N-Thiophosphorylated and *N*-Phosphorylated Iminophosphoranes [$R_3P{=}N{-}P(X)R'_2$; X = O, S] as Models for Dendrimers: Synthesis, Reactivity and Crystal Structures

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Several $R_3P{=}N{-}P(X)R'_2$ and $Fe[C_5H_4Ph_2P{=}N{-}P(X)R'_2]_2$ derivatives (X = S, O) are readily obtained from Staudinger reactions between phosphanes and $N_3{-}P(X)R'_2$. The P=N–P=X groups are easily alkylated on the X atom with methyl or isopropyl triflates. The alkylation induces a lengthening of the P–X bond, as shown by X-ray diffraction studies. This corresponds to a weakening of the P–X bond which can be cleaved with $P(NMe_2)_3$ to yield [P=N–P:] linkages. The presence of tricoordinated phosphorus atoms opens the way to a versatile reactivity, including the reaction with alkyl iodides and functionalized azides. These molecules are good models for screening which types of reagents and reactions could be used with macromolecules possessing also P=N–P=X linkages, such as dendrimers.

Introduction

N-Thiophosphorylated iminophosphoranes are known since more than 40 years, but have only attracted a moderate interest up to now as illustrated by the relative small number of $R_3P{=}N{-}P(S)R'_2$ compounds already described[1] (approximately 100). However, we have recently demonstrated the great synthetic interest of the P=N−P=S linkage for the building of very complex hyperbranched nanosized macromolecules, namely dendrimers.[2] Furthermore, the P=N−P=S linkages included in phosphorus-containing dendrimers[3] display a versatile and chemoselective reactivity[4] which leads to the unprecedented grafting of various functional groups[5] or new branches[6] within the dendritic architecture when and where desired.

The chemistry of dendrimers is fascinating but generally suffers from two drawbacks: the synthesis requires multistep procedures which are time-consuming, and the reactivity (as well as the synthesis) necessitates to use only reactions with quantitative yields. Thus, it is highly desirable to have models for dendrimers, in order to study the reactivity on small molecules easy to synthesize and to characterize, and to choose the type of reactions and reagents which could be used later with dendrimers. In this paper, we describe the synthesis of various *N*-thiophosphorylated iminophosphoranes, their reactivity toward strong electrophiles such as alkyl triflates, their desulfurization reactions leading to [P=N−P:] linkages, and Staudinger reactions of these linkages with functionalized azides. A few *N*-phosphorylated iminophosphoranes (P=N−P=O linkages) are also described to be compared with their thiophosphorylated analogues. The structure of four derivatives of ferrocene possessing two P=N−P=X or two [P−N−P−X−Me]$^+$ (X = S, O) groups determined by X-ray diffraction is also presented.

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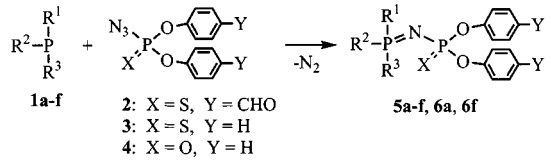
Results and Discussion

Syntheses

The method of synthesis we have used to obtain the P=N−P=X (X = S, O) linkages is the Staudinger reaction between phosphanes **1a−f** and phosphorylated azides **2−4** (Scheme 1). In all cases, the reaction proceeds rapidly at room temperature with evolution of nitrogen as sole by-product, and leads to compounds **5** (X = S) and **6** (X = O) in quantitative yields as crude products and in very good yields after work up, with the exception of compound **5d** which is isolated only in 70% yield. This lower yield is presumably due to the presence of two C≡C groups in compound **1d**, which are known to undergo cycloaddition reac-



1a-f **2**: X = S, Y = CHO; **3**: X = S, Y = H; **4**: X = O, Y = H **5a-f, 6a, 6f**

Compounds **5** and **6**	R^1	R^2	R^3	X	Y
5a	Ph	Ph	Ph	S	CHO
5b	*p*Cl-C_6H_4	*p*Cl-C_6H_4	*p*Cl-C_6H_4	S	CHO
5c	CH_2CH_2CN	CH_2CH_2CN	CH_2CH_2CN	S	CHO
5d	tBu	C≡C-Ph	C≡C-Ph	S	CHO
5e	Ph			S	H
5f	Me	Ph	Ph	S	H
6a	Ph	Ph	Ph	O	H
6f	Me	Ph	Ph	O	H

Scheme 1. Synthesis of *N*-(thio)-phosphorylated iminophosphoranes

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tions with azides,[7] lowering the amount of the desired product **5d**.

