A. S. *J. Org. Chem.* **1993**, *58*, 2272.

(21) It is worth noting the unusually strong basic character of a nitrogen atom bound to phosphorus in the case of bicyclic aminophosphanes 8-P-3: Grec, D.; Hubert-Pfalzgraf, L. G.; Riess, J. G.; Grand, A. *J. Am. Chem. Soc.* **1980**, *102*, 7134.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) from X-ray Data for 28M[a]

$O11_{ax}$−P1	1.656(1)	$N5_{ax}$−C4	1.501(3)
$O2_{eq}$−P1	1.607(2)	$N5_{ax}$−C6	1.486(2)
$N5_{ax}$−P1	1.932(2)	$N8_{eq}$−C7	1.453(2)
$N8_{eq}$−P1	1.640(2)	$N8_{eq}$−C9	1.461(3)
B18−$N5_{ax}$	1.624(3)	C3−C4	1.515(3)
$O2_{eq}$−C3	1.438(4)	C6−C7	1.520(3)
$O11_{ax}$−C10	1.424(3)	C9−C10	1.530(3)
$N5_{ax}$−P1−$O2_{eq}$	90.1(1)	C9−$N8_{eq}$−C7	120.7(2)
$N8_{eq}$−P1−$N5_{ax}$	87.2(1)	$N5_{ax}$−C4−C3	104.8(2)
$O11_{ax}$−P1−$O2_{eq}$	93.1(1)	$N5_{ax}$−C6−C7	106.3(1)
$O11_{ax}$−P1−$N8_{eq}$	91.0(1)	$N8_{eq}$−C7−C6	104.7(1)
$O11_{ax}$−P1−$N5_{ax}$	176.7(1)	$N8_{eq}$−C9−C10	102.4(2)
$N8_{eq}$−P1−$O2_{eq}$	122.6(1)	$O2_{eq}$−C4−C3	107.7(2)
C3−$O2_{eq}$−P1	118.3(1)	$O11_{ax}$−C10−C9	107.3(2)
C10−$O11_{ax}$−P1	113.5(1)	B18−$N5_{ax}$−P1	106.3(1)
C6−$N5_{ax}$−P1	105.6(1)	B18−$N5_{ax}$−C4	115.2(2)
C4−$N5_{ax}$−P1	104.5(1)	B18−$N5_{ax}$−C6	111.4(2)
C9−$N8_{eq}$−P1	117.8(1)	C15−C9−$N8_{eq}$	112.9(2)
C7−$N8_{eq}$−P1	121.4(1)	C12−C4−$N5_{ax}$	116.9(2)
C6−$N5_{ax}$−C4	112.8(1)	C12−C4−C3	113.3(2)

[a] Esd's are given in parentheses.

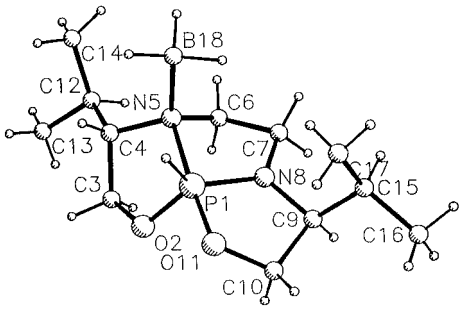
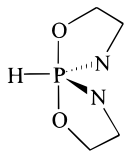


Figure 1. X-ray structure of the major diastereomer of triquinphosphorane−borane adduct **28** (**28M**).

toward the ideal SP (100%), P−H being the pivotal ligand in the pseudorotation process.[19,22] This distortion should be compared with that of the cyclenphosphorane bis(borane) adduct **1** that was shifted by 10.4% along the Berry coordinate from the ideal TBP.[2c]

As indicated before, the boron atom is in a *syn* position with respect to the P−H bond and an *anti* position toward the pseudoaxial isopropyl substituent. In this diastereomer the phosphorus atom exhibits an *S* configuration.

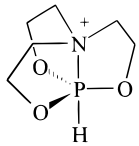
As expected, the equatorial P−O bond (1.607(2) Å) is shorter than the axial one (1.656(2) Å). The latter could be compared to the value found for the simple spirophosphorane **35** (1.709 Å),[23] although it is displaced by



35

24.5% along the Berry coordinate from the ideal TBP.[24] The equatorial P−N bond (1.640(2) Å) lies in the lower part of the usual range (1.62−1.71 Å) for such bonds.[19,25] Its shortness with respect to the above standards can in part be assigned to hyperconjugation between the phosphorus center and the equatorial nitrogen atom that exhibits a sp^2 type (sum of bond angles around N_{eq} is 359.9(2)°).[26]

The axial P−N bond is remarkably longer (1.932(2) Å)[27,28] than all those yet reported for phosphoranes (1.70−1.83 Å)[19] or for the cyclenphosphorane bis(borane) adduct **1** (average bond length 1.865 Å).[2a] Nevertheless, this value comes closer to the axial P→N dative bond (1.986 Å) reported by Verkade *et al.*[29] for the cation **36**



36

that is displaced by only 13.0% from the ideal TBP along the Berry coordinate.[24] The importance of symmetry factors underlined by Ramirez and co-workers[30] could explain the fact that the equatorial P−N bond lengths are longer in **1** (average value 1.650 Å) than in **28** (1.640(2) Å) and the axial bonds shorter in **1** (average value 1.865 Å) than in **28** (1.932(2) Å).

It is also remarkable that the N−B bond length in **28** (1.624(3) Å) lies within the usual range reported for N−BH_3 bonds (1.56−1.66 Å).[3a,31] This bond is longer than those reported for **2** (1.597 and 1.604 Å).[2a] The N−B bond length in **28** thus further implies a definite basicity of the axial nitrogen atom toward borane. This trend is confirmed by the sum of bond angles around N_{ax} in the phosphorane moiety (322.9(4)°) that is unusually low and reveals a pyramidal distortion of the axial nitrogen atom bound to borane.

Theoretical Study. Although we established that the triquinphosphorane borane adduct **28** presents a nearly ideal TBP structure, for the moment the structure of free triquinphosphoranes remains unknown.[32] We thus carried out theoretical calculations to address this question.

Simple pentacoordinated phosphorus compounds such as the hypothetical PH_5 and PH_3F_2 species, PF_5, or cyclic

(22) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.
(23) Meunier, P. F.; Dieters, J. A.; Holmes, R. R. *Inorg. Chem.* **1976**, *15*(10), 2577.
(24) This percentage of deformation has been calculated by our team: Llinas, J. R. Thesis, University of Marseilles, 1979.
(25) (a) Day, R. O.; Schmidpeter, A.; Holmes, R. R. *Inorg. Chem.* **1982**, *21*, 3916. (b) Day, R. O.; Schmidpeter, A.; Holmes, R. R. *Inorg. Chem.* **1983**, *22*, 3696.
(26) Gilheany, D. G. *Chem. Rev.* **1994**, *94*(5), 1339−1374.
(27) This P−N bond length is close to the covalent radius, 1.85 Å: Sutton, L., Ed. *Tables of Interatomic Distances and Configuration in Molecules and Ions*; The Chemical Society: London, 1958 and 1965; Special Publications Nos. 11 and 18.
(28) This P−N bond may be compared with the P−N bond in the neutral hexacoordinated phosphorus compounds obtained by Lewis acid−base interactions between pentacoordinated phosphorus compounds and nitrogen donor atom; see Table 2 of: Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927. See also Table 2 of: Wong, C. Y.; Kennepohl, D. K.; Cavell, R. G. *Chem. Rev.* **1996**, *96*, 1917.
(29) Clardy, J. C.; Milbrath, D. S.; Springer, J. P.; Verkade, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 623.
(30) (a) Ramirez, F.; Ugi, I. In *Advances in Physical Organic Chemistry*; Gold, V., Ed.; Academic Press: New York, 1971; Vol. 9. (b) Ramirez, F.; Ugi, I. *Bull. Soc. Chim. Fr.* **1974**, 453. (c) Ramirez, F.; Pfohl, S.; Tsolig, E. A.; Pilot, J. F.; Smith, C. P.; Ugi, I.; Marquarding, D.; Gillespie, P.; Hoffmann, P. *Phosphorus Relat. Group V Elem.* **1971**, *1*, 1.
(31) (a) Andrionov, V. I.; Atovmyan, L. O.; Golovina, N. I.; Klitskaya, G. A. *Zh. Strukt. Khim.* **1967**, *8*, 303. (b) Cassoux, P.; Kuczkowski, R. L.; Brian, P. S.; Taylor, R. C. *Inorg. Chem.* **1975**, *14*, 126. (c) Colquhoun, H. M.; Jones, G.; Maud, J. M.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1984**, 63.
(32) Despite numerous attempts, we could not obtain any crystals of solid phosphoranes **17** and **18** suitable for X-ray diffraction.

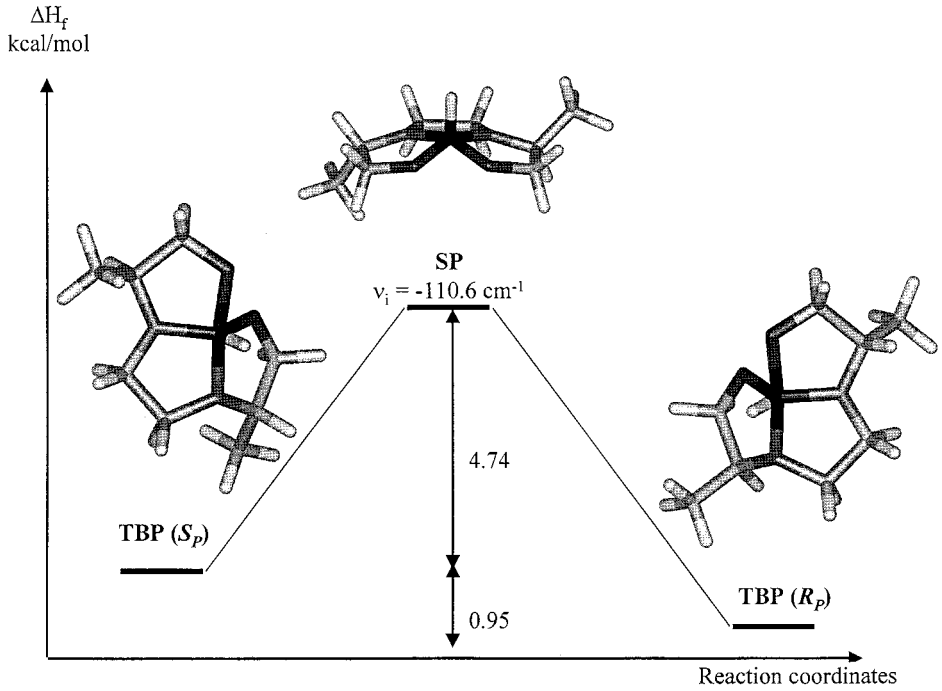


Figure 2. Calculated energy profile for the pseudorotation process of triquinphosphoranes **13**.

pentaoxyphosphoranes have been extensively studied with high-level *ab initio* theory.[33−36] Their structures and the mechanisms associated with their intramolecular rearrangement processes have been examined. For PH_5, Kutzelnigg and Wasilewski demonstrated that the ground state is a TBP structure (D_{3h}) that undergoes a Berry pseudorotation process via a square-pyramidal (C_{4v}) transition state, with an energetic barrier of about 2 kcal/mol.[36]

Because *ab initio* molecular orbital calculations on chiral triquinphosphoranes should require extensive computational resources, we resorted to semiempirical methods. Methods such as AM1[37] and PM3[38] have been successfully applied in the field of organophosphorus compounds.[39] For instance, pentacoordinated oxaphosphetanes involved in the Wittig reaction were correctly represented at this theoretical level.[40] Therefore, all calculations were carried out using the AM1 method implemented in the AMPAC 2.18 program.[41] In every case, all independent geometric variables were optimized, and the force constant matrix was calculated for each stationary point to ensure it to be either a minimum or a transition state on the potential energy hypersurface.

