Halogenation of Bis(phosphonio)isophosphindolide Salts: Oxidation versus Substitution

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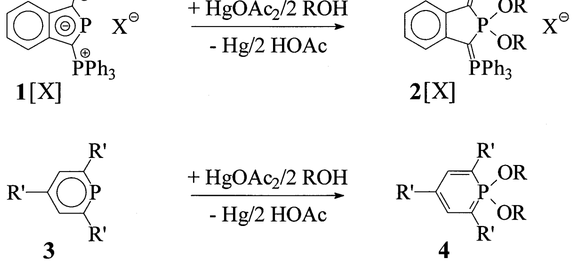
Bis(phosphonio)isophosphindolide iodide **1**[I] reacts with an equimolar amount of I_2 to yield the trihalide **1**[I_3], while treatment of **1**[X] (X = Br, OTf) with excess Br_2 furnishes the dibromophosphonium salt **6c**[X]. The bromo-substituted bis(phosphonio)isophosphindolide cations **5a** and **5b** are identified as intermediates in this reaction; **5b**[Br] is also obtained in pure form by reaction of **6c**[Br] with Zn or NEt_3. Reaction of **1**[OTf] with one equivalent of $PhICl_2$ (**7**) affords the dichlorophosphonium salt **8a**[OTf], which undergoes further substitution reactions in the presence of excess **7** and reacts with Me_3SiI to give a mixture of **1**[OTf] and I_2 rather than a substitution product **9**[OTf]. The results of a crystal-structure determination of **8a**[OTf] are reported and the mechanistic aspects of the different oxidation/substitution reactions are discussed.

In the course of our investigation of the coordination chemistry of bis(phosphonio)isophosphindolide ions, we found that the cation **1**[1] easily undergoes oxidative alcoholysis reactions in the coordination sphere of Hg^{2+} or Pd^{2+} ions to yield dialkoxy-substituted phosphonium ions **2** (Scheme 1)[2]. This reaction is related to the conversion of σ^2,λ^3-phosphinines **3** into 1,1-dialkoxy-σ^4,λ^5-phosphinines **4** (Scheme 1), which takes place under similar conditions[3]. In looking for a way to achieve oxidation of bis(phosphonio)isophosphindolides without the assistance of transition metals, we investigated the behaviour of the salts **1**[X] (X = halide, triflate) towards halogens, anticipating that a similar reaction as the oxidative halogenation of σ^2,λ^3-phosphinines[3] should occur. The results of these studies are presented here. The studies revealed, however, a more complex reactivity pattern which is characterised by competition between the expected oxidation with substitution reactions at the fused ring system.

Scheme 1. (X = Br, OTf)



Results

Reactions

Treatment of a CH_2Cl_2 solution of **1**[I] with an equimolar amount of I_2 produced almost instantaneously a brown solution. While ^1H- and ^{31}P-NMR data indicated the presence of the unchanged cation **1**, UV/Vis and Raman spectra showed bands attributable to I_3^- anions [UV/Vis: λ_{max} = 361, 294 nm (ref.[4]: 360, 290 nm); Raman: $\tilde{\nu}$ = 112, 145 cm^{-1} (ref.[5]: 52, 114, 145 cm^{-1})], suggesting the formation of a salt **1**[I_3] by electrophilic attack of iodine on the halide anion of the starting material (Scheme 2). The crude product was isolated as a dark brown, highly moisture-sensitive solid after evaporation of all volatiles, but decomposed during attempts to achieve any further purification by recrystallisation.

Reaction of **1**[Br] or **1**[OTf] with a substoichiometric amount of Br_2 (0.5 to 0.9 equiv.) in CH_2Cl_2 produced, according to a ^{31}P-NMR-spectroscopic assay, a mixture of the unreacted cation **1** with two further products which displayed ABX or A_2X patterns with $\delta^{31}P$ and $^2J_{PP}$ values very similar to those of **1**. Analysis of (+)-FAB mass spectra and two-dimensional $^1H,^{31}P$-HMQC/HMQC-TOCSY NMR spectra of the product mixture allowed the identification of the reaction products as the bromo-substituted bis(phosphonio)isophosphindolide ions **5a** and **5b**. This suggests that a bromination at the fused ring system of **1** with conservation of the two-coordinate phosphorus atom had occurred.