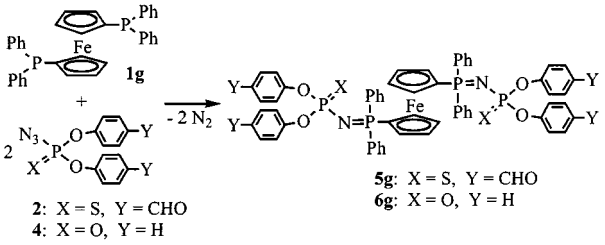
The occurrence of the Staudinger reaction is characterized in the ^{31}P-NMR spectra by the appearance of a system of two doublets, with $^2J_{PP} \approx 30$ Hz for all compounds except for **5d** (Table 1). The chemical shift is $\delta \approx 51$ for the P=S groups, and $\delta \approx -7$ for the P=O groups, for all compounds. The chemical shift of the $R^1R^2R^3P{=}N$ groups strongly depends on the $R^1R^2R^3$ substituents linked to this phosphorus atom, but is almost insensitive to the presence of sulfur or oxygen double bonded to the other phosphorus atom, as shown by the comparison between **5a** [X = S; δ(P=N) = 14.9] and **6a** [X = O; δ(P=N) = 13.7].

Table 1. ^{31}P-NMR data

	Compounds **5**, **6**			Compounds **7**–**11**		
	δ(P=N)	δ(P=X)	$^2J_{PP}$	δ(P=N)	δ(P=X)	$^2J_{PP}$
5a, **7a**	14.9	50.5	30[a]	22.8	23.4	20[a]
9a				22.4*	21.5*	17[a]
5b, **7b**	12.9	50.5	32[b]	26.2	31.4	23[b]
5c, **7c**	30.5	50.5	28[b]	45.7	28.9	10[b]
5d, **7d**	−8.9	52.2	6[a]	−4.7	28.5	5[a]
5e, **7e**	47.9	52.6	29[a]	53.7	24.6	12[a]
5f, **7f**	15.3	52.8	32[a]	24.2*	23.2*	20[a]
5g, **7g**	16.1	49.2	32[a]	25.4	23.9	23[a]
6a, **8a**	13.7	−7.9	32[a]	21.8	−10.0	35[a]
10a				21.7	−12.1	21[a]
6f, **8f**	15.2	−6.2	31[a]	24.2	−9.3	32[a]
11f				23.2	−18.6	33[a]
6g, **8g**	14.5	−8.6	37[a]	25.2	−9.7	35[a]

[a] In $CDCl_3$. – [b] In CD_3COCD_3. – * In these cases, the assignment of the chemical shift to P=N or P–S–R is ambiguous.

Analogous reactions applied to the 4,4′-bis(diphenylphosphanyl)ferrocene **1g** and compounds **2** and **4** lead to the quantitative formation of derivatives **5g** (X = S, Y = CHO) and **6g** (X = O, Y = H) possessing two P=N–P=X linkages (Scheme 2). These compounds display characteristic ^{31}P-NMR data (Table 1).



Scheme 2. Synthesis of bis[*N*-(thio)-phosphorylated iminophosphoranyl]ferrocenes

The structure of both compounds was also determined by X-ray diffraction studies (Table 2). Selected bond lengths and bond angles are gathered in Table 3. Figures 1 and 2 show the molecular structure of compounds **5g** and **6g**, respectively. The dihedral angle between the substituents of the Cp rings is 142.73° for compounds **5g** and 180° for compound **6g**. This position favors a large distance between the "branches", thus compound **5g** has been used as a tetrafunctional core for the synthesis of dendrimers.[8] The P=N–P moieties of the P=N–P=X linkage is very similar for both compounds **5g** and **6g**. Furthermore, the P–N bond lengths are almost equal {*d*[P(1)–N(1)] = 1.559(4) Å and *d*[N(1)–P(2)] = 1.569(4) Å for **5g**; 1.568(2) Å and 1.578(2) Å, respectively, for **6g**}. The P=S [1.918(2) Å] and P=O [1.450(2) Å] bond lengths are classical.