Theoretical Results

Two model chiral triquinphosphoranes were first examined: the parent structure **5** and the (4*S*,9*S*)-dimethyl derivative **13** that is prototypic of triquinphosphoranes derived from α-amino acids. For both phosphoranes, three geometries were computed: two TBP structures with inverse absolute configurations at the phosphorus atom, TBP(S_P) and TBP(R_P), and the square pyramid SP. In both cases, the two TBP structures appeared to be stable ground states, whereas the SP species were first-order transition states ($\nu_i = -118.1$ cm^{-1}, **5**; $\nu_i = -110.6$ cm^{-1}, **13**). The structures and energy profile for **13** are presented in Figure 2.

The geometries of the ground-state structures are close to the ideal TBP (Table 4). Bond angles in the equatorial plane are about 120°, and the axial−equatorial angles are about 90°. As expected, the axial bonds are longer than the equatorial ones; *e.g.*, $P-N_{ax} = 1.675$ Å/$P-N_{eq} = 1.609$ Å and $P-O_{ax} = 1.700$ Å/$P-O_{eq} = 1.660$ Å for **5**. Moreover, the two nitrogen atoms present clearly different hybridizations, the equatorial nitrogen atoms being clearly of sp^2 type (e.g. sum of bond angles around N_{eq} in **5** is 360°) while the axial ones exhibit typical sp^3 geometries (the sum of bond angles around N_{ax} in **5** is 346.6°).[42]

For each model, intrinsic reaction coordinate calculations were performed, starting from the SP species and following the transition vector. They showed that the deformation of the SP led to both TBP structures. TBP-

(33) (a) Shih, S. K.; Peyerimhoff, S. D. *J. Chem. Soc., Faraday Trans.* **1979**, *75*(2), 379. (b) Trinquier, G.; Daudey, J.-P.; Caruana, G.; Madaule, Y. *J. Am. Chem. Soc.* **1984**, *106*, 4794. (c) Reed, A. E.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1987**, *133*, 553. (d) Ewig, C. S.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 1552. (e) Wang, P.; Agrafiotis, D. K.; Streitwieser, A.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1990**, 201. (f) Ding, F.-J.; Zhang, L.-F. *Int. J. Quantum Chem.* **1996**, *60*, 1037.

(34) (a) Holmes, R. R.; Deiters, J. A. *Inorg. Chem.* **1994**, *33*, 3235. (b) Deiters, J. A.; Holmes, R. R. *Organometallics* **1996**, *15*, 3944.

(35) (a) Moc, J.; Morokuma, K. *J. Am. Chem. Soc.* **1995**, *117*, 11790 and references therein. (b) Uchimaru, T.; Uebayashi, M.; Hirose, T.; Tsuzuki, S.; Yliniemelä, A.; Tanabe, K.; Taria, K. *J. Org. Chem.* **1996**, *61*, 1599. (c) Wasada, H.; Hirao, K. *J. Am. Chem. Soc.* **1992**, *114*, 16.

(36) Kutzelnigg, W.; Wasilewski, J. *J. Am. Chem. Soc.* **1982**, *104*, 953.

(37) Dewar, M. J. S.; Zoebisch, E. F.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(38) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

(39) Dewar, M. J. S.; Jie, C. *J. Mol. Struct. (THEOCHEM)* **1989**, *187*, 1.

(40) Mari, F.; Lahti, P. M.; McEwen, E. *J. Am. Chem. Soc.* **1992**, *114*, 813.

(41) Dewar, M. J. S. Stewart, J. J. P. *QCPE Bull.* **1986**, *6*, 24; QCPE Program 506. All calculations were performed with the AMPAC 4.5 code (Semichem, Shawnee, KS 66216).

Table 4. Theoretical and Experimental Bond Lengths (Å) and Angles (deg) around the Phosphorus Atom[a]

	theoretical data (AM1)					X-ray
	5	**13**	**6**	**6′**	**28**	data (**28M**)
Bond Lengths						
$P-O_{eq}$	1.66	1.66	1.65	1.67	1.65	1.607(2)
$P-O_{ax}$	1.70	1.70	1.69	1.69	1.69	1.656(1)
$P-N_{ax}$	1.67	1.67	1.79	1.66	1.80	1.932(2)
$P-N_{eq}$	1.61	1.61	1.60	1.71	1.60	1.640(2)
Bond Angles						
$O_{ax}-P-N_{ax}$	173.4	173.1	173.3	171.9	173.0	176.7(1)
$O_{eq}-P-N_{eq}$	120.2	120.4	115.9	117.5	120.9	122.6(1)
$O_{eq}-P-N_{ax}$	93.3	93.1	91.8	91.2	92.7	90.1(1)
$N_{ax}-P-N_{eq}$	94.6	94.9	93.8	94.7	94.2	87.2(1)
$N_{eq}-P-O_{ax}$	92.0	92.0	92.7	90.7	93.1	91.0(1)
$O_{ax}-P-O_{eq}$	82.9	82.9	84.1	80.9	84.8	93.1(1)

[a] Esd's are given in parentheses.

(S_P) and TBP(R_P) are thus connected by a continuous reaction pathway corresponding to a Berry pseudorotation mechanism and involving a SP transition state. The corresponding calculated enthalpies of activation are about 5 kcal/mol (see Table 5). The two stereomeric TBP species would thus be in a very fast equilibrium relative to the time scale of NMR studies, in complete agreement with our experimental results. In the case of compound **13**, the equilibrium constant between the two diastereomeric TBP forms could be easily estimated. In fact, it is reasonable to assume that the entropy variation between the two TBP structures is negligible. Therefore, the difference in calculated formation enthalpy between TBP(S_P) and TBP(R_P) ($\Delta\Delta H_f = 0.95$ kcal/mol; Table 5, entry 2) affords a good approximation of the free enthalpy of equilibrium ΔG_e. The related equilibrium constant is 4.92 and corresponds to a TBP(S_P):TBP(R_P) ratio of 17:83. The greater stability of TBP(R_P) relative to TBP(S_P) should be due to some steric repulsion between the pseudoaxial methyl substituent and the axial−equatorial diazaphospholidine ring that can occur in the latter but not in the former.

To evaluate how the nature of the substituents affects the relative stability of the diastereomeric TBPs, we studied (4*S*,9*S*)-diisopropyl (**15**) and (4*S*,9*S*)-diphenyl (**17**) triquinphosphoranes. Because the isopropyl and phenyl groups can freely rotate around the C_4-R and C_9-R bonds and give rise to several conformers, we carried out a systematic conformational search on each TBP structure with the standard two-bond drive technique (grid method). Both driven torsion angles Θ_1 and Θ_2 defined for the isopropyl or phenyl substituents were changed in 15° steps to completely explore the conformational space (Figure 3).[43] Each minimum on the surface was then fully optimized.

In the case of compound **15**, we found nine stable conformers for each TBP structure, which correspond to the three rotamers expected for each $C(sp^3)-C(sp^3)$ bond between the triquinphosphorane skeleton and an isopropyl substituent (Figure 3). However, all the conformers of TBP(R_P) exhibit lower energy than those of TBP(S_P). In fact, in the latter structures, the pseudoaxial isopropyl group should induce a steric repulsion with the diazaphospholidine ring, whatever the torsion angle, just as in the case of phosphorane **13**. By locating one of the possible SP transition states, we verified that the inversion barrier between TBP(S_P) and TBP(R_P) remains nearly constant (about 5 kcal/mol) and seems insensitive to the steric hindrance of the substituents in 4,9-positions (Table 5, entry 3). Such a low pseudorotation barrier agrees very well with the experimental ^{31}P NMR studies, in which only one average signal was observed. The calculated Boltzmann populations of the 18 stereomeric TBP species in rapid equilibrium, by either internal rotation of the substituents or pseudorotation of the phosphorus ligands, indicated that the (R_P) form constitutes about 97% of triquinphosphorane **15**.

In the case of triquinphosphorane **17** bearing phenyl substituents, a single conformer was found for each TBP structure. Just like compounds **13** and **15**, the TBP(R_P) structure is more stable by about 1 kcal/mol than the TBP(S_P) form, the diastereomeric ratio being 86:14 (Table 5, entry 4). The inversion barrier corresponding to the SP transition structure is still 5 kcal/mol, which confirms that the nature of the substituents in 4,9-positions has very little influence on the pseudorotation process.

To compare the above family of 4*S*,9*S*-substituted triquinphosphoranes with species bearing substituents in other positions, similar calculations were performed on the (6*S*,7*S*)-diphenyl (**22**) and (3*R*,10*R*)-diphenyl (**24**, coming from (*R*)-mandelic acid) derivatives. Apart from the fact that these compounds were studied experimentally, phenyl substituents were chosen for their ability to produce significant steric interactions together with a limited conformational space due to their high local symmetry, the driven torsion angles Θ_1 and Θ_2 being changed from 0 to 180°. They exhibit a single potential well. Indeed, for the two triquinphosphoranes, a single conformer was found for each TBP structure. As was the case in the previous series of derivatives, they present only an slightly distorted TBP structure, indicating that the position of the substituents does not affect the skeleton geometry. Triquinphosphorane **24** behaves essentially like its 4,9-isomer **17**: TBP(S_P) is disfavored toward TBP(R_P), although this is to a slightly lesser extent (0.87 *versus* 1.07 kcal/mol; Table 5, entry 6). In a way similar to that for **17**, this should be due to steric repulsion in TBP(S_P) between the diazaphospholidine ring and, in this instance, the pseudoequatorial phenyl substituent. However, such a steric interaction cannot occur with triquinphosphorane **22**, because the phenyl groups are borne by the diazaphospholidine ring itself. The difference between the computed formation enthalpies of the diastereomeric TBP forms should result from steric interactions between the pseudoaxial phenyl group and the adjacent oxazaphospholidine ring ($N_{ax}-O_{eq}$) that disfavor the TBP(R_P). Nevertheless, this effect should be partially counterbalanced by a similar, although weaker, interaction that must exist in the TBP(S_P) between the pseudoequatorial substituent and the ($N_{ax}-O_{eq}$) oxazaphospholidine ring. As a result of such antagonistic effects, the computed energy differ-

(42) These values should be compared with the sum of experimental bond angles around axial and equatorial nitrogen atoms in cyclenphosphorane, which are 348 and 356°, respectively: Lattman, M.; Olmstead, M. M.; Power, P. P.; Rankin, D. W. H.; Robertson, H. E. *Inorg. Chem*. **1988**, *27*, 3012.

(43) Torsion angles changed from −180 to 180° for isopropyl groups and from 0 to 180° for phenyl substituents.