Addition of more Br_2 did not result in further conversion of **1** into **5a** and **5b**, but rather in the formation of two new species whose ^{31}P-NMR signals displayed ABX or A_2X patterns with much smaller values of $^2J_{PP}$ and a marked up-

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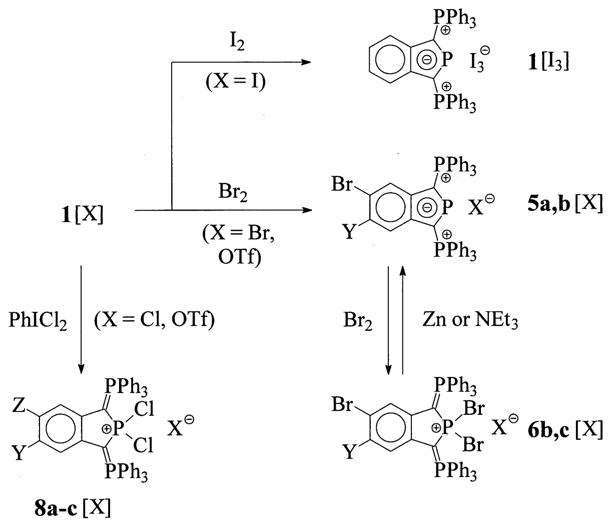
Scheme 2



	5a,6b	5b,6c	8a	8b	8c
Y	H	Br	H	Cl	Cl
Z	-	-	H	H	Cl

field shift of the P^X resonance. On this basis the new species were found to be the oxidation products **6b** and **6c**. Complete conversion of all intermediates into **6c** was finally observed after four equivalents of Br_2 had been added. Evaporation of the solution formed gave a brown, highly moisture-sensitive residue of crude **6c**[X] which contained approximately 3−5% of nonphosphorus-containing compounds as impurities. Although attempts towards further purification failed because of decomposition of the highly reactive dihalo-phosphonium moiety, the constitution of the cation was unambiguously confirmed by means of multinuclear NMR investigations.

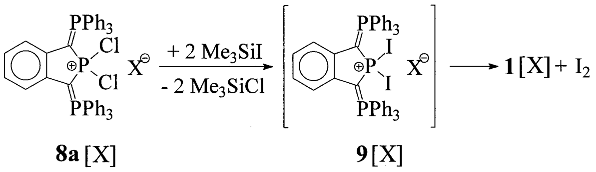
A further chemical proof of the identity of **6c** was obtained from its reactions with Zn or, alternatively, with excess NEt_3, which afforded the dibromo-substituted bis(phosphonio)isophosphindolide **5b** by selective reduction of the Br_2P unit. The salt **5b**[Br] was isolated in analytically pure form as a white solid that was fairly stable to both air and moisture and was characterised by NMR spectroscopy. The monobrominated cation **5a**, which was not accessible in preparative amounts by this procedure, was formed as the main product (70% of phosphorus-containing species) in the reaction of a mixture of **6b** and **6c** (prepared in situ from the reaction of **1**[OTf] with 2.5 equiv. of Br_2) with an equimolar amount of **1**[OTf]. Chromatographic workup produced a small quantity of crude **5a**[OTf] which, although still contaminated by small amounts of **1** and **5b**, proved sufficient for an unambiguous NMR-spectroscopic structure elucidation.

Reaction of **1**[X] (X = Cl, OTf) with an equimolar amount of $PhICl_2$ (**7**), which was chosen as a chlorinating agent because of its superior handling as compared to elemental Cl_2, furnished selectively the oxidation products **8a**[X]. The triflate salt **8a**[OTf] was precipitated by addition of ether and isolated after recrystallisation as a light yellow, moisture-sensitive solid which is readily soluble in aprotic dipolar solvents such as CH_2Cl_2 or THF. The product was characterised by means of NMR spectroscopy and an X-ray crystal-structure determination.

Further reaction of **8a**[X] with an excess of **7** in the presence of NEt_3 as an acid scavenger was found to proceed in a more complicated way than the reaction with Br_2 and yielded a mixture of several species rather than a single final product. Attempts towards isolation of single components remained unsuccessful, but inspection of ^{31}P-NMR spectra of the mixtures allowed the identification of two species which displayed ABX and A_2X coupling patterns with very similar values for $\delta^{31}P$ and J_{PP} as **8a** and were tentatively formulated as the chlorinated cations **8b** and **8c**. The additional presence of a singlet resonance attributable to $[ClPPh_3]^+$, together with several unidentified AX-type multiplets, suggested that in addition to the H/Cl exchange, partial decomposition of the molecular skeleton by cleavage of an exocyclic phosphonio substituent had also occurred. Initial formation of **8b** and **8c** as the main products was likewise observed upon treatment of **1**[OTf] with an excess of **7** in pure CH_2Cl_2, but the products were found to decompose completely during the further course of the reaction.