Reactivity

A few alkylations of the sulfur atom of P=N–P=S linkages have already been reported,[9] for instance with methyl iodide,[9a] but this reagent does not react neither with compounds **5**, nor with compounds **6**, so stronger electrophiles are needed. For this purpose, methyl trifluoromethanesulfonate is first used as alkylating agent. The reaction carried out with compounds **5a–g**, **6a**, **6f**, and **6g** leads immediately, and in quantitative yield except for compound **7d**, to the formation of cationic compounds possessing one (**7a–f**, **8a**, **8f**) or two (**7g**, **8g**) $[P{-}N{=}P{-}X{-}Me]^+$ linkages (Scheme 3).

Two different behaviors are observed in the ^{31}P-NMR spectra, depending on the nature of the X atom. The alkylation of the thiophosphoryl groups induces a large shielding of the signal corresponding to the P=S group, from $\delta \approx 51$ to $\delta \approx 25$, while the signal corresponding to the P=N group is deshielded (Table 1). In several cases, the chemical-shift values corresponding to the P=N and P–S–Me groups are very close, but their attribution is unambiguous, on the basis of ^{31}P-NMR spectra with proton couplings, except for compound **7f**. On the other hand, the alkylation of the phosphoryl groups induces only a slight shielding of the signal corresponding to the P=O groups ($\Delta\delta_{max} = 3$) and a deshielding of the signal corresponding to the P=N groups ($\Delta\delta \approx 10$). The value of the $^2J_{PP}$ coupling constant is lowered when X = S (for the transformation **5** → **7**), and slightly increased when X = O (**6** → **8**) (Table 1).

To ascertain the occurrence of the alkylation reaction on the sulfur or oxygen and not on the nitrogen atom or on the aldehyde groups, the structure of compounds **7g** and **8g** was determined by X-ray diffraction (Table 2). Figures 3 and 4 show the molecular structure of the cationic moieties of compounds **7g** and **8g**, respectively. These drawings confirm without any ambiguity that alkylation took place on the sulfur (**7g**) and oxygen atom (**8g**). Selected bond lengths and bond angles for both compounds are gathered in Table 3. The alkylation induces in both cases a lengthening of the P=N [P(1)–N(1)], P=X [P(2)–S(2) or P(2)–O(3)], and O–C(Ar) bond lengths and a shortening of the N–P [N(1)–P(2)] and P–O [P(2)–O(1) and P(2)–O(2)] bond lengths; the six P–O bond lengths are equivalent for compound **8g**. All these phenomena, as well as the deshielding observed for the signal of the P=N groups in the ^{31}P-NMR spectra, indicate that the positive charge is partly localized on this phosphorus atom.

Other triflates can react with the P=N–P=X linkages, for instance isopropyl trifluoromethanesulfonate. The reaction proceeds in the same conditions than with methyl triflate, to afford compounds **9a** and **10a**, from **5a** and **6a**,

Table 2. Crystal data for compounds **5g**, **6g**, **7g** and **8g**

	5g	**6g**	**7g**	**8g**
Emp. formula	$C_{62}H_{48}N_2O_8P_4S_2Fe$	$C_{58}H_{48}N_2O_6P_4Fe$	$C_{64}H_{54}N_2O_8P_4S_2Fe[CF_3SO_3]_2 \cdot 3/2CH_2Cl_2$	$C_{60}H_{54}N_2O_6P_4Fe[CF_3SO_3]_2$
Mol. mass	1192.94	1048.76	1648.52	1376.96
Cryst. system	monoclinic	triclinic	triclinic	monoclinic
Space group	*C*2/*c*	$P\bar{1}$	*P*1	*C*2/*c*
a [Å]	14.420(3)	9.463(2)	10.855(2)	16.844(2)
b [Å]	13.994(4)	10.945(2)	11.091(2)	12.520(2)
c [Å]	28.927(5)	11.961(3)	16.416(2)	29.807(3)
α [°]		88.35(2)	75.41(2)	
β [°]	103.70(2)	86.20(2)	84.91(2)	97.415(9)
γ [°]		89.21(2)	75.84(2)	
V [Å^3]	5673(3)	1235(2)	1854(2)	6233(2)
Z	4	1	1	4