Table 5. Calculated Enthalpies (kcal/mol) and Boltzmann Populations (273 K) of Triquinphosphoranes

			ΔH_f					Boltzmann pop. (%)	
entry no.	molecule	substituent	TBP(S_P)	TBP(R_P)	SP	$\Delta H^{\ddagger}$	ΔH_r[a]	TBP(S_P)	TBP (R_P)
1	**5**		−107.49	−107.49	−102.16	5.33	0	50	50
2	**13**	4,9-Me	−115.84	−116.79	−111.10	4.74	0.95	17	83
3	**15**	4,9-iPr	−134.16[b]	−135.82[b]	−129.39	5.06[b]	1.77	3	97
4	**17**	4,9-Ph	−46.44	−47.51	−41.43	5.01	1.07	14	86
5	**22**	6,7-Ph	−47.05	−46.31			−0.74	78	22
7	**28**	4,9-iPr(BH_3)	−119.07[b]	−111.87[b]			−7.20		

[a] TBP(S_P) − TBP(R_P). [b] Weighted value for the nine conformers.

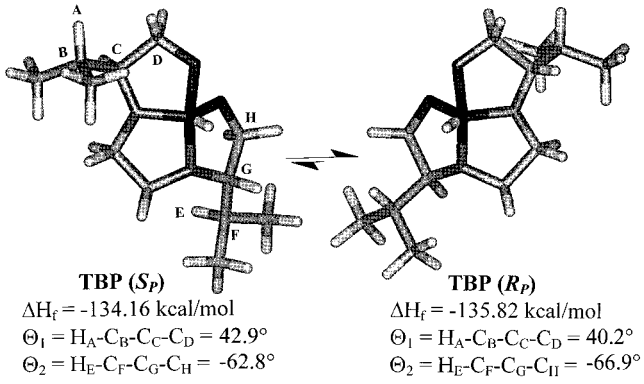


Figure 3. Two conformers of phosphorane **15** in equilibrium *via* epimerization at the phosphorus atom. The characteristic torsion angles of the two isopropyl substituents are indicated. The average calculated enthalpy for the nine conformers of each TBP is indicated.

ence between the diastereomeric TBP structures is lower for **22** than for its isomers **17** and **24** (Table 5, entry 5).

Remarkably, the ground-state species located at the AM1 theoretical level for all the triquinphosphoranes studied exhibit nearly ideal TBP structures, whatever the nature and the position of the substituents. The relative stabilities of two diastereomeric TBP structures are governed by steric factors that allow us to predict the prevalence of one form. The low calculated energy barriers for the pseudorotation process are in perfect qualitative accordance with the experimental ^{31}P dynamic NMR data.

Finally, we computed triquinphosphorane−borane adducts. We envisaged three species resulting from borane addition to the parent triquinphosphorane on either the axial or the equatorial nitrogen atom, in the latter case in either a *syn* or an *anti* position toward the P−H bond (Figure 4). Remarkably, all the structures found are only slightly distorted from the ideal TBP (Table 4). However, as expected from the respective hybridization of the two nitrogen atoms, species **6** bearing borane at the axial sp^3 nitrogen is by far the most stable and lies about 6 kcal/mol below the two other ones, **6′** and **6″**. The changes in hyperconjugation induced by complexation of the borane to the sp^2 equatorial nitrogen atom should account for the lower stabilities of **6′** and **6″**. In fact, the P−N_{eq} bond length increases from 1.61 Å in the free phosphorane **5** to 1.71 Å in the *syn* N_{eq}−BH_3 complex **6′** and becomes higher than the P−N_{ax} length (1.66 Å, Table 4). The sum of bond angles around N_{eq} is 338.4° for species **6′** instead of 360.0° for **5** and 359.4° for **6**, revealing a typical sp^3 hybridization. Conversely, the geometry of the axial nitrogen atom is not affected by complexing BH_3 to N_{eq}, the sum of bond angles around N_{ax} remaining about 346°.

Starting from the *anti* borane complex **6″**, we were unable to locate any stable species resulting from a pseudorotation process. In fact, **6″** would only result from the unlikely complexation of borane at the sp^2 equatorial nitrogen atom of the free phosphorane **5** and should not be experimentally observed. Conversely, the stable N_{ax}−BH_3 complex **6** undergoes a pseudorotation process to yield TBP *syn* **6′** with opposite absolute configuration at the phosphorus center and in which the nitrogen atom bearing borane is in an equatorial position. We located the corresponding transition structure that is depicted in Figure 4. It features a highly distorted SP geometry with H−P−X (X = N, O) bond angles between 98.8 and 110.0° (average value 103.7°). The nitrogen atom bound to the borane unit remains in a sp^3 hybridization (sum of bond angles 343.6°), whereas the second one is still in a sp^2 hybridization (sum of bond angles 358.4°). The activation enthalpy related to this transition state is 9.25 kcal/mol from **6**. This higher pseudorotation barrier compared to the free triquinphosphorane **5** (5.33 kcal/mol; Table 5, entry 1) reveals an enhanced apicophilicity of the nitrogen atom bearing borane. Nevertheless, the activation enthalpy is still low, supporting a fast pseudorotation equilibrium between **6** and **6′**. However, owing to the large difference in stability between these species, the N_{ax}−BH_3 complex **6** must be the only significant form. This result is in accordance with the experimental ^{31}P NMR data, since a single borane adduct was observed in this case (Table 1, entry 1). Despite careful potential energy surface explorations, we were unable to characterize any borane exchange process between the two nitrogen atoms (or dissociation of the borane complexes) during the pseudorotation course. Such a process should have led to the enantiomeric TBP structure with borane at the axial nitrogen atom. Thus, this strongly supports that there is no interconversion pathway between TBP(S_P) and TBP(R_P) borane complexes, in accordance with the dynamic ^{31}P NMR results on diastereomeric complexes **28** (*vide supra*).

To compare the geometry obtained by the AM1 calculations with the available X-ray structure, the adduct **28** of 4,9-diisopropylphosphorane **15** with borane at the axial nitrogen atom was finally studied in the same way as for the free phosphorane. Just as was previously found, nine conformers were located for each TBP. However, TBP(S_P) and TBP(R_P) borane complexes are no longer in equilibrium through a pseudorotation process, as discussed before. Remarkably, the TBP(S_P) complexes are much more stable than the TBP(R_P) ones, the weighted enthalpy difference being 7.20 kcal/mol

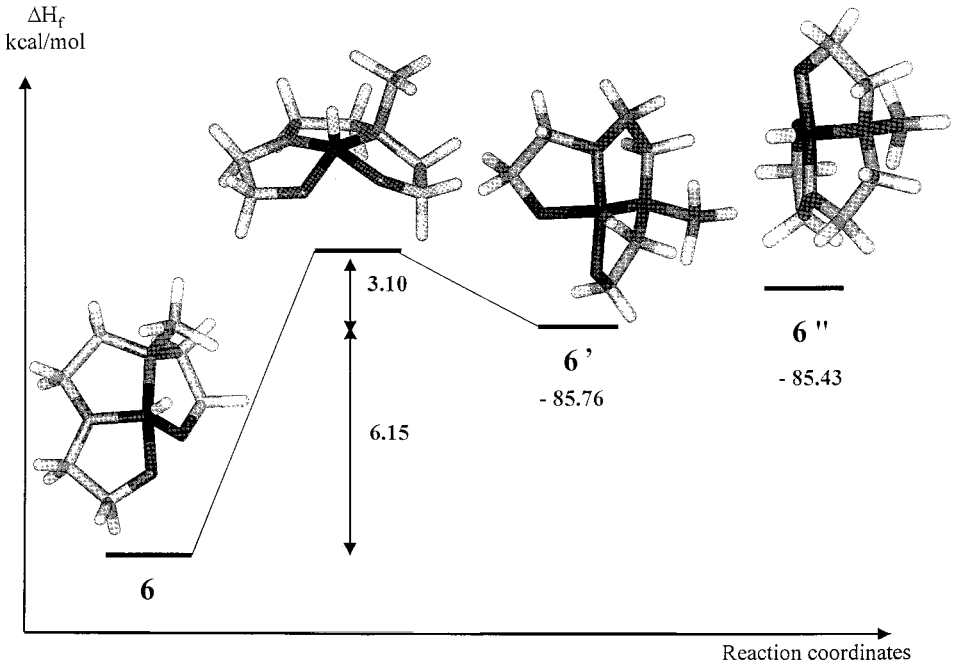


Figure 4. Calculated energy profile for the interconversion of triquinphosphorane−borane complexes **6** (TBP(R_P), N_{ax}−BH_3) and **6′** (TBP(S_P), N_{eq}−BH_3 *syn*) through a distorted PC transition state. The N_{eq}−BH_3 *anti* complex **6″** is also represented.

(Table 5, entry 7), whereas it was the opposite situation in the case of the free phosphorane **15**. This must be due to a large steric repulsion between the borane unit and the pseudoaxial isopropyl substituent, which are in *syn* positions in the TBP(R_P) structures, whereas they are in an *anti* positions in the TBP(S_P) structures, as can be seen in the case of the most stable conformer. Since similar steric interactions must occur during the borane attack on the free triquinphosphorane, the reaction rate of borane addition on TBP(S_P) must be much higher than that on TBP(R_P). Consequently, the experimentally observed diastereoselectivity in favor of TBP(S_P) should result from a kinetically controlled process which obeys the Curtin−Hammett principle:[44] the minor TBP(S_P) of free triquinphosphorane **15** is in fast equilibrium with the major TBP(R_P) and reacts faster than this latter one to afford the major diastereomer **28M** (TBP(S_P)) of the borane complex. This also accounts for the decline of diastereomeric excess at very low temperatures (less than −50 °C). In fact, when the equilibrium between TBP(S_P) and TBP(R_P) becomes much slower, consumption of the faster reacting TBP(S_P) increases the concentration of the slower reacting TBP(R_P) and thus the proportion of the (R_P)-borane adduct **28m**, providing that the relative borane addition rate remains unchanged. Indeed, the product composition is formally related to the relative concentrations of the diastereomeric phosphoranes and the respective rate constant of their reactions with borane.

The AM1 semiempirical calculations succeed in predicting the predominance of the (S_P)-borane complex, whose structure was obtained by X-ray diffraction. However, as might be expected, the gas-phase theoretical conformation of the most stable rotamer is distinct from the conformation experimentally observed in the crystal (Figure 1) that should be imposed by the cell packing. The computed bond lengths and angles around the phosphorus atom of the most stable complex are compared to the experimental values in Table 4. The average difference between them is less than 4%. The most significant discrepancy concerns the unusually long P−N_{ax} bond. Although the calculated value (1.80 Å) lies within the usual range (*vide supra*), it is considerably shorter than the crystallographic length (1.932 Å). This discrepancy should result from the approximations inherent to semiempirical methods and some defects in the parametrization. Concerning the B−N_{ax} bond length, the calculated value (1.62 Å) reproduces exactly the experimental one (1.624 Å).

In summary, AM1 semiempirical calculations allowed us to account for the main experimental data concerning the structure of chiral triquinphosphoranes and their epimerization process as well as for the high diastereoselectivities observed in their additions with borane.[45]

(44) (a) Curtin, D. Y. *Rec. Chem. Prog.* **1954**, *15*, 111. (b) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83. (c) Seeman, J. I. *J. Chem. Educ.* **1986**, *63*, 42.