Reaction of **8a**[OTf] with two equivalents of Me_3SiI proceeded with quantitative formation of **1**[OTf] and I_2. No evidence for the formation of a substitution product **9**[OTf] was obtained; this compound is presumably unstable with respect to disproportionation (Scheme 3). A slow, but selective conversion of **8a** into **1** was also observed upon addition of pyridine or NEt_3 to CH_2Cl_2 solutions of **8a**[OTf] and keeping the resulting mixtures for several days; in this case, the nature of the oxidation products was not elucidated.

Scheme 3. (X = Cl, OTf)



NMR-Spectroscopic Investigations

The $\delta^{31}P$ values for the two-coordinate phosphorus atoms in the cations **1** and **5a** and **5b** are shifted to lower field with increasing number of Br substituents, while the resonances of the nuclei in the phosphonio groups and those of the quaternary C-1/C-3 carbon atoms remain essentially unchanged (Table 1). Likewise, the values of both $^2JP^AP^X$ and $^4JP^AP^B$ are very similar for all three compounds. The position of the bromine atom in **5a** follows immediately from the $^1H\{^{31}P\}$-NMR spectrum; the resonances of the hydrogen atoms at the central ring appear as an AMX-type pattern whose middle proton shows a splitting by a large and a small coupling which is characteristic of a 1,2,4-substituted benzene moiety. The $^{1}H\{^{31}P\}$-NMR spectrum of **5b** displays a singlet for the protons adjacent to the bromine atoms which splits into an apparent doublet in an undecoupled spectrum. A correlation peak with the upfield ^{31}P resonance in a $^{1}H,^{31}P$-HMQC spectrum revealed that the splitting must arise from coupling with the two exocyclic phosphorus nuclei rather than the single endocyclic phosphorus nucleus. The magnitude of the $^{n}J_{HP}$ couplings [J = +(−)3.3 and −(+)1.7 Hz] which were determined by iterative analysis suggested attachment of the hydrogen atoms in the 4,7 rather than in the remote 5,6 positions of the fused ring system. This hypothesis was further corroborated by a strong correlation peak connecting the 4-H/7-H and C-1/C-3 signals in a $^{1}H,^{13}C$-HMBC spectrum which is in accord with the presence of a three-bond coupling pathway.

Table 1. ^{31}P-NMR and selected ^{13}C-NMR data of **1, 5a, 5b, 6b, 6c**, and **8a−c**; chemical shifts are given in ppm, coupling constants in Hz; P^A, P^B, and P^X denote the phosphorus nuclei in ABX- or A_2X-spin systems, respectively

	$\delta^{31}P$				$\delta^{13}C$	J_{PC}	
	P^A, P^B	P^X	$^{2}JP^{A,B}P^X$	$^{4}JP^AP^B$	C-1/C-3	$^{1}J_{PC}$	$^{3}J_{PC}$
1[a][b]	16.3	241.8	−91.4	+8.6[c]	109.0	+96.6 (P^A) −56.0 (P^X)	+14.0
5a	16.2 16.1	246.9	90.6 90.3	8.5	110.5 110.3	110 56 (P^X) 112 57 (P^X)	1415
5b	16.0	2 52.9	88.4	8.6[c]	112.00	141.3 (P^A) 58.3 (P^X)	13.7
6b	11.83 11.80	−34.7	44.5	4.5	–	–	–
6c	11.9	−33.0	44.5	4.6[c]	49.53	119.3 123.7	8.1
8a	11.3	49.2	44.7	4.6[c]	46.18	142.2 126.2	7.7
8b	11.40 11.43	50.3	43.9	4.5	–	–	–
8c	11.4	51.7	43.2	–	–	–	–

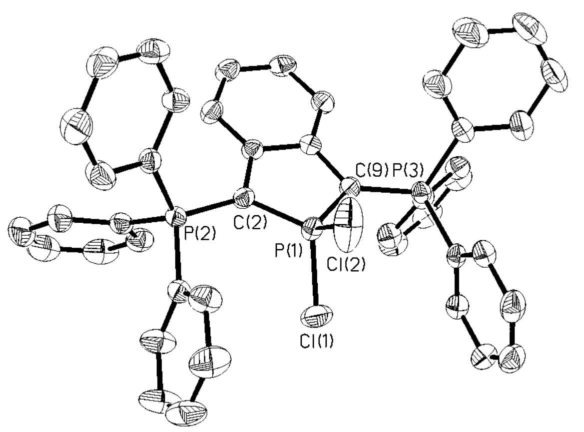
[a] $\delta^{31}P$, $\delta^{13}C$, and $^{2}J_{PP}$ from ref.[1]. – [b] Signs of coupling constants were determined from a two-dimensional $^{31}P,^{13}C$ shift correlation. – [c] Values of $^{4}JP^AP^{A'}$ were obtained from analysis of appropriate ^{13}C satellites in the ^{31}P-NMR spectra.

