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Electrophile Induced Addition Reactions of Bis-phosphonio-isophosphindolide Cations

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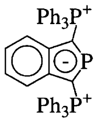
Abstract—Bis-triphenylphosphonio-isophosphindolide cations **1** react with triflic acid to give C-protonated products **4**, **5** which show an enhanced reactivity to undergo addition of H_2O or MeOH to the cyclic π-system. This reaction is the first step of the hydrolytic decomposition of the heterocycle which was monitored by NMR spectroscopic studies. No evidence for direct P-protonation or P-alkylation (which had been postulated in a previous study) was obtained. Addition of H_2O or H_2S to the cyclic π-system of **1** is also promoted by oxidizing agents such as I_3^- or sulfur and affords novel zwitterionic (thio)-phosphinates **11**, **13**. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Introduction

The cation **1**[1] can be regarded as a benzophospholide anion with a delocalized 10π-electron system and two positively charged phosphonio substituents.[2,3] The two-coordinate phosphorus atom in the ring is ambiphilic and may behave in chemical reactions both as an electrophile and a nucleophile.[1–3] However, since the π-electron delocalization and charge compensation reduce both the nucleophilicity and electrophilicity,[1,3] bis-phosphonio-isophosphindolides are less reactive than other types of phosphorus-containing multiple-bond systems. In particular, **1** lacks the notorious sensitivity of many of these species to react under insertion into the O–H bonds of water or alcohols,[4] and may be handled in aqueous or alcoholic media without decomposition.[1] We have recently established, however, that the reactivity of bis-phosphonio-isophosphindolides can be greatly enhanced by coordination to transition metal cations such as Au^+ or Hg^{2+}. For instance, complexes of **1** with AuCl or $HgCl_2$ react with H_2O or alcohols under instantaneous addition to the cyclic π-electron system.[5,6]



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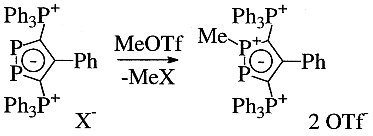

2[X] **3**[OTf]

Considering that the increase in reactivity upon coordination is in the first place attributable to the electron-withdrawing effect of the transition metal,[5,6] nonmetallic electrophiles are expected to exert a similar activating effect. The feasibility of alkylation and protonation of the two-coordinate phosphorus in phosphonio-substituted phospholide systems has been demonstrated by the synthesis of the structurally characterized dication **3** via methylation of **2**,[7] as well as by a preliminary report of methylation and protonation of **1**.[1] We have reinvestigated these reactions, paying particular attention to a possible activation of the heterocyclic π-electron system for subsequent hydrolysis reactions. The results presented here indicate that the interaction of **1** with strong Brønsted acids or alkylating agents does indeed induce a similar reactivity enhancement as metal coordination. Furthermore, our new studies indicate that some of the earlier structural assignments on the products formed during the protonation and alkylation of **1** have to be corrected.

Results

Reaction of 1 with (Lewis) acids/H_2O

Even if protonation or methylation of **1** has been claimed to

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Keywords: addition reactions; ambiphilic activity; phospholes; protonation.

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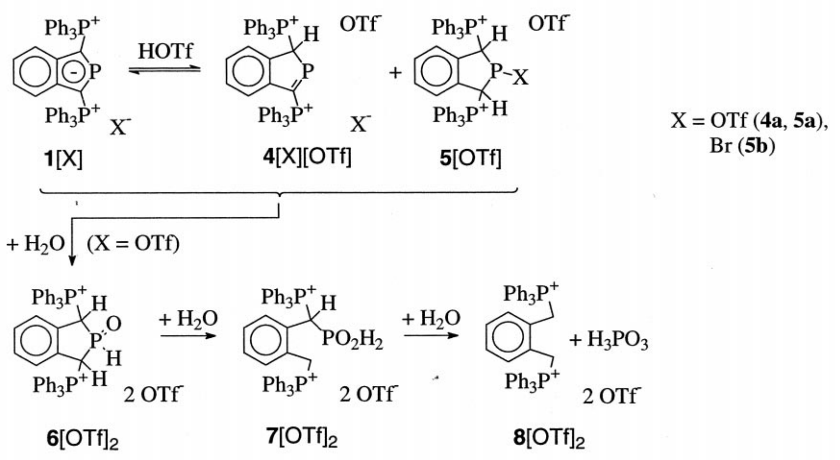


Scheme 1.

proceed similarly to the complexation via electrophilic attack at the two-coordinate phosphorus, identification of the formed products is so far based only on an incomplete set of NMR data.[1] To obtain a more comprehensive characterization, we initiated a detailed study of the reactions of **1**[OTf] with triflic acid (HOTf) and methyl triflate (MeOTf).