(45) One of the reviewers of our manuscript kindly offered us his complementary results and valuable comments about the use of the AM1 method in this case: "The question might arise as to whether it would be worthwhile undertaking a more rigorous theoretical study of one or two key members of the large series of compounds studied here, to see whether the AM1 predictions are maintained. (...) I decided to study compounds **5** and **6** at the DZP/SCF level of theory, a combination that is usually very reliable for molecular geometries of main-group compounds. While a less inaccurate value was indeed obtained for the P−N_{ax} bond length (1.82 Å in **5**, 1.88 Å in **6**), the P−O_{ax} bond lengths were disappointingly long (1.75 Å in both **5** and **6**); for this parameter, the AM1 method is more successful. Most strikingly, the DZP/SCF method failed to predict a bonding interaction between BH_3 and N5 in compound **6**. I then turned to DFT, which provides a better description of coordinate bonds of the type present between N5 and BH_3. A bound system was indeed predicted, but the B−N bond is far too long if a DZP basis is used (the so-called "B3LYP" version of SFT was adopted) and the error for the P−O_{ax} bond is scarcely reduced. These disappointing observations show that rather elaborate theoretical methods will be needed to describe these intriguing compounds properly. The use of the semiempirical AM1 approach therefore seems to be particularly appropriate for the present compounds, even if the reasons why it should be more successful than SCF or B3LYP techniques are not immediately apparent."

Conclusion

According to both the experimental and the theoretical studies, triquinphosphoranes deriving from chiral enantiopure diamino diols should exist as two diastereomeric TBP species in rapid equilibrium *via* an SP transition structure. In the former, the axial nitrogen atoms exhibit a marked basicity toward borane, whereas the equatorial ones do not behave as coordination centers. The borane addition seems very sensitive to the steric hindrance at the axial nitrogen site, which differs in each diastereomeric TBP form. Thus, the relative reaction rate governs the diastereoselectivity of the addition. The irreversibility of borane addition together with the hindrance to epimerization of the borane adducts allowed us to isolate for the first time a stable enantiopure hydridophosphorane. This opens the way to the use of chiral triquinphosphoranes in reactions toward other electrophilic reagents to afford derivatives with high diastereomeric excesses.[46]

Experimental Section

General Remarks. All reactions and manipulations were carried out under an atmosphere of purified nitrogen unless otherwise indicated. The solvents were purchased from commercial sources, rigorously dried according to described procedures, and deoxygenated prior to use.[47] Melting points were measured on a Büchi apparatus in glass capillaries and are uncorrected. Elemental analyses were performed by the Service de Microanalyse, Faculté des Sciences et Techniques de St Jérôme, Marseille, France. Optical rotations were obtained on a Perkin-Elmer 241 MC variable-wavelength polarimeter. Infrared (IR) spectra were recorded on a Perkin-Elmer 1700 X IR-FT spectrophotometer as neat films on KBr windows. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 200 and Bruker AMX 400 NMR spectrometers using $SiMe_4$ as an external standard. ^{31}P and ^{11}B NMR spectra were recorded on a Bruker AC 100 spectrometer using 85% aqueous H_3PO_4 and $BH_3{\cdot}SMe_2$ as external standards, respectively. The following abbreviations are used: br = broad, s = singulet, d = doublet, t = triplet, q = quartet, m = multiplet. Chemical shifts (δ) are reported in ppm.

The $BH_3{\cdot}SMe_2$ complex, *N*,*N*′-bis(hydroxyethyl)ethylenediamine, (2*S*,7*S*)-2,7-diethyl-3,6-diazaoctane-1,8-diol (**8**) (in its hydrochloride salt form), and *trans*-cyclohexanediamine were obtained commercially and used without further purification. (1*S*,2*S*)-1,2-Diphenylethylene-1,2-diamine has been prepared by the method proposed by Pikul and Corey.[48] (1*R*,2*R*)-Cyclohexanediamine was obtained according to the method described by Galsbøl et al.[49]

Preparation of Diamino Diols. General Procedure for the Synthesis of (2*S*,7*S*)-Dialkyl-3,6-diazaoctane-1,8-diols *7*−*12*. These ligands were prepared in three steps: (A) methyl esterification of amino acids, (B) condensation of the amino acid methyl esters with oxalyl chloride to give the corresponding diamide diesters (*N*,*N*′-bis(1-alkyl-2-hydroxyethyl)oxalamide), and (C) reduction to give the diamino diols (*N*,*N*′-bis-(1-alkyl-2-hydroxyethyl)ethylenediamine).

A. To a cold solution of 0.5 mol of amino acid in 350 mL of anhydrous MeOH was added dropwise at 0 °C 0.5 mol (59 g) of thionyl chloride. The mixture was stirred for 3 h at room temperature, concentrated, and diluted with diethyl oxide. Solids were filtered, and the filtrate was concentrated. These operations were repeated until no more solids appeared. The hydrochloride salt was then dried over P_2O_5 *in vacuo*.

B. To a cold suspension of 0.5 mol of the methyl ester hydrochloride salt in 800 mL of CH_2Cl_2 were added 0.5 mol (51 g) of triethylamine in 100 mL of CH_2Cl_2, 0.25 mol (32 g) of oxalyl chloride in 100 mL of CH_2Cl_2, and 0.5 mol (51 g) of triethylamine in 100 mL of CH_2Cl_2 at 0−5 °C. The mixture was stirred for 10 h at room temperature and then washed with 0.1 M aqueous hydrochloric acid and with distilled water. The organic layer was dried on $MgSO_4$ and concentrated to give a residue which can be recrystallized in a mixture of ethyl acetate and petroleum spirit. The product was then dried over P_2O_5 *in vacuo*.

C. To 400 mL of anhydrous THF at 0−5 °C were added successively 0.45 mol (17 g) of $AlLiH_4$ and 0.1 mol of the previous diamide diester. The mixture was warmed to room temperature and then refluxed for 10 h with stirring. The resulting suspension was cooled to 0−5 °C, hydrolyzed with 30 mL of 5 N aqueous potassium hydroxide, and stirred at room temperature for 10 h, and the solvent was removed *in vacuo* to give a white powder. This solid was extracted three times with CH_2Cl_2 and the organic layer was dried over Na_2SO_4 and concentrated in vacuo to give analytically pure diamino diol.

(2*S*,7*S*)-2,7-Dimethyl-3,6-diazaoctane-1,8-diol (7). Yield: 80%. $Bp_{0.001}$ = 96 °C. $[\alpha]_D^{20}$ = +38.0 (*c* 0.99, MeOH). Anal. Calcd for $C_8H_{20}N_2O_2$: C, 54.50; H, 11.44; N, 15.89. Found: C, 54.75; H, 11.50; N, 15.60. IR (cm^{-1}): 3600−2800 (OH), 3280, 3290 (NH), 1120, 1090, 1070, 1045 (C−O and C−N). ^{1}H NMR ($CDCl_3$): δ 3.70 (s, 4H, OH + NH), 3.60 (dd, 2H, $^2J_{H-H}$ = 3.90 Hz, $^3J_{H-H}$ = 11.0 Hz, CH_2O), 3.34 (dd, 2H, $^2J_{H-H}$ = 7.62 Hz, $^3J_{H-H}$ = 11.0 Hz, CH_2O), 2.95−2.70 (m, 6H, CH_2N + C*H*N), 1.03 (d, 6H, $^3J_{H-H}$ = 6.48 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 65.7 (*C*H_2O), 54.6 (*C*HN), 46.4 (*C*H_2N), 16.7 (*C*H_3).

(2*S*,7*S*)-2,7-Diethyl-3,6-diazaoctane-1,8-diol (8). Compound **8** was obtained from its commercially available HCl salt. Yield: 87%. Mp: 88 °C. $[\alpha]_D^{20}$ = +36.7 (*c* 1.0, MeOH). Anal. Calcd for $C_{10}H_{24}N_2O_2$: C, 58.82; H, 11.76; N, 13.73. Found: C, 58.81; H, 11.70; N, 13.74. IR (cm^{-1}): 3600−2800 (OH + NH), 1100 (C−O and C−N). ^{1}H NMR ($CDCl_3$): δ 3.64 (dd, 2H, $^3J_{H-H}$ = 3.8 Hz, CH_2O), 3.36 (dd, 2H, $^3J_{H-H}$ = 7.0 Hz, CH_2O), 2.91 (s, 4H, O*H* + N*H*), 2.85−2.40 (m, 6H, CH_2N + C*H*N), 1.4 (dq, 4H, $^3J_{H-H}$ = 6.6 Hz, $^3J_{H-H}$ = 1.8 Hz, CH_2), 0.92 (t, 6H, $^3J_{H-H}$ = 6.6 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 63.4 (*C*H_2O), 60.6 (*C*HN), 46.8 (*C*H_2N), 24.3 (*C*H_2), 10.6 (*C*H_3).

(2*S*,7*S*)-2,7-Diisopropyl-3,6-diazaoctane-1,8-diol (9). Yield: 95%. $Bp_{0.001}$: 175 °C. $[\alpha]_D^{20}$ = +9.4 (*c* 1.0, MeOH). Anal. Calcd for $C_{12}H_{28}N_2O_2$: C, 62.04; H, 12.15; N, 12.06. Found: C, 62.00; H, 11.99; N, 10.86. IR (cm^{-1}): 3600−2800 (OH + NH), 1100 (C−O and C−N). ^{1}H NMR ($CDCl_3$): δ 3.68 (m, 2H, $^2J_{H-H}$ = 10.8 Hz, $^3J_{H-H}$ = 4.13 Hz, CH_2O), 3.38 (m, 2H, $^2J_{H-H}$ = 10.8 Hz, $^3J_{H-H}$ = 7.60 Hz, CH_2O), 3.15 (s, 4H, O*H* + N*H*), 2.79 (m, 4H, CH_2N), 2.40 (m, 2H, C*H*N), 1.73 (m, 2H, C*H*), 0.96 (d, 6H,

(46) When this paper was completed, we knew about the work by Contreras *et al*. (Tlahuextl, M.; Martínez-Martínez, F. J.; Rosales-Hoz, M. J.; Contreras, R. *Phosphorus, Sulfur Silicon Relat. Elem*. **1997**, *123*, 5−19), who obtained an X-ray diffraction structure of the triquinphosphorane derived from *N*,*N*′-bis[(−)-norephedrine]ethylene. In this structure, the phosphorus atom adopts a TBP geometry that agrees remarkably well with our computational results. Moreover, the absolute configuration of the phosphorus atom corresponds to the one predicted in our study for phosphoranes of similar type. The addition of borane on this compound led to a main adduct with the opposite absolute configuration at the phosphorus atom. The authors concluded that this resulted from an attack of BH_3 on the equatorial nitrogen atom followed by epimerization of the phosphorus atom, giving the molecule with the N−BH_3 group in an axial position, whereas we demonstrate here that this reaction proceeds only on the axial nitrogen atom and obeys the Curtin−Hammett principle. Taken together, these data strongly support our own conclusions and validate the results of AM1 calculations on the free triquinphosphoranes.

(47) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. In *Purification of Laboratory Compounds*; 2nd ed.; Pergamon Press: Oxford, U.K., 1980.