The $\delta^{31}P$ values of the endocyclic phosphorus atoms in the oxidation products **6b** and **6c** range between those of acyclic dichlorophosphonium salts ($\delta^{31}P$ = 66−104[6]) and 1,1-dichloro-λ^5,σ^4-phosphinines ($\delta^{31}P$ = 7−17[7]), while formal replacement of Cl by Br in **8b** and **8c** induces a comparable upfield shift of d^{31}P as in the cyclophosphazene system[8]. The magnitudes of $^{2}JP^AP^X$ and $^{4}JP^AP^B$ are about half as large as in **1**, **5a** and **5b**. The ^{13}C-NMR signals of the quaternary C-1/C-3 atoms in **6c** and **8a** reveal similar upfield shifts with respect to **1**, **5b** as were previously found for the 1,1-dialkoxy-substituted cations **2**[2], suggesting a pronounced ylidic character for the exocyclic P−C bonds. As in **5b**, the resonance of the 4-H/7-H atoms of **6c** and **8c** appears as a singlet in the $^{1}H\{^{31}P\}$-NMR spectrum and splits to a triplet in the undecoupled spectrum due to coupling with the two exocyclic ^{31}P nuclei.

Molecular Structure of 8a

Crystalline **8a**[OTf] consists of discrete anions and cations and contains an additional solvent molecule per formula unit. No contacts closer than van der Waals distances are exhibited by any of the single components. As in **1**[9], the fused ring system in the cation **8a** (Figure 1) is planar, with a standard deviation of the ring atoms and the two exocyclic phosphorus atoms from the mean plane of 0.030 Å. The difference between endocyclic [1.695(4), 1.697(4) Å] and exocyclic P−C bond lengths [1.723(4), 1.729(4) Å] is similar to **1**[9], but both types of bonds are somewhat shorter than there. The two P−Cl bonds [1.991(2), 2.063(2) Å] differ in length. Both exceed the bond length of 1.91 Å in $[PCl_4][FeCl_4]$[10] and lie between the values of equatorial and axial bonds in PCl_5 (2.02, 2.14 Å[10]). The central P(1) atom displays a distorted tetrahedral coordination, with the C(2)−P(1)−C(9) [99.5(2)°] and Cl(1)−P(1)−Cl(2) angles [97.4(1)°] being significantly more acute than the ideal angle of 109.4°. Interestingly, the two chlorine atoms exhibit a slightly asymmetric arrangement with respect to the plane through P(1), C(2), and C(9), with the longer P(1)−Cl(2) bond showing a larger tilt angle with respect to this plane. Regarding, however, the large thermal ellipsoid at Cl(2) (Figure 1), it remains uncertain if this effect indicates a real structural distortion or is merely the consequence of larger librational motion of the chlorine atom.

Figure 1. ORTEP view (50-% probability ellipsoids) of the cation in crystalline **8a** [OTf][a]

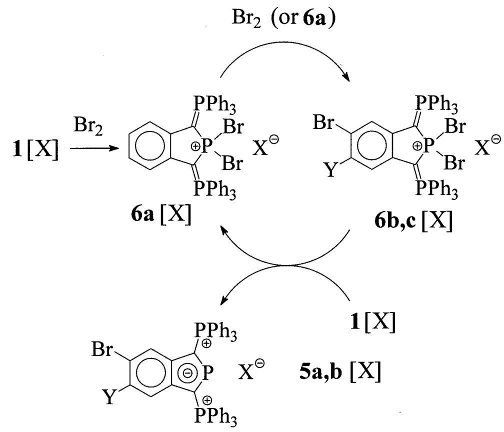


[a] Selected bond lengths [Å] and angles [°]: Cl(1)−P(1) 1.991(2), Cl(2)−P(1) 2.063(2), P(1)−C(2) 1.695(4), P(1)−C(9) 1.697(4), C(2)−P(2) 1.729(4), C(9)−P(3) 1.723(4); Cl(1)−P(1)−Cl(2) 97.4(1), C(2)−P(1)−C(9) 99.5(2), C(2)−P(1)−Cl(1) 116.2(1), C(2)−P(1)−Cl(2) 115.1(2), C(9)−P(1)−Cl(1) 116.9(1), C(9)−P(1)−Cl(2) 112.8(1).