Table 3. Selected bond lengths and bond angles for compounds **5g**, **6g**, **7g** and **8g**

Bond lengths [Å] Bond angles [°]	**5g**	**6g**	**7g**	**8g**
d[P(1)−N(1)]	1.559(4)	1.568(2)	1.60(1)	1.583(4)
d[P(2)−N(1)]	1.569(4)	1.578(2)	1.53(1)	1.535(4)
d[P(2)−S(2)]	1.918(2)		2.045(4)	
d[P(2)−O(3)]		1.450(2)		1.547(4)
d[P(2)−O(1)]	1.630(3)	1.604(2)	1.587(8)	1.553(4)
d[P(2)−O(2)]	1.632(3)	1.607(2)	1.564(9)	1.551(4)
d[O(1)−C(211)]	1.373(6)	1.404(2)	1.38(2)	1.423(6)
d[O(2)−C(221)]	1.389(6)	1.396(2)	1.42(2)	1.421(6)
d[S(2)−C(11)]			1.88(2)	
d[O(3)−C(6)]				1.447(7)
P(1)−N(1)−P(2)	137.2(3)	136.8(1)	140.7(6)	137.5(3)
N(1)−P(2)−S(2)	121.9(2)		113.6(4)	
N(1)−P(2)−O(3)		120.43(9)		117.7(2)
Dihedral angle between the substituents of the Cp rings [°]	142.73	180	148.87	116.95

respectively (Scheme 4, Table 1). An analogous behavior is observed with trimethylsilyl triflate. The oxophilicity of silicon induces the formation of the cationic compound **11f** from **6f** (Scheme 5). The ^{31}P-NMR spectrum displays the expected shielding of the signal corresponding to the PO groups from δ = −6.2 to −18.6 (Table 1). However, it must be noted that this compound is much more sensitive to moisture than the corresponding methylated analogue, thus for practical purposes, the use of trimethylsilyl triflate has not been extended to other compounds, and only the reactivity of cationic compounds **7** and **8** has been explored.

In fact, we have focused our attention on the reactivity of compounds **7**, because the methylation reaction of compounds **5** is more easily monitored by ^{31}P-NMR spectroscopy than that of compounds **6**. The lengthening of the P=S bond after methylation [1.918(2) Å for **5g**, 2.034(5) and 2.040(5) Å for **7g**] should induce a weakening of this bond which could be cleaved, leading to the formation of [P=N−P:] linkages incorporating a tricoordinated phosphorus atom. First experiments are conducted with compound **7f** which is the best model for dendrimers. The desulfurization reaction occurs easily at room temperature when tris(dimethylamino)phosphane is added to a solution of **7f** in CH_2Cl_2.[10] The reaction proceeds with a transfer of the S−Me$^+$ group from **7f** to $P(NMe_2)_3$, leading to compound **12f** and $[MeS-P(NMe_2)_3]^+$ (Scheme 6).

The reaction is monitored by ^{31}P-NMR spectroscopy, which shows the appearance of two doublets at δ = 143.9 (P:) and 9.9 (P=N) ($^2J_{PP}$ = 32 Hz) for **12f** and one singlet at δ = 68 for $[MeS-P(NMe_2)_3]^+$. These data indicate that only the P−S bond is cleaved, and not the P−O or P−N bonds. Compound **12f** is very sensitive toward oxidation, therefore it is not really isolated but only cleared of $[MeS-P(NMe_2)_3][CF_3SO_3]$. The presence of a tricoordinated phosphorus atom in compound **12f** should lead to a versatile reactivity. For instance, compound **12f** can react with electrophiles such as allyl iodide (Scheme 6). The formation of the phosphonium salt **13f** is characterized by ^{31}P-NMR spectroscopy, with the appearance of two doublets at δ = 27.3 and 28.9 ($^2J_{PP}$ = 20 Hz). This reaction, which allows the grafting of functional groups, has been extended to the reactivity of the internal layers of dendrimers.[5b]