(48) Pikul, S.; Corey, E. J. *Synthesis* **1993**, 22−29.

(49) Galsbøl, F.; Steebøl, P.; Sørensen, B. S. *Acta Chem. Scand*. **1972**, *26*, 3605.

$^3J_{H-H}$ = 6.32 Hz, CH_3), 0.90 (d, 6H, $^3J_{H-H}$ = 6.54 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 64.7 (*C*H_2O), 61.7 (*C*HN), 43.7 (*C*H_2N), 29.2 (*C*H), 19.5 and 18.6 (*C*H_3).

(2*S*,7*S*)-2,7-Diisobutyl-3,6-diazaoctane-1,8-diol (10). Yield: 85%. Mp: 37 °C. $[\alpha]_D^{20}$ = +12.7 (*c* 1.0, THF). Anal. Calcd for $C_{14}H_{32}N_2O_2$: C, 64.61; H, 12.31; N, 10.77. Found: C, 64.57; H, 12.28; N, 10.82. IR (cm^{-1}): 3600−2800 (OH + NH), 1100 (C−O and C−N). ^{1}H NMR ($CDCl_3$): δ 3.70−3.25 (m, 8H, CH_2O + O*H* + N*H*), 2.73 (s, 4H, CH_2N), 2.85−2.45 (m, 2H, C*H*N), 1.63 (m, 2H, CH_2C*H*Me_2), 1.27 (m, 4H, CH_2CHMe_2), 0.93 (d, 12H, $^3J_{H-H}$ = 5.4 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 64.5 (*C*H_2O), 58.4 (*C*HN), 47.3 (*C*H_2N), 41.8 (*C*H_2CHMe_2), 26.0 (CH_2*C*HMe_2), 23.4 and 23.2 (*C*H_3).

(2*S*,7*S*)-2,7-Diphenyl-3,6-diazaoctane-1,8-diol (11). Yield: 50%. $Bp_{0.001}$: 200 °C. $[\alpha]_D^{20}$ = −57.6 (*c* 1.0, MeOH). Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 72.00; H, 8.00; N, 9.33. Found: C, 72.09; H, 7.97; N, 9.30. IR (cm^{-1}): 3700−3000 (OH + NH), 1080, 1040 (C−O + C−N). ^{1}H NMR ($CDCl_3$): δ 7.35−7.21 (m, 10H, Ar *H*), 3.76−3.61 (m, 6H, CH_2O + C*H*N), 3.49 (s, 2H, N*H*), 3.43 (s, 2H, O*H*), 2.67−2.52 (m, 4H, CH_2N). ^{13}C NMR ($CDCl_3$): δ 140.4, 128.6, 127.6, 127.3, 126.6 (Ar), 66.8 (*C*H_2O), 64.8 (*C*HN), 46.7 (*C*H_2N).

(2*S*,7*S*)-2,7-Dibenzyl-3,6-diazaoctane-1,8-diol (12). Yield: 61%. Mp: 94 °C. $[\alpha]_D^{20}$ = −8.5 (*c* 1.0, THF). Anal. Calcd for $C_{20}H_{28}N_2O_2$: C, 73.14; H, 8.59; N, 8.53. Found: C, 73.33; H, 8.52; N, 8.40. IR (cm^{-1}): 3500−2800 (OH), 3290 and 3275 (NH), 1100, 1050, 1040 (C−O + C−N). ^{1}H NMR (CD_2Cl_2): δ 7.30−7.10 (m, 10H, Ar *H*), 3.54 (m, 2H, $^2J_{H-H}$ = 11.1 Hz, $^3J_{H-H}$ = 3.48 Hz, CH_2O), 3.29 (m, 2H, $^2J_{H-H}$ = 11.1 Hz, $^3J_{H-H}$ = 5.63 Hz, CH_2O), 2.83 (m, 2H, C*H*N), 2.70 (s, 4H, CH_2N), 2.64 (d, 4H, $^3J_{H-H}$ = 2.51 Hz, CH_2), 2.40−2.20 (m, 4H, O*H* + N*H*). ^{13}C NMR (CD_2Cl_2): δ 139.3, 129.6, 128.8, 126.6 (Ar), 63.4 (*C*H_2O), 60.9 (*C*HN), 47.1 (*C*H_2N), 38.4 (*C*H_2).

General Procedure for the Synthesis of 4,5-Dialkyl-3,6-diazaoctane-1,8-diols. To a cold solution of 0.02 mol (2.73 g) of ethyloxalyl chloride in 5 mL of methylene chloride were added dropwise 0.01 mol of 1,2-dialkyl-1,2-diamine and 0.02 mol (2.24 g) of DABCO in 5 mL of methylene chloride. The mixture was stirred at room temperature for 20 h and filtered. The solids were dissolved in water, and the solution was extracted three times with methylene chloride. The combined organic extracts were dried over anhydrous sodium sulfate, and the solvent was removed to give white crystals. Successively, 0.04 mol (1.52 g) of $AlLiH_4$ and 0.01 mol of the diamide diester previously obtained were added to 50 mL of THF at 0−5 °C. The mixture was refluxed for 20 h, cooled to room temperature, and hydrolyzed with 5 mL of 5 N aqueous potassium hydroxide. The lithium and aluminum hydroxides were filtered off and extracted three times with methylene chloride. The combined organic extracts were dried over anhydrous sodium sulfate and filtered, and the solvent was removed *in vacuo* to give a ^{1}H NMR spectroscopically pure white solid that was recrystallized from toluene.

***N*,*N*′-(Bis(hydroxyethyl)ethylene)-(1*R*,2*R*)-1,2-cyclohexyl-1,2-diamine (19).** Yield: 75%. $Bp_{2\times10^{-6}}$: 50 °C. $[\alpha]_D^{20}$ = −91.3 (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{10}H_{22}N_2O_2$: C, 59.41; H, 10.89; N, 13.86. Found: C, 59.46; H, 10.81; N, 13.79. IR (cm^{-1}): 3400−3250 (NH + OH), 1100 and 1060 (C−O + C−N). ^{1}H NMR ($CDCl_3$): δ 3.69−3.57 (m, 4H, CH_2O), 3.25 (s, 4H, *H*N overlapping with *H*O), 2.94−2.57 (m, 4H, CH_2N), 2.23−2.19 (m, 2H, C*H*N), 2.09−2.03 (m, 4H, CH_2−CHN), 1.74−1.69 (m, 4H, CH_2−CH_2). ^{13}C NMR ($CDCl_3$): δ 61.5 (*C*HN), 61.4 (*C*H_2O), 48.6 (*C*H_2N), 32.0 (*C*H_2−CHN), 25.2 (*C*H_2−CH_2).

***N*,*N*′-(Bis(hydroxyethyl)ethylene)-(1*S*,2*S*)-1,2-diphenyl-1,2-diamine (20).** Yield: 75%. Mp: 77 °C. $[\alpha]_D^{20}$ = −23.3 (*c* 0.7, CH_2Cl_2). Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.05; N, 9.33. Found: C, 71.93; H, 8.11; N, 9.26. IR (cm^{-1}): 3360−3020 (NH + OH), 1140, 1100, 1070 (C−O + C−N). ^{1}H NMR (CD_3OD): δ 7.21−7.05 (m, 10H, Ar *H*), 4.93 (s, 4H, *H*N overlapping with *H*O), 3.71 (s, 2H, C*H*N), 3.61 (t, 4H, $^3J_{H-H}$ = 4.9 Hz, CH_2O), 2.56 (t, 4H, $^3J_{H-H}$ = 5.3 Hz, CH_2N). ^{13}C NMR (CD_3OD): δ 142.0, 129.3, 129.0, 128.0 (Ar), 70.1 (*C*HN), 62.1 (*C*H_2O), 50.3 (*C*H_2N).

Synthesis of (1*R*,8*R*)-1,8-diphenyl-3,6-diazaoctane-1,8-diol (23). A.[50] ***(R)*-Acetoxymandelic Acid.** To hot (100 °C) acetic acid (25 mL) was added 0.05 equiv (0.90 g) of zinc dichloride and 0.13 mol (20.0 g) of D-mandelic acid. The solution was stirred for 1 h at 100 °C and poured into ice-cold water (250 mL). After $^1/_2$ h, the solids were filtered off and washed several times with cold water until neutral. The solid was recrystallized from water/ethyl alcohol to give colorless needles. Yield: 73%. Mp: 40 °C. $[\alpha]_D^{20}$ −90.8° (*c* 1,0; CH_2Cl_2). IR cm^{-1}: 3500−2800 (OH), 1720 (CO). ^{1}H NMR ($CDCl_3$): δ 8.75 (s, 1H, COO*H*); 7.61−7.33 (m, 5H, Ar *H*); 5.93 (s, 1H, C*H*); 2.19 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 172.4 (*C*═O); 170.6 (CH_3*C*═O); 133.2, 129.5, 128.9, 127.7 (Ar); 74.2 (Ar*C*HO); 20,7 (*C*H_3).

B. **(*R*)-α-Acetoxybenzeneacetyl Chloride.** To a cold solution of 5.2 mmol (1.00 g) of acetylmandelic acid in 15 mL of methylene chloride was added dropwise 1.1 equiv (0.68 g) of thionyl chloride. After the mixture was refluxed for 2 h, the solvent was removed and the yellowish oil was distilled under reduced pressure. Yield: 95%. $bp_{7\times10^{-3}}$: 80 °C. $[\alpha]_D^{20}$ −173.6 °C (*c* 1.2, CH_2Cl_2). IR (cm^{-1}): 1795 and 1750 (CO), 1220 (C−O). ^{1}H NMR ($CDCl_3$): δ 7.61−7.33 (m, 5H, Ar); 5.93 (s, 1H, C*H*−O); 2.19 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.6 (CH_3*C*═O); 169.8 (Cl*C*═O); 130.7, 130.1, 129.1, 128.3 (Ar); 80.7 (*C*H−O); 20.2 (*C*H_3).

C. **1,8-Diacetoxy-(1*R*,8*R*)-1,8-diphenyl-3,6-diazaoctane-2,7-dione.** To a cold solution (0−5 °C) of 1.31×10^{-2} mol (0.79 g) of freshly distilled ethylenediamine, 1.5 equiv (2.00 g) of triethylamine, and 10% (0.16 g) of DMAP in 25 mL of THF was added dropwise a solution of the previously synthesized acyl chloride (2.2 equiv, 6.13 g) in 25 mL of THF. The mixture was stirred for 2 h at room temperature. The precipitate that appeared was filtered off, and the organic layer was washed successively with 10% aqueous HCl, 10% aqueous $NaHCO_3$, and brine. The combined extracts were dried over $MgSO_4$ and concentrated to give a white solid that was recrystallized from toluene. Yield: 69%. Mp: 157 °C. $[\alpha]_D^{20}$ = −119.0° (*c* 1.0; CH_2Cl_2). IR (cm^{-1}): 3300 and 3050 (NH), 1795 and 1750 (CO). ^{1}H NMR ($CDCl_3$): δ 7.40−7.31 (m, 12H, N*H* + Ar); 5.98 (s, 2H, Ar C*H*); 3.31 (m, 4H, NCH_2); 2.16 (s, 6H, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.6 (NH*C*═O); 169.7 (O*C*(O)CH_3); 135.5, 128.9, 128.7, 127.4 (Ar), 75.4 (*C*HO), 39.7 (N*C*H_2); 20.9 (*C*H_3).