The oxidation of the bis(phosphonio)isophosphindolide cation **1** to the 1,1-dihalogeno derivatives **6b, 6c** and **8a**, as well as the corresponding retro reaction (that is reduction of the formed products to give **1, 5a** and **5b**, respectively) resemble similar reactions of phosphinines[3][7]. The bonding in the products **6** and **8** may be described, as is suggested by the drawings in Scheme 2, in terms of a bis-ylide which receives additional electronic stabilisation by negative hyperconjugation into the central dihalophosphonium moiety[11]. The instability of the corresponding 1,1-diiodo derivative **9** which becomes evident both in the failure to observe oxidation of **1** with I_2 as well as in the formation of **1** and I_2 after treatment of **8a** with Me_3SiI, reflects the lower oxidative power of the heavier halogen.

The reaction of **1** with Br_2 in which the formation of the substituted bis(phosphonio)isophosphindolides **5a** and **5b** precedes the formation of the oxidation products **6b** and **6c** deserves some further comment. In principle, **5a** and **5b** may be generated by either of two mechanisms: (a) direct electrophilic substitution of **1**, or (b) a multistep pathway (Scheme 4) involving initial oxidation of **1** to **6a**, subsequent substitution of the oxidation product to give **6b** and **6c**, and final reaction of these species with **1** under formation of **5a** and **5b** and regeneration of **6a** (because of the recursive nature of the overall reaction, **6a** needs to be present only in a catalytic quantity).

Scheme 4. Proposed mechanism for the formation of **5a** and **5b** during the reaction of **1** with Br_2 (X = Br, OTf; Y = H, Br)



The available experimental results do not allow a definitive determination of the reaction mechanism to be made; however, we favour the second alternative because it allows an explanation of the observed reactions of **1** with Br_2 and $PhICl_2$ in terms of a common mechanism. Moreover, this mechanism is equivalent to the "indirect" electrophilic substitution of λ^3-phosphinines[3], and all crucial steps in the sequence had been verified independently. Thus, reduction of a 1,1-dibromobis(phosphonio)isophosphindolide by **1** is involved in the conproportionation of **6a** and **1** to give **5a** (see above). Furthermore, it was recently shown by Schmidpeter[12] that ylide substituents may activate aromatic ring systems for electrophilic substitution so that a particularly high reactivity for the double ylide substituted benzene moieties in **6a** (and **8a**) is expected. Considering the *o-/p*-directing capability of ylide groups[12], exchange of all four hydrogen atoms in **6a** should in principle be possible. The observed regioselectivity indicates a higher reactivity at the 5,6 positions, while tri- and tetrasubstitution are presumably prevented by the deactivating influence (−I effect) of the halide substituents. The failure to observe **6a** in significant concentration beside the substitution products **6b** and **6c** suggests that either electrophilic substitution of **6a** occurs at a much higher rate or that **6a** exhibits a higher tendency for reductive debromination than **6b** and **6c**; both explanations again highlight the importance of deactivation of the aromatic system by halide substituents. The difference in the reactions of **1** with Br_2, where the formation of the substitution products **5a** and **5b** apparently precedes that of the oxidation product, and with **7**, where this is not the case, may be attributable to a higher kinetic lability and/or lower thermodynamic stability of **6a** as compared to **8a**. This is also in accord with the observed different rates of amine-induced reductive elimination reactions, and was predicted by the lower stability of 1,1-dibromo- as compared to 1,1-dichlorophosphinines[4].