In contrast to the reported alkylation of **1**[Br] by [Me_3O][BF_4],[1] we observed that in the absence of water treatment of **1**[OTf] with one equivalent of MeOTf gave no reaction at all. In contrast, reaction of equimolar amounts of **1**[OTf] and HOTf afforded two new products (Scheme 1) which were found to exist only in equilibrium with excess of **1**[OTf] and HOTf and thus could not be isolated. Elucidation of the constitution as the protonated species **4a**, **5a** was feasible from ^{1}H and ^{31}P NMR spectra of the equilibrium mixture recorded at −30°C (at higher temperatures, chemical exchange leads to a broadening of all signals). The dication **4a** displays in the ^{31}P{^{1}H} NMR spectrum three signals of an AMX spin system (Table 1) whose most deshielded signal exhibits a chemical shift in the typical range of phosphaalkenes.[8] Protonation of one of the C-1/C-3-carbon atoms in the ring is revealed by additional doublet splittings of the resonances of both adjacent phosphorus atoms in an undecoupled ^{31}P NMR spectrum (signal assignments were confirmed by 2D-^{1}H,^{31}P shift correlations, Fig. 1). Compound **5a** gives rise in the ^{31}P{^{1}H} NMR spectrum to a characteristic AX_2 pattern whose A-signal displays an additional triplet splitting when proton decoupling is switched off, indicating that protonation of both C-1/C-3-carbon atoms has occurred. Since $^{2}J_{P,H}$ is much smaller and $^{2}J_{P,P}$ much larger than in other derivatives of **1** which exhibit protonated C-1/C-3-carbon atoms and a four coordinate phosphorus atom (Table 1), we assume a coordination number of three at the endocyclic phosphorus atom. A product with very similar spectroscopic data and suggested constitution **5b** was formed when **1**[Br] was reacted with HOTf under otherwise identical conditions; in this case, no mono-protonated species **4b** was detected. Both **4a** and **5a,b** were transformed back into **1** upon addition of an excess of NEt_3.

Repeated addition of small amounts of moist THF to acidified solutions of **1**[OTf] leads to almost instantaneous hydrolysis of the cation. A ^{31}P NMR spectroscopic assay revealed a multistep pathway which proceeded via several intermediates and gave as final products the phosphonium cation **8**, which was isolated as a bis-triflate salt, and phosphorous acid. Even if attempts to isolate any of the intermediates failed, structural assignments were possible on the basis of the observed ^{31}P and ^{31}P{^{1}H} NMR spectra. Thus, the first stage of the reaction proceeds via addition of one molecule of H_2O to **4a** (or formal HOTf / H_2O metathesis in **5a**, respectively) and subsequent tautomerization to give the

Table 1. ^{31}P NMR Data of **4**–**8**, **10**, **11**, and **13** (in CH_2Cl_2, 30 °C)