D. To a cold suspension of $AlLiH_4$ (3.13 mmol, 0.12 g) in THF (30 mL) was added 6.25 mmol of the previously prepared diamide diester. The mixture was stirred for 12 h at room temperature and then for 4 h at solvent reflux. The mixture was cooled to 0−5 °C and hydrolyzed with 3 mL of 30% aqueous KOH. The lithium and aluminum hydroxides were filtered off and extracted three times with CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated *in vacuo* to give a yellow oil. After recrystallization from toluene, the white solid was dried over P_2O_5 *in vacuo*. Yield: 72%. Mp: 115 °C. $[\alpha]_D^{20}$ = −72.0 (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 71.97; H, 8.05; N, 9.33. Found: C, 72.04; H, 8.09; N, 9.31. IR (cm^{-1}): 3320 (OH), 3090−3050 (NH), 1130, 1070 (C−O + C−N), 760−710 (Ar). ^{1}H NMR ($CDCl_3$): δ 7.36−7.18 (m, 10H, Ar *H*), 4.75 (t, 2H, $^3J_{H-H}$ = 6.29 Hz, C*H*O), 4.39 (s, 4H, *H*N overlapping with *H*O), 2.80−2.76 (m, 4H, C*H*N + CH_2N). ^{13}C NMR ($CDCl_3$): δ 142.5, 128.1, 127.3, 125.5 (Ar), 71.8 (*C*HO), 56.6 (*C*H_2N), 48.0 (*C*H_2N).

General Procedure for the Synthesis of Triquinphosphoranes. To a solution of 0.01 mol (1.63 g) of tris(dimethylamino)phosphine in 20 mL of toluene was added 0.01 mol of diamino diol in 20 mL of toluene. The mixture was refluxed for 30 min and cooled to room temperature. The solvent was

(50) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. Vogel's *Textbook of Practical Organic Chemistry*, 5th ed.; Longman Scientific & Technical and Wiley: New York, 1989; p 644.

then removed *in vacuo* and the crude product distilled under reduced pressure.

2,11-Dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (5). Yield: 80%. $bp_{0.05:}$ 75 °C. Anal. Calcd for $C_6H_{13}N_2O_2P$: C, 40.91; H, 7.43; N, 15.90. Found: C, 40.98; H, 7.39; N, 15.92. IR (cm^{-1}): 2350 (PH). ^{1}H NMR (C_6D_6): δ 7.10 (d, 1H, $^1J_{P-H}$ = 721 Hz, P*H*), 3.76−3.52 (m, 4H, CH_2O), 3.03−2.44 (m, 8H, CH_2N). ^{13}C NMR (C_6D_6): δ 59.1 (*C*H_2O), 44.9 (d, $^2J_{P-C}$ = 13.0 Hz, *C*H_2N), 43.4 (d, $^2J_{P-C}$ = 9.7 Hz, *C*H_2N). ^{31}P NMR (C_6D_6): δ −37.3 ($^1J_{P-H}$ = 721 Hz).

(4*S*,9*S*)-4,9-Dimethyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (13). Yield: 82%. $bp_{0.05}$: 80 °C. $[\alpha]_D^{20}$ = +94.0 (*c* 1.2, toluene). IR (cm^{-1}): 2360 (PH). ^{1}H NMR (C_6D_6): δ 7.29 (d, 1H, $^1J_{P-H}$ = 708 Hz, P*H*), 3.97−3.78 (m, 2H, CH_2O), 3.48−3.27 (m, 2H, CH_2O), 3.07−2.40 (m, 6H, CH_2N + C*H*N), 0.91 (d, 3H, $^3J_{H-H}$ = 0.67 Hz, CH_3), 0.88 (d, 3H, $^3J_{H-H}$ = 0.85 Hz, CH_3). ^{13}C NMR (C_6D_6): δ 67.0 (*C*H_2O), 65.7 (*C*H_2O), 51.7 (d, $^2J_{P-C}$ = 7.70 Hz, *C*HN), 48.7 (d, $^2J_{P-C}$ = 6.00 Hz, *C*HN), 42.7 (d, $^2J_{P-C}$ = 5.50 Hz, *C*H_2N), 38.6 (d, $^2J_{P-C}$ = 19.0 Hz, *C*H_2N), 19.2 (d, $^3J_{P-C}$ = 10.3 Hz, *C*H_3), 17.8 (d, $^3J_{P-C}$ = 5.00 Hz, *C*H_3). ^{31}P NMR (C_6D_6): δ −37.1 ($^1J_{P-H}$ = 711 Hz).

(4*S*,9*S*)-4,9-Diethyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (14). Yield: 90%. $Bp_{8\times10^{-3:}}$ 90 °C. $[\alpha]_D^{20}$ = +66.6 (*c* 1.0, toluene). Anal. Calcd for $C_{10}H_{21}N_2O_2P$: C, 51.72; H, 10.78; N, 12.07. Found: C, 51.69; H, 10.94; N, 12.13. IR (cm^{-1}): 2356 (PH). ^{1}H NMR (C_6D_6): δ 7.11 (d, 1H, $^1J_{P-H}$ = 707 Hz, P*H*), 3.94−3.68 (m, 1H, CH_2O), 3.78 (dd, 1H, $^3J_{P-H}$ = 1.95 Hz, $^3J_{H-H}$ = 6.40 Hz, C*H*N), 3.43−3.28 (m, 2H, CH_2O), 3.34 (dd, 1H, $^2J_{P-H}$ = 1.23 Hz, $^3J_{H-H}$ = 8.76 Hz, C*H*N), 3.20−2.88 (m, 1H, CH_2O), 2.84−2.42 (m, 4H, CH_2N), 1.55−1.32 (m, 2H, CH_2), 1.29−1.06 (m, 2H, CH_2), 0.70 (t, 3H, $^3J_{H-H}$ = 7.34 Hz, CH_3), 0.69 (t, 3H, $^3J_{H-H}$ = 7.46 Hz, CH_3). ^{13}C NMR (C_6D_6): δ 64.6 (*C*H_2O), 63.2 (*C*H_2O), 57.2 (d, $^2J_{P-C}$ = 7.62 Hz, *C*HN), 53.5 (d, $^2J_{P-C}$ = 16.0 Hz, *C*HN), 43.7 (d, $^2J_{P-C}$ = 5.93 Hz, *C*H_2N), 39.0 (d, $^2J_{P-C}$ = 17.2 Hz, *C*H_2N), 27.2 (d, $^3J_{P-C}$ = 8.74 Hz, *C*H_2), 24.8 (d, $^3J_{P-C}$ = 5.65 Hz, *C*H_2), 9.3 (*C*H_3). ^{31}P (C_6D_6): δ - 36.3 ($^1J_{P-H}$ = 704 Hz).

(4*S*,9*S*)-4,9-Diisopropyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (15). Yield: 85%. $Bp_{0.05}$: 110 °C. $[\alpha]_D^{20}$ = +28.6 (*c* 1.1, toluene). Anal. Calcd for $C_{12}H_{25}N_2O_2P$: C, 50.85; H, 10.59; N, 11.28. Found: C, 50.79; H, 10.51; N, 11.35. IR (cm^{-1}): 2340 (PH). ^{1}H NMR (C_6D_6): δ 7.10 (d, 1H, $^1J_{P-H}$ = 712 Hz, P*H*), 3.84−3.42 (m, 4H, CH_2O), 3.07−2.84 (m, 1H, C*H*N), 2.69−2.48 (m, 5H, C*H*N + CH_2N), 1.70−1.48 (m, 2H, C*H*), 0.80−0.70 (m, 12H, CH_3). ^{13}C NMR (C_6D_6): δ 61.8 (d, $^2J_{P-C}$ = 8.42 Hz, *C*HN), 60.7 (*C*H_2O), 59.6 (d, $^2J_{P-C}$ = 2.13 Hz, *C*H_2O), 57.3 (d, $^2J_{P-C}$ = 14.86 Hz, *C*HN), 44.9 (d, $^2J_{P-C}$ = 5.88 Hz, *C*H_2N), 39.3 (d, $^2J_{P-C}$ = 14.0 Hz, *C*H_2N), 31.2 (d, $^3J_{P-C}$ = 7.01 Hz, *C*H), 28.3 (d, $^3J_{P-C}$ = 4.59 Hz, *C*H), 19.1, 18.3, 17.1, 16.3 (*C*H_3). ^{31}P NMR (C_6D_6): δ −35.2 ($^1J_{P-H}$ = 712 Hz).

(4*S*,9*S*)-4,9-Diisobutyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (16). Yield: 85%. $bp_{0.015}$: 140 °C. $[\alpha]_D^{20}$ = +46.1 (*c* 1.3, toluene). Anal. Calcd for $C_{14}H_{29}N_2O_2P$: C, 58.25; H, 10.06; N, 9.71. Found: C, 58.32; H, 10.01; N, 9.64. IR (cm^{-1}): 2365 (PH). ^{1}H NMR (C_6D_6): δ 7.17 (d, 1H, $^1J_{P-H}$ = 710 Hz, P*H*), 3.96−3.71 (m, 2H, CH_2O), 3.54−3.31 (m, 2H, CH_2O), 3.14−2.87 (m, 2H, C*H*N), 2.85−2.42 (m, 4H, CH_2N), 1.52−1.29 (m, 4H, CH_2), 1.17−1.03 (m, 2H, C*H*), 0.78−0.73 (m, 12H, CH_3). ^{13}C NMR (C_6D_6): δ 65.2 (*C*H_2O), 64.0 (*C*H_2O), 54.7 (d, $^2J_{P-C}$ = 8.60 Hz, *C*HN), 51.0 (d, $^2J_{P-C}$ = 15.86 Hz, *C*HN), 44.0 (d, $^2J_{P-C}$ = 11.3 Hz, *C*H_2N), 43.9 (d, $^3J_{P-C}$ = 10.2 Hz, *C*H_2), 41.3 (d, $^2J_{P-C}$ = 5.80 Hz, *C*H_2N), 39.2 (d, $^3J_{P-C}$ = 14.59 Hz, *C*H_2), 25.2 and 24.9 (*C*H), 23.7, 23.6, 22.7, 22.5 (*C*H_3). ^{31}P NMR (C_6D_6): δ −36.9 ($^1J_{P-H}$ = 710 Hz).

(4*S*,9*S*)-4,9-Diphenyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (17). Yield: 87%. Mp: 146 °C. $[\alpha]_D^{20}$ = −235.3 (*c* 0.7, CH_2Cl_2). Anal. Calcd for $C_{18}H_{21}N_2O_2P$: C, 65.85; H, 6.39; N, 8.53. Found: C, 65.80; H, 6.80; N, 8.50. IR (cm^{-1}): 2365 (PH). ^{1}H NMR (C_6D_6): δ 7.50 (d, 1H, $^1J_{P-H}$ = 717 Hz, P*H*), 7.32−7.22 (m, 10H, Ar *H*), 4.22−4.02 (m, 2H, CH_2O + C*H*N), 3.97−3.78 (m, 3H, CH_2O + C*H*N), 3.69−3.58 (m, 1H, CH_2O), 2.98−2.48 (m, 4H, CH_2N). ^{13}C NMR (C_6D_6): δ 128.9, 128.7, 127.9, 127.7, 127.3, 127.2 (Ar), 68.2 (*C*H_2O), 66.6 (*C*H_2O), 62.4 (d, $^2J_{P-C}$ = 8.37 Hz, *C*HN), 57.7 (d, $^2J_{P-C}$ = 18.4 Hz, *C*HN), 43.0 (d, $^2J_{P-C}$ = 5.73 Hz, *C*H_2N), 39.0 (d, $^2J_{P-C}$ = 21.3 Hz, *C*H_2N). ^{31}P NMR (C_6D_6): δ −37.4 ($^1J_{P-H}$ = 710 Hz).