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Experimental Section

General: All manipulations were carried out under dry argon. Solvents were dried using standard procedures. − NMR spectra: Bruker AMX 300 (^1H: 300.13 MHz, ^{13}C: 75.46 MHz, ^{31}P: 121.5 MHz). ^1H,^{31}P(^{13}C)-HMQC- and HMQC-TOCSY spectra were measured using standard pulse sequences from the Bruker Pulse Program library. Spectra of samples in nondeuterated solvents were recorded with suppression of the solvent resonances by presaturation. Chemical shifts were referenced to ext. TMS (^1H 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 4-H to 7-H, and atoms within the C_6H_5 substituents by $C(H)^{para}$, $C(H)^{meta}$; the assignment of the resonances was derived from 2D ^1H,^{13}C-HMQC/HMBC spectra. For ^{13}C-NMR signals which are the X part of AA′MX- or AA′X-spin systems, ΣJ denotes the absolute value of the sum of the couplings to the exocyclic phosphorus nuclei, and J_M the coupling to the endocyclic phosphorus atom. − UV/Vis: Uvikon 860. − Raman Spectra: Bruker RFS 100. − MS: Kratos Concept 1 H, Xe-FAB, *m*-nitrobenzaldehyde matrix; molecular masses refer to the most abundant isotopes. − Melting points were determined in sealed capillaries. − Elemental analyses: Heraeus CHNO-Rapid or Mikroanalytisches Labor Pascher, Remagen.

Reaction of **1**[I] *with* I_2: To a solution of 0.63 g (0.81 mmol) of **1**[I] in 20 ml of CH_2Cl_2 was added 0.21 g (0.81 mmol) of I_2, and the mixture stirred for 30 min at ambient temperature until a clear solution was obtained. Removal of all volatiles in vacuo produced a brown, highly moisture- and air-sensitive solid whose ^1H- and ^{31}P-NMR spectra were identical with those of **1**[I]. UV/Vis and Raman spectroscopy (for data see text) indicated the presence of I_3^- ions, suggesting the formation of **1**[I_3^-]. Attempts at recrystallisation of the product from CH_2Cl_2/Et_2O mixtures failed due to the onset of extensive decomposition reactions.

Reaction of **1**[Br] *with* Br_2: A solution of 4.86 g (30.4 mmol) of Br_2 in 70 ml of CH_2Cl_2 was added dropwise within 2 h to a solution of 5.60 g (7.60 mmol) of **1**[Br] in 30 ml of CH_2Cl_2. Interrupting the reaction at different stages and subjecting an aliquot of the reaction mixture to ^1H- and ^{31}P-NMR-spectroscopic analysis allowed the identification of cations **5a, 5b** and **6b** as reaction intermediates. The red-brown solution resulting at the end of the reaction was concentrated to dryness and the residue redissolved in CH_2Cl_2. Inspection of ^1H-, ^{13}C-, and ^{31}P-NMR spectra revealed the presence of **6c** as the only phosphorus-containing component, together with small amounts (3−5% by integration of ^1H-NMR spectra) of nonphosphorus-containing impurities which were not analysed further. Attempts to purify the crude product by recrystallisation from different solvent mixtures were unsuccessful and promoted increasing decomposition of **6c**.

6b: ^1H NMR (CH_2Cl_2): δ = 7.9−7.7 (m, 30 H, C_6H_5), 6.47 (m, 1 H, 6-H), 6.23 (m, 1 H, 4-H), 6.07 (m, 1 H, 7-H). − $^1H\{^{31}P\}$ NMR (CH_2Cl_2): δ = 7.9−7.7 (m, 30 H, C_6H_5), 6.47 (dd, J_{HH} = 8.3, 1.9 Hz, 1 H, 6-H), 6.23 (d, J_{HH} = 1.9 Hz, 1 H, 4-H), 6.07 (d, J_{HH} = 8.3 Hz, 1 H, 7-H).

6c: ^1H NMR (CH_2Cl_2): δ = 7.88−7.75 (m, 18 H, H^{meta}, H^{para}), 7.71 (m, 12 H, H^{ortho}), 6.30 (t, ΣJ = 3.6 Hz, 2 H, H-4,7). − $^1H\{^{31}P\}$ NMR (CH_2Cl_2): δ = 7.88−7.75 (m, 18 H, H^{meta}, H^{para}), 7.71 (m, 12 H, H^{ortho}), 6.30 (s, 1 H, 4,7-H). − ^{13}C NMR (CH_2Cl_2): δ = 137.48 (m, ΣJ = 18.7 Hz, J_M = 31.2 Hz, C-3a,7a), 134.74 (m, ΣJ = 2.5 Hz, C^{para}), 134.51 (m, ΣJ = 10.9 Hz, C^{ortho}), 130.03 (m, ΣJ = 13.2 Hz, C^{meta}), 121.49 (m, ΣJ = 3.7 Hz, J_M = 18.3 Hz, C-4,7), 119.69 (m, ΣJ = 95.5 Hz, $^3J_{PC}$ = 3.0 Hz, C^{ipso}), 113.3 (d, J_{PC} = 2.5 Hz, C-5,6), 49.53 (ddd, $^1J_{PC}$ = 119.3, 123.7 Hz,$^3J_{PC}$ = 8.1 Hz, C-1,3).