	Spin system	$\delta\,^{31}$P	^{2}J(P,P) [Hz]	^{n}J(P,H) [Hz][a]
4a[b]	AMX	329.7 (A), 23.1 (M), 15.6 (X)	78.2 (J_{AX}), 19.8(J_{AM})	18.7 ($^{2}J_{H,M}$)
5a[b]	AX_2	105.5 (A), 23.5 (X)	64.5	11.6 ($^{2}J_{H,X}$), 3.9 ($^{2}J_{H,A}$)
5b[b]	AX_2	107.3 (A), 21.9 (X)	62.3	[c]
6	AX_2	40.7 (A), 21.9 (X)	12.1	581 ($^{1}J_{H,A}$), 11.4 ($^{2}J_{H,A}$)
7	AMX	25.9 (A), 22.6 (M), 17.6 (X)	3.1 (J_{AM}), 1.3 (J_{MX})	607 ($^{1}J_{H,A}$), 17.8 ($^{2}J_{H,A}$)
8	A_2	21.3	–	–
10	AX_2	69.3 (A), 22.4 (X)	11.0	16.2 ($^{2}J_{H,X}$), 12.8 ($^{2}J_{H,A}$), 11.2 ($^{2}J_{H,A}$)
11[d]	AX_2	28.0 (A), 22.6 (X)	3.8	15.7 ($^{2}J_{H,A}$)
13[d]	AX_2	81.6 (A), 20.2 (X)	1.1	27.9 ($^{2}J_{H,A}$), 27 ($^{2}J_{H,X}$)

[a] To benzylic protons at C-1/C-3.
[b] At −40 °C.
[c] Not determined.
[d] In MeOH.

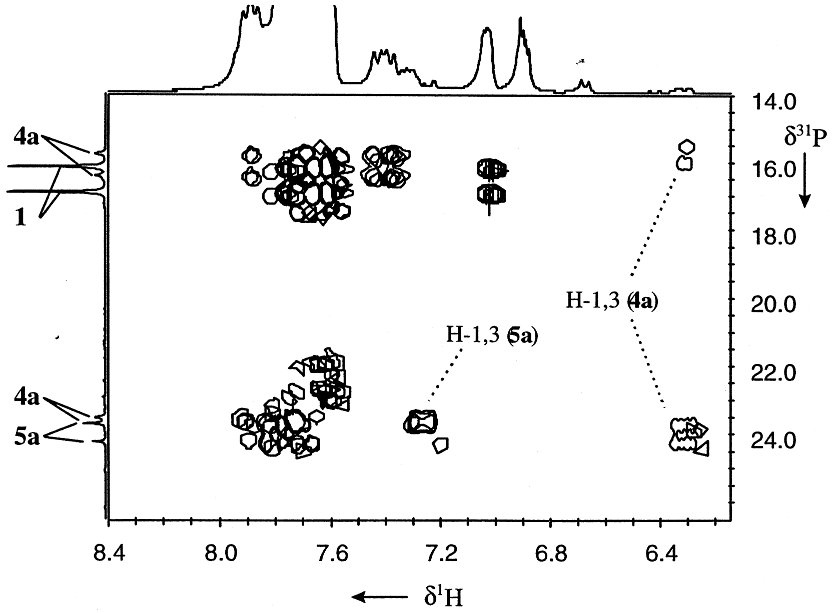


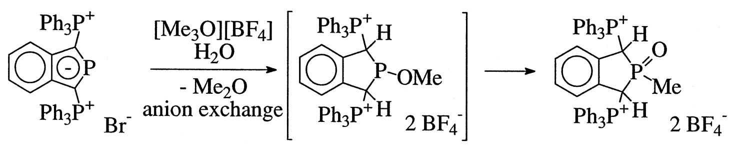
Figure 1. Expansion of the $^1H,^{31}P$ HMQC spectrum (−30°C, CH_2Cl_2) of a **1**[OTf]/ HOTf mixture with corresponding 1D ^1H (top) and $^{31}P\{^1H\}$ spectra (left). Correlation signals of the H-1,3 atoms of **4a** (at $\delta^1H=6.31$) and **5a** (at $\delta^1H=7.28$) are marked.

phosphoryl cation **6** which is characterized in the ^{31}P NMR spectrum by an AX_2 pattern whose A-signal is further split by characteristic couplings to one directly attached proton and two remote benzylic protons (Table 1). Further reaction of **6** with H_2O proceeds by P–C bond cleavage to afford the phosphinic acid derivative **7** which gives rise to an AMX-type spectrum whose A-signal displays coupling to one directly bonded and only one remote proton. Hydrolytic cleavage of the remaining P–C bond finally gives **8** and H_3PO_3 during the last stage of the reaction.