Compound **12f** also reacts with azides, such as 4-azidophenyl isothiocyanate. The Staudinger reaction occurs readily to give compound **14f**, characterized in the ^{31}P-NMR spectrum by the presence of two doublets at δ = 15.3 (P=N) and −7.7 (N−P=N) ($^2J_{PP}$ = 16 Hz). This compound can be isolated to be characterized also by ^{1}H- and ^{13}C-NMR spectroscopy, but it decomposes within a few days when left in solution, to give compound **5f** as the sole phosphorus-containing compound. The decomposition probably proceeds by an aza Wittig reaction between the P=N and

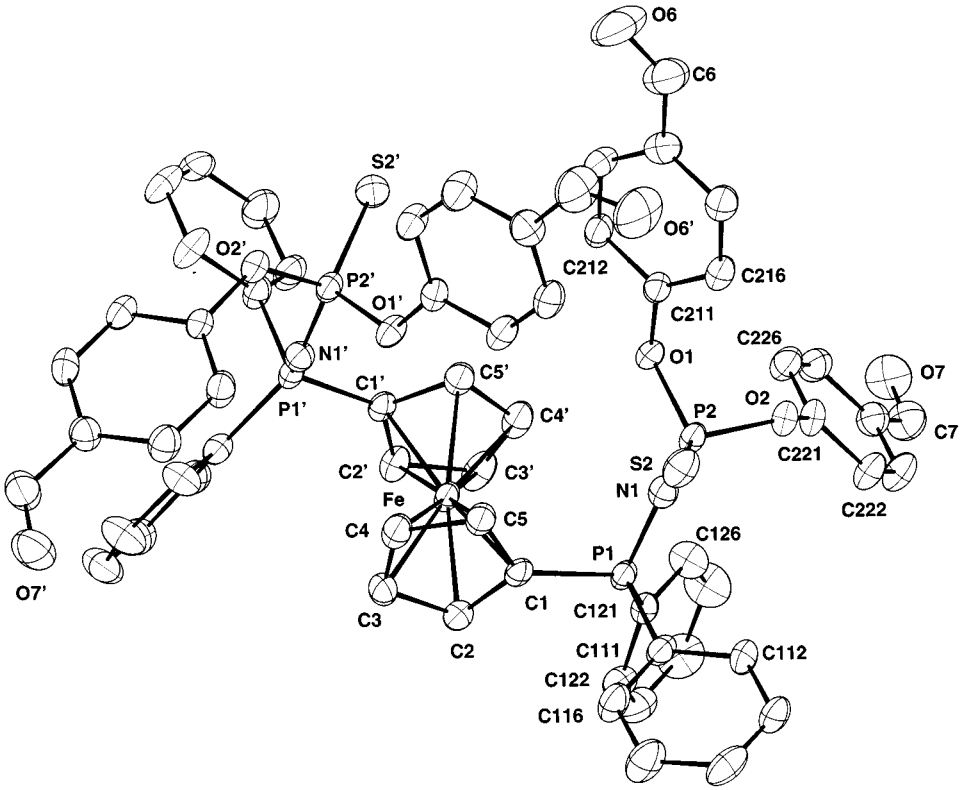


Figure 1. Molecular structure of compound **5g**

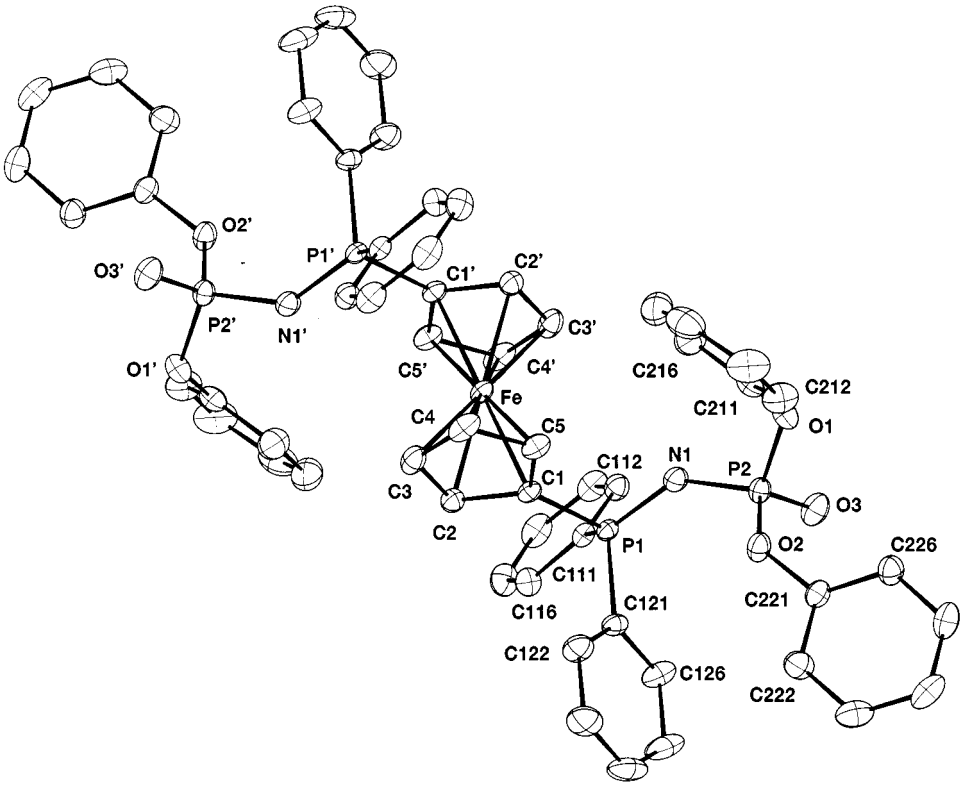