Reduction of **6b and 6c**: To a stirred solution of crude **6c**[Br], which was prepared as described above, was added 3.64 g (36.0 mmol) of dry NEt_3. After continued stirring for 30 min, the reaction mixture was concentrated to dryness, the remaining solid redissolved in 40 ml CH_2Cl_2, and the resulting solution extracted twice with 25 ml of water. The organic phase was separated and dried with Na_2SO_4. Slow addition of 30 ml of ether produced a yellow precipitate which was collected by filtration and washed twice with 20 ml of ether. Recrystallisation from CH_2Cl_2/Et_2O gave 4.48 g of **5b**[Br]$\cdot CH_2Cl_2$ (60%) as a light yellow powder, m.p. 186°C. For the preparation of compound **5a**, 1.00 g of **1**[OTf] and 50 mg (3 mmol) of Br_2 were treated as described above. To the resulting solution, which contained according to an ^{31}P-NMR-spectroscopic analysis approx. 70% of **6b**, was added with stirring 1.00 g (1.24 mmol) of **1**[OTf]. Chromatographic workup (silica gel, eluent: CH_2Cl_2) furnished 100 mg of a white solid which consisted of a mixture of **5a** (60%), **5b** (35%), and **1** (5%) according to an NMR-spectroscopic assay. No further separation by fractional crystallisation was achieved, and NMR-spectroscopic characterisation of **6b** was performed with the crude product mixture.

5a[OTf]: ^1H NMR ($CDCl_3$): δ = 7.72−7.55 (m, 30 H, C_6H_5), 7.03 (br. d, J_{HH} = 1.8 Hz, 1 H, 4-H), 6.95 (dd, J_{HH} = 1.8, 8.7 Hz, 1 H, 6-H), 6.80 (dd, J_{HH} = 8.7 Hz, ΣJ_{PH} = 2 Hz, 1 H, 7-H). − $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ = 7.72−7.55 (m, 30 H, C_6H_5), 7.03 (d, J_{HH} = 1.8 Hz, 1 H, 4-H), 6.95 (dd, J_{HH} = 1.8, 8.7 Hz, 1 H, 6-H), 6.80 (d, J_{HH} = 8.7 Hz, 1 H, 7-H). − ^{13}C NMR ($CDCl_3$): δ = 146.6 (m, C-3a), 144.12 (m, C-7a), 134.52 (s, C^{para}), 134.48 (s, C^{para}), 133.9−133.7 (m, C^{ortho}), 130.20−129.9 (m, C^{meta}), 124.49 (br. s, C-4), 124.47 (br. s, C-6), 122.67 (ddd, J_{PC} = 92/3/3 Hz, C^{ipso}), 122.01 (br. m, C-7), 121.90 (ddd, J_{PC} = 92/2/1 Hz, C^{ipso}), 117.85 (s, C-5), 110.5 (ddd, $^1J_{PC}$ = 110/56 Hz,$^3J_{PC}$ = 14 Hz, C-1,3), 110.3 (ddd, $^1J_{PC}$ = 112/57 Hz,$^3J_{PC}$ = 15 Hz, C-1,3).

5b[Br]: $C_{44}H_{32}Br_3P_3\cdot CH_2Cl_2$ (895.39): calcd. C 55.13, H 3.70; found C 55.41, H 3.88. − UV/Vis (CH_2Cl_2): λ_{max} (lg ε_{max}) = 370 (sh), 345 (4.1), 274 (sh), 261 (4.5) nm. − ^1H NMR ($CDCl_3$): δ = 7.77−7.57 (m, 30 H, C_6H_5), 7.12 {m, iterative analysis as an $[AX]_2$ spin system gave J_{PH} = +(−)3.4, −(+)1.7 Hz, J_{HH} = 0.9 Hz, 2 H, 4,7-H}. − ^{13}C NMR ($CDCl_3$): δ = 144.49 (m, ΣJ = 24.0 Hz, J_M = 2.7 Hz, C-3a,7a), 135.02 (m, ΣJ = 2.3 Hz, C^{para}), 134.23 (m, ΣJ = 9.9 Hz, C^{ortho}), 130.503 (m, ΣJ = 20.2 Hz, C^{meta}), 124.79 (br. m, C-4,7), 121.90 (m, ΣJ = 92.6 Hz, $^3J_{PC}$ = 2.8 Hz, C^{ipso}), 120.52 (q, J_{FC} = 320.2 Hz, CF_3SO_3), 118.09 (s, C-5,6), 112.00 (ddd, $^1J_{PC}$ = 96.9, 58.2 Hz,$^3J_{PC}$ = 13.7 Hz, C-1,3).