Formation of exactly the same products was observed when a mixture of **1**[OTf] and MeOTf was allowed to age in contact with moist air, or when water was deliberately added. We assume that in this case the first reaction step involves hydrolysis of the ester to give MeOH and free acid, and that subsequent protonation and further hydrolytic decomposition of **1** takes place as described above.

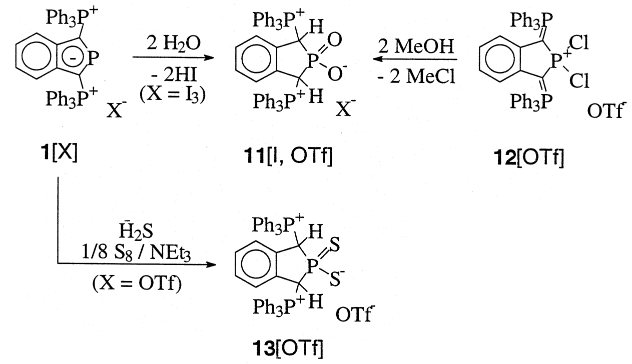
The ^{31}P-NMR data of **6** bear close similarity to those of the product obtained from **1**[Br] and HBF_4 which was first formulated as a protonated bis-phosphonio-isophosphindolide dication.[1] Comparison of the spectra revealed that in fact the cations of both compounds are identical; the splitting by coupling with the benzylic protons at C-1/C-3 had originally been overlooked due to exchange-induced signal broadening. Since these findings suggest that likewise the structural assignment of the product arising from methylation of **1** with $[Me_3O][BF_4]$ is erroneous, we decided to reinvestigate this process. As in the case of the interaction of **1**[OTf] with MeOTf, the reaction of **1**[Br] with $[Me_3O][BF_4]$ took several hours for completion and afforded, besides small amounts of the cations **5b** and **6**, a main product which displayed identical $^{31}P\{^1H\}$ NMR data as reported previously.[1] The compound was isolated after precipitation with THF and its identification as the salt **10**$[BF_4]_2$ (Scheme 2) by analytic and spectroscopic techniques confirmed that solvolysis had also occurred in this case.

The alkylation at phosphorus and protonation at the C-1/C-3 ring carbon atoms in **10** follows unequivocally from the signal multiplicities in ^{31}P, ^1H, and $^{13}C\{^1H\}$-DEPT spectra and the identical coupling constants $^2J_{H,P}$ of the two benzylic protons in the ^{31}P NMR spectrum, and the elemental composition was further confirmed by a (+)-FAB mass spectrum. The observed AX_2 pattern in the $^{31}P\{^1H\}$ NMR spectrum indicates a *cis*-arrangement of the phosphonio substituents, but the signal broadening in both ^{31}P and $^{13}C\{^1H\}$ NMR spectra suggests that dynamic *cis-trans* isomerisation may take place.[9] Presumably, the reaction of $[Me_3O][BF_4]$ with **1** is initiated, as the one with MeOTf, by interaction of the oxonium ion with a trace amount of H_2O[10] to give MeOH and fluoroboric acid. The formation of **10** is then accomplished by protonation of **1**, subsequent 1,2-addition of MeOH to give **9**, and a final Michaelis–Arbusov



1[Br] **9**$[BF_4]_2$ **10**$[BF_4]_2$

Scheme 2.



Scheme 3.

rearrangement. Attempts to speed up the reaction by deliberate addition of H_2O yielded similar product mixtures as observed during the acid promoted hydrolysis reactions, suggesting that either MeOH adds slower than H_2O, or the hydrolysis of **9** is faster than the Michaelis–Arbusov reaction, so that in the presence of excess H_2O, formation of **10** is not observed.