(4*S*,9*S*)-4,9-Dibenzyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (18). Yield: 61%. Mp: 94 °C. $[\alpha]_D^{20}$ = +49.5 (*c* 1.0, toluene). Anal. Calcd for $C_{20}H_{25}N_2O_2P$: C, 67.40; H, 7.07; N, 7.86. Found: C, 67.36; H, 7.15; N, 7.90. IR (cm^{-1}): 2430 (PH). ^{1}H NMR (C_6D_6): δ 7.21 (d, 1H, $^1J_{P-H}$ = 722 Hz, P*H*), 7.20−6.90 (m, 10H, Ar *H*), 3.85−3.35 (m, 4H, CH_2O), 3.10−2.14 (m, 10H, CH_2N + C*H*N + CH_2). ^{13}C NMR (C_6D_6): δ 138.8, 129.5, 126.5 (Ar), 64.9 (*C*H_2O), 63.1 (*C*H_2O), 58.7 (d, $^2J_{P-C}$ = 9.13 Hz, *C*HN), 54.2 (d, $^2J_{P-C}$ = 16.4 Hz, *C*HN), 44.3 (d, $^2J_{P-C}$ = 4.78 Hz, *C*H_2N), 41.7 (d, $^2J_{P-C}$ = 8.42 Hz, *C*H_2N), 39.8 (*C*H_2), 39.3 (*C*H_2). ^{31}P NMR (C_6D_6): δ −36.3 ($^1J_{P-H}$ = 723 Hz).

(6*R*,7*R*)-6,7-Cyclohexyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (21). Yield: 72%. $[\alpha]_D^{20}$ = −66.8 (*c* 1.7, CH_2Cl_2). Anal. Calcd for $C_{10}H_{19}N_2O_2P$: C, 52.12; H, 8.25; N, 12.16. Found: C, 52.17; H, 8.20; N, 12.21. IR (cm^{-1}): 2360 (PH). ^{1}H NMR (C_6D_6): δ 7.15 (d, 1H, $^1J_{P-H}$ = 716 Hz, P*H*), 3.85−3.76 (m, 2H, C*H*N), 3.61−3.49 (m, 4H, CH_2O), 2.90−2.56 (m, 4H, CH_2N), 1.76−1.62 (br, 4H, CH_2CHN), 1.35−1.10 (br, 4H, CH_2CH$_2$). ^{13}C NMR (C_6D_6): δ 61.5 (*C*H_2O), 59.1 (d, $^2J_{P-C}$ = 7.19 Hz, *C*HN), 58.7 (*C*HN), 58.5 (*C*H_2O), 42.6 (d, $^2J_{P-C}$ = 9.42 Hz, *C*H_2N), 40.6 (d, $^2J_{P-C}$ = 16.3 Hz, *C*H_2N), 30.6 (d, $^3J_{P-C}$ = 11.7 Hz, *C*H$_2$CHN), 29.9 (d, $^3J_{P-C}$ = 7.49 Hz, *C*H$_2$CHN), 24.8 (*C*H$_2$CH$_2$). ^{31}P NMR (C_6D_6): δ −34.5 ($^1J_{P-H}$ = 719 Hz).

(6*S*,7*S*)-6,7-Diphenyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (22). Yield: 82%. Mp: 146 °C. $[\alpha]_D^{20}$ = −1.7 (*c* 1.8, CH_2Cl_2). Anal. Calcd for $C_{18}H_{21}N_2O_2P$: C, 65.85; H, 6.39; N, 8.53. Found: C, 65.45; H, 6.80; N, 8.48. ^{1}H NMR (C_6D_6): δ 7.49 (d, 1H, $^1J_{P-H}$ = 711 Hz, P*H*); 7.23−7.08 (m, 10H, Ar *H*); 3.96−3.52 (m, 6H, CH_2O overlapping with C*H*N); 2.95−2.33 (m, 4H, CH_2N). ^{13}C NMR (C_6D_6): δ 142.3 (d, $^3J_{P-C}$ = 10.8 Hz); 139.9 (d, $^3J_{P-C}$ = 6.6 Hz); 128.6, 128.3, 127.9, 127.6 (Ar); 70.3 (*C*HN); 66.4 (d, $^2J_{P-C}$ = 13.0 Hz, *C*HN); 59.4 (d, $^2J_{P-C}$ = 6.1 Hz, *C*H$_2$O); 57.9 (*C*H$_2$O); 44.6 (d, $^2J_{P-C}$ = 10.3 Hz, *C*H$_2$N); 41.4 (d, $^2J_{P-C}$ = 18.7 Hz, *C*H$_2$N). ^{31}P NMR (C_6D_6): δ −37.8 ($^1J_{P-H}$ = 716 Hz).

(3*R*,10*R*)-3,10-Diphenyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (24). Yield: 98%. $Bp_{7.5\times10^{-3:}}$ 200 °C. $[\alpha]_D^{20}$ = −43.4 (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{18}H_{21}N_2O_2P$: C, 65.85; H, 6.39; N, 8.53. Found: C, 65.70; H, 6.57; N, 8.60. ^{1}H NMR (C_6D_6): δ 7.27−6.99 (m, 10H, Ar *H*); 6.69 (d, 1H, $^1J_{P-H}$ = 700 Hz, P*H*); 5.73 (dt, 1H, $^4J_{H-H}$ = 2.36 Hz, $^3J_{H-H}$ = 8.76 Hz, C*H*O); 5.47 (dt, 1H, $^4J_{H-H}$ = 1.93 Hz, $^3J_{H-H}$ = 10.0 Hz, C*H*O); 3.36−2.35 (m, 8H, CH_2N). ^{13}C NMR (C_6D_6): δ 139.6 (d, $^2J_{P-C}$ = 8.80 Hz); 137.8, 129.3, 128.8, 128.7, 128.5, 128.2, 126.6, 126.4, 126.1, 126.0, 125.8, 125.6 (Ar); 79.7 (d, $^2J_{P-C}$ = 7.35 Hz, *C*HO); 76.6 (d, $^2J_{P-C}$ = 8.25 Hz, *C*HO); 56.8 (d, $^2J_{P-C}$ = 4.28 Hz, *C*H$_2$N); 55.6 (d, $^2J_{P-C}$ = 4.36 Hz, *C*H$_2$N); 48.4 (*C*H$_2$N); 46.3 (*C*H$_2$N). ^{31}P NMR (C_6D_6): δ −38.1 ($^1J_{P-H}$ = 727 Hz).

General Procedure for the Preparation of Triquinphosphorane−Borane Adducts. To a solution of 0.01 mol of triquinphosphorane in 40 mL of toluene was added at room temperature 0.01 mol (0.76 g) of BH_3·SMe_2 complex. The solution was stirred for 20 min, and the solvent was removed under reduced pressure to give the crude product, which can be recrystallized from diethyl ether. The following data concern the major diastereomer. No elemental analyses are reported for the adducts because they decompose upon analysis, leading to erroneous values (including for the pure crystallized compounds **28**).

2,11-Dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]-undecane−BH_3 (6). Yield: 90%. Mp: 110 °C. ^{1}H NMR (C_6D_6): δ 7.34 (d, 1H, $^1J_{P-H}$ = 820 Hz, P*H*), 4.20−4.10 (m, 4H, CH_2O), 4.02−3.92 (m, 2H, CH_2O), 3.31−3.02 (m, 6H, CH_2N), 2.92−2.84 (m, 2H, CH_2N). ^{13}C NMR (C_6D_6): δ 61.3 (d, $^2J_{P-C}$ = 4.03 Hz, *C*H$_2$O), 58.6 (d, $^2J_{P-C}$ = 2.91 Hz, *C*H$_2$O), 51.9 (d, $^2J_{P-C}$ =

10.0 Hz, *C*H_2N), 50.7 (d, $^2J_{P-C}$ = 6.58 Hz, *C*H_2N), 44.1 (d, $^2J_{P-C}$ = 17.5 Hz, *C*H_2N), 40.0 (d, $^2J_{P-C}$ = 11.8 Hz, *C*H_2N). ^{31}P NMR (C_6D_6): δ −24.5 ($^1J_{P-H}$ = 820 Hz). ^{11}B NMR (C_6D_6): δ −15.6 ($^1J_{B-H}$ = 93 Hz).

(4*S*,9*S*)-4,9-Dimethyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane−BH_3 (26). Yield: 90%. De: 54%. ^{13}C NMR (C_6D_6): δ 64.6 (*C*H_2O), 64.3 (*C*H_2O), 55.9 (d, $^2J_{P-C}$ = 11.6 Hz, *C*HN), 49.4 (d, $^2J_{P-C}$ = 16.9 Hz, *C*HN), 41.8 (d, $^2J_{P-C}$ = 5.70 Hz, *C*H_2N), 38.1 (d, $^2J_{P-C}$ = 9.80 Hz, *C*H_2N), 16.8 (d, $^3J_{P-C}$ = 2.40 Hz, *C*H_3), 9.4 (d, $^3J_{P-C}$ = 3.70 Hz, *C*H_3). ^{31}P NMR (C_6D_6): δ M −24.1, m −19.0.

(4*S*,9*S*)-4,9-Diethyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane−BH_3 (27). Yield: 88%. Mp: 119 °C. De: 63%. ^{1}H NMR ($CDCl_3$): δ 6.90 (d, 1H, $^1J_{P-H}$ = 817 Hz, P*H*), 4.20−3.94 (m, 2H, CH_2O + C*H*N), 3.76−3.46 (m, 3H, CH_2O + C*H*N + CH_2O), 3.26−3.11 (m, 1H, CH_2O), 2.99−2.11 (m, 4H, CH_2N), 1.88−1.10 (m, 4H, CH_2), 0.92 (t, 6H, $^3J_{H-H}$ = 7.59 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 64.8 (*C*H_2O), 63.0 (*C*H_2O), 62.7 (d, $^2J_{P-C}$ = 10.2 Hz, *C*HN), 55.8 (d, $^2J_{P-C}$ = 15.5 Hz, *C*HN), 43.5 (d, $^2J_{P-C}$ = 5.83 Hz, *C*H_2N), 39.9 (d, $^2J_{P-C}$ = 10.0 Hz, *C*H_2N), 25.0 (d, $^3J_{P-C}$ = 2.16 Hz, *C*H_2), 19.5 (d, $^3J_{P-C}$ = 3.67 Hz, *C*H_2), 10.7 (*C*H_3), 8.6 (*C*H_3). ^{31}P NMR ($CDCl_3$): δ M −21.8 ($^1J_{P-H}$ = 817 Hz), m −15.8. ^{11}B NMR ($CDCl_3$): δ −16.3.