Reaction of **1**[OTf] *with* $PhICl_2$: To a stirred solution of 1.50 g (1.86 mmol) of **1**[OTf] in 20 ml of CH_2Cl_2 was added dropwise a solution of 0.51 g (1.86 mmol) of $PhICl_2$ in 20 ml of CH_2Cl_2. Subsequent dropwise addition of 15 ml of Et_2O to the yellow fluorescing solution produced a yellow precipitate which was collected by filtration, washed with Et_2O and dried in vacuo to give 1.48 g of **8a**[OTf]$\cdot CH_2Cl_2$ (91%), m.p. 201°C. The same product was obtained when the reaction was conducted in the presence of 0.55 ml of NEt_3. Reaction of **1**[OTf] with an excess of $PhICl_2$ (1.5 to 4 equiv.) under the same conditions produced, according to ^{31}P-NMR-spectroscopic analysis, complex product mixtures which contained beside unreacted **8a** various amounts of the supposed substitution products **8b** and **8c** and several components whose resonances appeared as singlets or AX-type patterns. With the exception of a singlet at δ = 63.4 which was assigned to $[ClPPh_3]^+$ by comparison with an authentic sample, none of these products was identified. Separation of the mixtures and isolation of individual compunds proved not to be feasible.

8a[OTf]: $C_{45}H_{34}Cl_2F_3P_3SO_3\cdot CH_2Cl_2$ (960.58): calcd. C 57.52, H 3.78; found C 56.98, H 3.66. − ^1H NMR ($CDCl_3$): δ = 7.74−7.57 (m, 30 H, C_6H_5), 6.41 (m, 2 H, 5,6-H), 6.21 (m, 2 H, 4,7-H). − ^{13}C NMR ($CDCl_3$): δ = 135.69 (m, ΣJ = 18.7 Hz, J_M = 33.5 Hz, C-3a,7a), 134.86 (m, ΣJ = 3 Hz, C^{para}), 134.72 (m, ΣJ = 10.7 Hz, C^{ortho}), 130.33 (m, ΣJ = 13.0 Hz, C^{meta}), 121.36 (q, J_{FC} = 320.9 Hz, CF_3SO_3), 119.76 (d, J = 2.5 Hz, C-5,6), 118.66 (m, ΣJ = 4 Hz, J_M = 19.8, C-4,7), 121.38 (m, ΣJ = 92.7 Hz, $^3J_{PC}$ = 3.2 Hz, C^{ipso}), 46.18 (ddd, $^1J_{PC}$ = 142.2, 126.2 Hz,$^3J_{PC}$ = 7.7 Hz, C-1,3).

Crystal-Structure Determination of **8a**[OTf] *at 200(2) K:* $[C_{44}H_{34}Cl_2P_3][CF_3SO_3]\cdot CH_2Cl_2$, M = 960.52, yellow plates, crystal size 0.30 × 0.23 × 0.20 mm, monoclinic, space group $P2_1/c$ (no. 14): a = 12.4581(4), b = 22.5518(6), c = 16.5854(6) Å, β = 104.852(4)°, V = 4504.0(2) Å^3, Z = 4, $\rho_{calcd.}$ = 1.416 Mg m^{-3}, $F(000)$ = 1968, μ(Cu-K_α) = 4.28 mm^{-1}. 8443 reflections (8143 independent reflections with R_{int} = 0.032) were collected with an Enraf-Nonius MACH3 diffractometer (Cu-K_α radiation, graphite monochromator, $2\theta/\omega$ scans) in the range $3° \le \theta \le 68°$ $(-14 \le h \le 14, -27 \le k \le 0, 0 \le l \le 19)$. Of these, 8142 were used for structure solution (direct methods) and refinement (full-matrix least squares on F^2, 542 parameters and 82 restraints, nonhydrogen atoms anisotropic, hydrogen atoms with a "riding" model); wR_2 = 0.176 $\{R_1[I > 2\sigma(I)] = 0.066\}$. A semiempirical absorption correction on the basis of ψ scans and an extinction correction were applied. Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the number CCDC-100692. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: internat.+44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

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