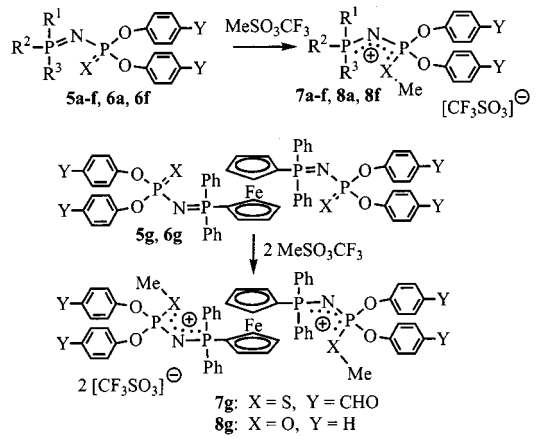


Figure 2. Molecular structure of compound **6g**

C=S bonds. This reaction is presumably intermolecular; indeed, the intramolecular reaction is unlikely from a geometric point of view. Furthermore, the use of the same azide in the internal layers of dendrimers gives stable com-



Scheme 3. Methylation of P=N−P=X linkages

(δ = 17.9, $^2J_{PP}$ = 23 Hz, *P*=N−P=N−P=S; δ = 45.9, $^2J_{PP}$ = 63 Hz, P=N−P=N−*P*=S) and one doublet of doublet (δ = −14.3, P=N−*P*=N−P=S) in the ^{31}P-NMR spectrum. The sequence of reactions **5g** → **7g** → **12g** → **15g** which allows the grafting of aldehyde groups is of crucial importance for the growing of new branches within a dendritic framework.[6]