Oxidation induced addition of H_2O/H_2S

As the chemical activation of the π-system of **1**[Br] by (Lewis-)acids relies mainly on electrophilicity enhancement by the electron-withdrawing effect of the reagent, it can be envisaged that the influence of oxidizing agents has a similar effect. An accidental confirmation of this idea was first obtained by the observation that the hydrolytic sensitivity of **1** increases markedly when the anion in the salt **1**[I] is replaced by the mildly oxidizing I_3^-.[11] Spectroscopic analysis of the products which formed upon prolonged exposure of solutions of **1**[I_3] to moist air allowed identification of a species tentatively formulated as the dication **11** (Scheme 3), which arises formally from oxidative hydrolysis of **1**, as the main reaction product. Even though all attempts towards its isolation from this reaction failed, the constitution of **11** was unequivocally established from spectroscopic characterization of an analytically pure sample of the salt **11**[OTf] which was synthesized independently via methanolysis of the λ^5-bis-phosphonio-isophosphindolide **12**.[11]

Since oxidation of low valent phosphorus compounds by sulfur is a widely used process, we studied the prospect of the reaction with S_8/H_2S to obtain so far unknown sulfide derivatives of **1**. In fact it was found that whereas salts **1**[X] gave a defined reaction with neither H_2S nor elemental sulfur (or S/NEt_3) alone, a smooth formation of a single product was observed in a tandem reaction with both components. The product was isolated after precipitation with Et_2O and recrystallization from MeOH, and its constitution established as **13** by analytical and spectroscopic techniques. Apart from a deshielding of the ^{31}P NMR signal of the endocyclic phosphorus which is characteristic of thioxo-substituted phosphorus compounds, all ^{31}P, ^{1}H, and ^{13}C NMR parameters closely match the corresponding data of **11**. Since no reaction intermediates were observable, detailed accounts on the mechanism of the formation of **13** cannot be made.

Dithiophosphinates have long been known as ligands to transition metals, and the utilization of the ylide-substituted derivative $Ph_3P{=}C(Ph)P(Et)S_2^-$ (**14**) as a ligand has been recently established.[12] We thus also considered studies on the ligand properties of **13** of interest. However, in contrast to **14**, complexation with $M(acac)_2$ or MCl_2 (M=Ni, Pt, Cd; acac=acetylacetonate) was observed neither for the cation **13** nor its conjugate base which was generated in situ by abstracting the benzylic protons with two equivalents of *n*-BuLi. Reaction of **13** (or its conjugate base) with AgOTf afforded, besides Ag_2S, a complicated product mixture whose NMR spectroscopic investigation allowed identification of **1** as the only known product.

Discussion

It has been shown that the bis-phosphonio-isophosphindolide cation **1** reacts as a weak base towards the strong acid HOTf. Protonation occurs exclusively at the C-1/C-3 ring carbon atoms which appear thus to be a more basic site than the lone pair at the two-coordinate phosphorus atom. This is in contrast to a previous report on the reaction of **1** with HBF_4[1] and the observation of P-alkylation for the diphospholide **2**,[7] but agrees with the occurrence of similar reactions for a vinylated derivative of **1**.[2] The observed dynamic behavior of **4**, **5** as well as their reaction with base indicates that the protonation of **1** is reversible. Unlike **2**,[7] direct alkylation of **1** could not be verified; the dication **10** which was originally formulated as a P-methyl derivative of **1** was shown to be actually a methanolysis product of the conjugate acid of **1**. It cannot be decided on the basis of the available information if the failure to observe direct P-alkylation of **1** is related to a lower nucleophilicity as compared to **2**, or with other factors such as steric protection of the nucleophilic C-1/C-3 carbons by two bulky adjacent Ph_3P substituents.

Protonation of **1** induces, similarly to its coordination to electrophilic transition metals,[5,6] a chemical activation of the cyclic 10π-electron system for reactions such as addition of H_2O, H_2S, or MeOH. Cases of enhanced reactivity in a tandem reaction with an electrophile and a nucleophile with respect to separate reactions with either substrate alone have been observed before for other phosphorus heterocycles.[13,14] The observed reactions of **1** provide a way to understand the general underlying mechanism of these processes. Comparison of metal- and acid-promoted addition reactions of **1** suggests that the driving force for the chemical activation is in the first case mainly the inductive withdrawal of electron density from the cyclic π-system,[5,6] whereas in the second case, the disruption of the cyclic π-system is also important. The site of coordination of the electrophile (at phosphorus or carbon) appears of secondary influence.