(4*S*,9*S*)-4,9-Diisopropyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane−BH_3 (28). Yield: 84%. Mp: 196 °C. De: 90%. ^{1}H NMR (C_6D_6): δ 6.84 (d, 1H, $^1J_{P-H}$ = 825 Hz, P*H*); 4.05−3.68 (m, 4H, CH_2O); 3.57−3.49 (m, 1H, C*H*N); 3.15−2.87 (m, 4H, CH_2N); 2.66−2.59 (m, 1H, C*H*N); 2.20−2.10 (m, 1H, C*H*);, 2.01−1.93 (m, 1H, C*H*); 1.21 (d, 3H, $^3J_{H-H}$ = 6.86 Hz, CH_3); 0.95 (t, 3H, $^3J_{H-H}$ = 6.88 Hz, CH_3); 0.88 (d, 3H, $^3J_{H-H}$ = 6.61 Hz, CH_3); 0.87 (t, 3H, $^3J_{H-H}$ = 6.55 Hz, CH_3); 1.80−0.80 (m, 3H, BH_3). ^{13}C NMR (C_6D_6): δ 66.4 (d, $^2J_{P-C}$ = 10.4 Hz, *C*HN); 62.9 (*C*H_2O); 59.7 (d, $^2J_{P-C}$ = 14.4 Hz, *C*HN); 59,6 (d, $^2J_{P-C}$ = 2.54 Hz, *C*H_2O); 43.9 (d, $^2J_{P-C}$ = 5.61 Hz, *C*H_2N); 40.5 (d, $^2J_{P-C}$ = 9.57 Hz, *C*H_2N); 29.5 (d, $^3J_{P-C}$ = 2.01 Hz, *C*H); 26.5 (d, $^3J_{P-C}$ = 4.52 Hz, *C*H); 22.8, 19.1, 18.0, 15.9 (*C*H_3). ^{31}P NMR (C_6D_6): δ M −20.2 ($^1J_{P-H}$ = 826 Hz), m −12.2 ($^1J_{P-H}$ = 828 Hz). ^{11}B NMR (C_6D_6): δ −15.5.

White parallelepiped crystals were obtained by slow evaporation from diethyl ether from a 95/5 **28**M/**28**m mixture. A suitable fragment was cut into a crystalline block (0.12 × 0.18 × 0.47 mm) and was used for the data collection. Crystals are monoclinic and belong to the space group $P2_1$. The unit cell parameters given in Table 2 have been refined by least squares from angular positions of 50 reflections. The intensities of 2778 reflections were collected with a Huber four-circle diffractometer. The structure was solved by direct methods (SHELX86).[51] Fourier synthesis allowed the location of hydrogen atoms. Anisotropic least-squares refinement (SHELX76)[52] was made on 2531 reflections to reach R_w and R values of 0.03.

(4*S*,9*S*)-4,9-Diisobutyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane−BH_3 (29). Yield: 77%. Mp: >250 °C. De: 86%. ^{1}H NMR (C_6D_6): δ 6.87 (d, 1H, $^1J_{P-H}$ = 814.3 Hz, P*H*); 4.94−4.18 (m, 3H, CH_2O + C*H*N); 3.74−3.40 (m, 3H, CH_2O + C*H*N); 2.92−2.41 (m, 4H, CH_2N); 1.70−1.10 (m, 6H, CH_2 + C*H*); 0.96−0.88 (m, 12H, CH_3); 1.80−0.80 (m, 3H, BH_3). ^{13}C NMR (C_6D_6): δ 64.9 (*C*H_2O); 63.7 (*C*H_2O); 59.5 (d, $^2J_{P-C}$ = 10.53 Hz, *C*HN); 53.3 (d, $^2J_{P-C}$ = 9.20 Hz, *C*HN),; 43.3 (d, $^2J_{P-C}$ = 5.21 Hz, *C*H_2N); 41.0 (d, $^3J_{P-C}$ = 2.52 Hz, *C*H_2N); 39.8 (d, $^2J_{P-C}$ = 9.21 Hz, *C*H_2N); 35.0 (d, $^3J_{P-C}$ = 3.10 Hz, *C*H_2); 25.1, 24.6 (*C*H); 23.8, 23.4, 22.0, 21.4 (*C*H_3). ^{31}P NMR (C_6D_6): δ M −23.0 ($^1J_{P-H}$ = 816 Hz), m −16.9 ($^1J_{P-H}$ = 842 Hz). ^{11}B NMR (C_6D_6): δ −17.1.

(4*S*,9*S*)-4,9-Diphenyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane−BH_3 (30). Yield: 68%. Mp: >250 °C. De: 64%. ^{1}H NMR (CD_3OD): δ 7.58 (d, 1H, $^1J_{P-H}$ = 816 Hz, P*H*); 7.35−7.25 (m, 10H, Ar *H*); 4.45−3.77 (m, 6H, CH_2O + C*H*N); 3.05−2.19 (m, 4H, CH_2N). ^{13}C NMR (CD_3OD): δ 137.2, 128.3, 128.1, 126.8 (Ar); 70.6 (*C*H_2O); 64.9 (*C*H_2O); 53.6 (*C*HN); 50.5 (*C*HN); 48.4 (*C*H_2N); 48.1 (*C*H_2N). ^{31}P NMR (CD_3OD): δ M −21.6 ($^1J_{P-H}$ = 814 Hz), m −17.6 ($^1J_{P-H}$ = 831 Hz). ^{11}B NMR (CD_3OD): δ −16.3.

(4*S*,9*S*)-4,9-Dibenzyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane−BH_3 (31). Yield: 82%. Mp: >250 °C. De: 65%. ^{1}H NMR (C_6D_6): δ 7.32 (d, 1H, $^1J_{P-H}$ = 818 Hz, P*H*); 7.29−6.90 (m, 10H, Ar *H*); 3.56−2.83 (m, 6H, CH_2O + C*H*N); 2.61−2.34 (m, 4H, CH_2N); 2.20−1.96 (m, 4H, CH_2); 1.43 (br, 2H, BH_3); 1.02 (br, 1H, BH_3). ^{13}C NMR (C_6D_6): δ 138.0, 136.7, 129.2, 129.1, 128.9, 128.8, 126.9, 126.8 (Ar); 64.4 (*C*H_2O); 62.9 (d, $^2J_{P-C}$ = 10.5 Hz, *C*HN); 62.7 (*C*H_2O), 57.4 (d, $^2J_{P-C}$ = 14.7 Hz, *C*HN); 43.7 (d, $^2J_{P-C}$ = 5.84 Hz, *C*H_2N); 40.6 (d, $^2J_{P-C}$ = 10.0 Hz, *C*H_2N); 39.1 (*C*H_2); 37.2 (*C*H_2). ^{31}P (C_6D_6): δ M − 22.0 ($^1J_{P-H}$ = 830 Hz), m − 15.3. ^{11}B (C_6D_6): δ − 16.2.

(6*R*,7*R*)-6,7-Cyclohexyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane−BH_3 (32). Yield: 70%. De: 10%. Due to the minus de, all the spectra have not been discussed. ^{1}H NMR (C_6D_6): δ m 7.64 (d, 1H, $^1J_{P-H}$ = 828 Hz, PH), M 7.59 (d, 1H, $^1J_{P-H}$ = 827 Hz, PH). ^{31}P NMR (C_6D_6): δ M −21.3 ($^1J_{P-H}$ = 847 Hz), m −17.4 ($^1J_{P-H}$ = 811 Hz). ^{11}B NMR (C_6D_6): δ M −13.2, m −18.7.

(6*S*,7*S*)-6,7-Diphenyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane−BH_3 (33). Yield: 79%. Mp: >250 °C. De: 60%. ^{1}H NMR (C_6D_6): δ 8.16 (d, 1H, $^1J_{P-H}$ = 833 Hz, P*H*); 7.50−6.99 (m, 10H, Ar *H*); 4.57−4.26 (m, 2H, C*H*N); 3.83−3.54 (m, 4H, CH_2O); 2.65−2.23 (m, 4H, CH_2N). ^{13}C NMR (C_6D_6): δ 132.6, 131.4, 129.3, 128.3 (Ar); 74.0 (d, $^2J_{P-C}$ = 5.92 Hz, *C*HN); 62.8 (d, $^2J_{P-C}$ = 6.07 Hz, *C*H_2O); 59.2 (d, $^2J_{P-C}$ = 4.00 Hz, *C*H_2O); 58.4 (d, $^2J_{P-C}$ = 12.2 Hz, *C*HN); 47.2 (d, $^2J_{P-C}$ = 8.58 Hz, *C*H_2N); 42.5 (d, $^2J_{P-C}$ = 15.7 Hz, *C*H_2N). ^{31}P NMR (C_6D_6): δ M −23.8 ($^1J_{P-H}$ = 834 Hz), m −17.7 ($^1J_{P-H}$ = 823 Hz). ^{11}B NMR (C_6D_6): δ M −13.4, m −15.9.

(3*R*,10*R*)-3,10-Diphenyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane−BH_3 (34). Yield: 86%. Mp: >250 °C. De: 28%. Due to the minus de, all the spectra have not been discussed. ^{1}H NMR (C_6D_6): δ m 7.69 (d, $^1J_{P-H}$ = 740 Hz, P*H*), M 7.40 (d, $^1J_{P-H}$ = 769 Hz, P*H*), 7.23−6.90 (m, 10H, Ar *H*). ^{13}C NMR (C_6D_6): δ 128.6, 128.7, 127.7, 127.3, 127.1 (Ar), 67.9 (*C*HO), 64.5 (*C*HO), 62.4 (CHO−*C*H_2N), 57.5 (CHO−*C*H_2N), 43.4 (*C*H_2N), 41.2 (*C*H_2N). ^{31}P NMR (C_6D_6): δ M −26.4 ($^1J_{P-H}$ = 769 Hz), m −25.4 ($^1J_{P-H}$ = 739 Hz). ^{11}B NMR (C_6D_6): δ M −13.6, m −15.5.

Acknowledgment. Financial support from the CNRS (UMR 6516) and a fellowship from the MESR (C.M.) are gratefully acknowledged. We are grateful to Dr. J. Feneau-Dupont and Dr. J. P. Declercq from the "Université Catholique de Louvain" for the X-ray structure determinations, to Dr. Y. Vanoorenberghe for preliminary studies on triquinphosphorane−borane complexes, and to Dr. O. Pardigon for practical assistance and helpful discussions. Calculations were performed on an IBM RISC SP2 supercomputer at the "Complexe de Calcul de Saint-Jérôme" with the support of the "Région Provence-Alpes-Côte d'Azur", whom we thank. Finally, we thank an anonymous reviewer of our manuscript who offered his results of additional calculations and helpful comments that we quoted.

Supporting Information Available: Tables of positional and thermal parameters, bond distances and angles, and torsion angles for **28M**, tables giving results of the conformational study of compounds **15** and **28**, and figures representing the lowest energy conformers of disubstituted compounds **17**, **22**, **24**, and **28**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM980774C

(51) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, D., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175−189.

(52) Sheldrick, G. M. SHELX76 Program for Crystal Structure Determination; University of Cambridge, Cambridge, U.K., 1976.