The chemical activation of the π-system of **1** can also be promoted by the presence of an oxidizing agent, even if the detailed mechanism of these reactions was not elucidated. The easily observed desulfurization of the disulfide **13** in reactions with Ag^+ parallels the previously noted instability of the 2,2-dihalogenated λ^5-bis-phosphonio-isophosphindolides towards reductive elimination reactions.[11]

Experimental

General

All manipulations were carried out under an atmosphere of dry argon. Solvents were dried using standard procedures. NMR spectra: Bruker AMX 300 (^{1}H: 300.13 MHz, ^{13}C: 75.46 MHz, ^{31}P: 121.5 MHz). ^{1}H,^{31}P-HMQC spectra were measured using standard pulse sequences. Spectra in nondeuterated solvents were recorded with suppression of the solvent resonances by presaturation. Chemical shifts were referenced to ext. TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P, Ξ=40.480747 MHz); a positive sign denotes a shift to lower frequencies. Coupling constants are given as absolute values. The atoms in the isophosphindole ring system are denoted by C-1 to C-7a and H-4 to H-7, and atoms within the C_6H_5 substituents by C(H)^{para}, C(H)^{meta}. For ^{13}C NMR signals which are the X-part of AA′MX- or AA′X-spin systems, $\sum J$ and J_M denote the absolute values of the sum of couplings to the exocyclic and endocyclic phosphorus nuclei, respectively. MS: Kratos Concept 1H, Xe-FAB, *m*-nitrobenzaldehyde matrix; molecular masses refer to the most abundant isotopes. Melting points were determined in sealed capillaries. Elemental analyses: Mikroanalytisches Labor der Humboldt-Universität, Berlin.

General procedure for reactions of 1[X] with HOTf (MeOTf)/H_2O

To a cooled (−78°C) solution of 1 mmol of **1**[X] (X=OTf, Br) in 5 ml of CH_2Cl_2 was added dropwise with stirring a solution of 1 mmol of HOTf (MeOTf) in 1 ml CH_2Cl_2. The reaction mixture was allowed to warm to ambient temperature and analyzed by ^{1}H and ^{31}P NMR spectroscopy (see text and Table 1). Hydrolysis of the reaction mixture was accomplished by repeated addition of a few drops of moist THF (see text and Table 1). The progress of the reaction was monitored by ^{31}P NMR spectroscopy after each addition. Isolation of hydrolysis products was attempted by reducing the volume of partially hydrolyzed solutions to approximately one-half, and adding the same amount of dry ether. Crystallization at temperatures between 0 and −25°C afforded varying amounts of colorless crystals which were identified as the salt **11**[BF_4]$_2$ by microanalysis (calcd. for $C_{44}H_{38}B_2F_8P_2$, C 65.87 H 4.77, found C 65.3 H 4. 5) and comparison of the ^{1}H and ^{31}P NMR spectra with those of an authentic sample.

Preparation of 10[BF_4]$_2$

Solutions of 0.74 g (1.00 mmol) of **1**[Br] and 0.15 g (1.00 mmol) of [Me_3O][BF_4] each in 10 ml of CH_2Cl_2 were mixed at ambient temperature and stirred for several hours until ^{31}P NMR control indicated complete consumption of the cation **1**. The solution was concentrated in vacuo, and the product precipitated by addition of THF. The formed off-white precipitate was filtered, washed several times with THF, and dried in vacuo to give 0.39 g (90% with respect to BF_4^-) of **10**[BF_4]$_2$, m.p. 240°C. Anal. calcd. for $C_{45}H_{39}B_2F_8P_3O\cdot CH_2Cl_2$, C 58.33 H 4.36; found C 58.8 H 4.9. ^{1}H NMR ($CDCl_3$): 8.00–7.40 (m, 30H, C_6H_5), 7.06 (m, 2H, H-5,6), 6.81 (m, 2H, H-4,7), 5.88 (dd, J_{PH}=16.2, 11.2 Hz, 2H, H-1,3), 0.74 (d, J_{PH}=13.6 Hz, 6H, PCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): 136.6 (m, $\sum J$=4.4 Hz, C^{para}), 135.1 (m, $\sum J$=8.7 Hz, C^{ortho}), 131.8 (ddd, J=11.0, 4.5, 2.8 Hz, C-3a,7a), 131.2 (d, J=13.0 Hz, C^{meta}), 130.3 (s, C-5,6), 128.7 (m, $\sum J$=13.4 Hz, C-4,7), 117.6 (br, C^{ipso}), 42.8 (m, $\sum J$=56.7 Hz, J_M=52.3 Hz, C-1,3). (+)-FAB-MS: *m*/*e* (%): 687 (55) [$C_{45}H_{38}P_3O^+$].

Preparation of 11[OTf]

0.65 g (0.75 mmol) of **12**[OTf] were dissolved in 15 ml of CH_2Cl_2 and treated with 0.13 ml (3.00 mmol) MeOH. Stirring the yellow solution overnight induced a fading of the color and precipitation of a colorless solid. The product was collected by filtration, washed with dry THF, then ether, and dried in vacuo to give 0.57 g (92 %) of **11**[OTf]·CH_2Cl_2, m.p. 236°C. Anal. calcd. for $C_{45}H_{36}F_3P_3O_5S\cdot CH_2Cl_2$, C 59.82 H 4.15 S 3.47, found C 60.00 H 4.15 S 3.44. ^{1}H NMR (CH_3OH/CD_3OD): 7.87–7.61 (m, 30H, C_6H_5), 7.14 (m, 2H, H-5,6), 6.90 (m, 2H, H-4,7), 4.66 (d, $^2J_{PH}$=15.9 Hz, CH). ^{1}H{^{31}P} NMR (CH_3OH/CD_3OD): 7.87–7.61 (m, 30H, C_6H_5), 7.14 (m, 2H, H-5,6), 6.90 (m, 2H, H-4,7), 4.66 (s, CH). ^{13}C{^{1}H} NMR ($CDCl_3$): 136.5 (m, $\sum J$=3.0 Hz, C^{para}), 136.1 (m, $\sum J$=10.3 Hz, C^{ortho}), 134.5 (m, C-3a,7a), 131.4 (m, $\sum J$=13.0 Hz, C^{meta}), 120.5 (m, $\sum J$=69.8 Hz, $^3J_{PC}$=5.3 Hz, C^{ipso}), 121.2 (m, C-5,6), 120.1 (m, C-4,7), 39.3 (dd, J_{PC} = 70.0 Hz, 46.3 Hz, C-1,3).

Preparation of 13[OTf]

Into a solution of 5.5 g (6.8 mmol) of **1**[OTf], 0.23 g (6.8 mmol) of sulfur and 0.1 ml of NEt_3 in 60 ml CH_2Cl_2, gaseous H_2S was bubbled for 10 min. The color changed from light yellow to dark red. The solution was stirred for additional 5 h during which time the color changed again to yellow, and a colorless solid precipitated. The product was collected by filtration, washed twice with 10 ml of CH_2Cl_2 and dried in vacuo to give 4.24 g (71%) of **13**[OTf]·CH_2Cl_2, m.p. 210°C. Anal. calcd. for $C_{45}H_{36}F_3O_3P_3S_3\cdot CH_2Cl_2$ C 57.81 H 4.01 S 10.06, found C 58.03 H 4.26 S 9.8. ^{1}H NMR (CD_3OD/DMSO-d$_6$): 6.94–6.74 (m, 30H, C_6H_5), 6.28 (m, 2H, H-5,6), 5.91 (m, 2H, H-4,7), 4.44 (dd, J_{HP}=27.9 Hz, 2H, H-1,3). ^{13}C{^{1}H} NMR (CD_3OD/DMSO-d$_6$): 136.1 (m, $\sum J$=10.3 Hz, C^{ortho}), 135.8 (m, $\sum J$=2.7 Hz, C^{para}), 135.3 (m, C-3a,7a), 130.5 (m, $\sum J$=13.4 Hz, C^{meta}), 119.5 (m, C^{ipso}), 121.2 (m, C-5,6), 120.0 (m, C-4,7), 57.6 (dd, C-1,3). (+)-FAB-MS: *m*/*e* (%): 721 (75) [$C_{44}H_{36}P_3S_2^+$].

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