The P=S group of the P=N−P=N−P=S linkage possesses the same properties than those included in P=N−P=S linkages. Indeed, methylation with $MeSO_3CF_3$ occurs on the sulfur atom, as shown by the large shielding of the doublet corresponding to the P=S groups in the ^{31}P-NMR spectrum from δ = 45.9 ($^2J_{PP}$ = 63.5 Hz) for **15g** to δ = 20.0 ($^2J_{PP}$ = 51 Hz) for **16g**. The slight deshielding observed for the doublet corresponding to the *P*=N−P=N−P=S groups from δ = 17.9 ($^2J_{PP}$ = 23.2 Hz) for **15g** to δ = 21.5

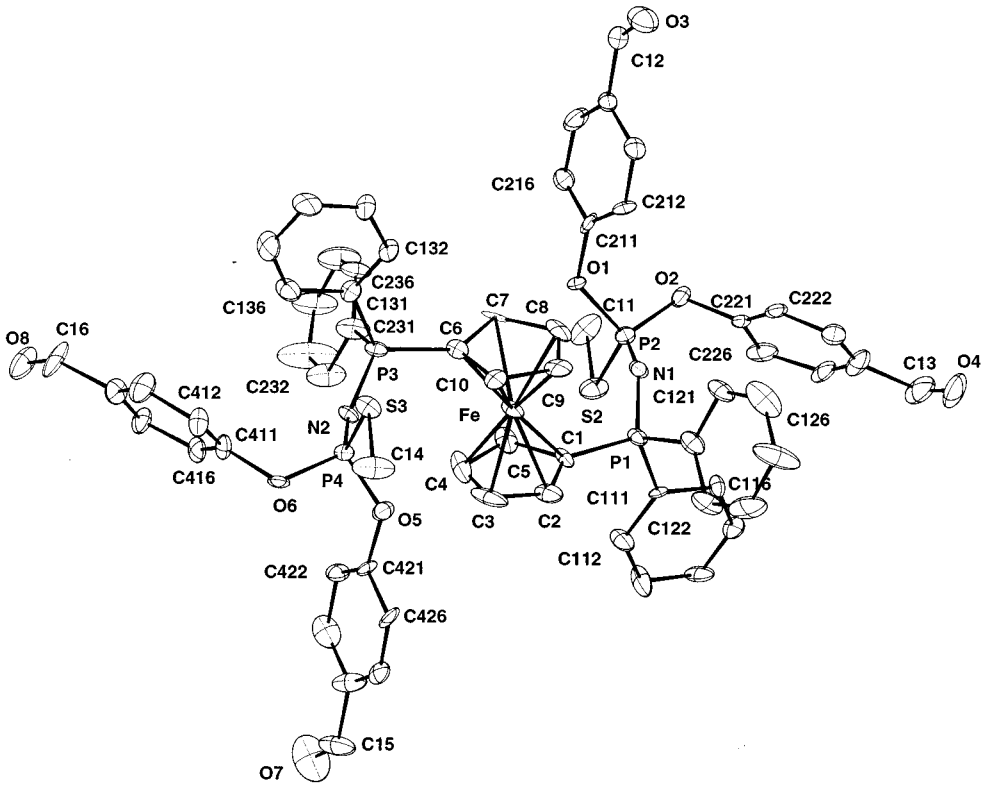


Figure 3. Molecular structure of compound **7g**; the anionic counterion is omitted for clarity

pounds which do not decompose within several days in solution. One can presume that the P=N and C=S bonds of the internal layers of two molecules of dendrimer cannot interact for steric reasons, and that the reaction between two branches of one dendrimer is also unlikely for geometric and topographic reasons.[5b]

The desulfurization reaction can be applied also to the dicationic ferrocene derivative **7g**, leading to the formation of compound **12g** (Scheme 7). The Staudinger reaction of two equivalents of the azide **2** with the ferrocene derivative **12g** affords compound **15g** in quantitative yield. The formation of both P=N−P=N−P=S linkages induces the appearance of a very characteristic system of two doublets ($^2J_{PP}$ = 30 Hz) for **16g**, indicates a delocalization of the positive charge all along this linkage. The chemical shift of the doublet of doublet corresponding to P=N−*P*=N−P=S is almost insensitive to this reaction (δ = −14.3 for **15g**, δ = −16.9 for **16g**).

Conclusion

Various compounds possessing P=N−P=X (X = S, O) linkages have been prepared and their reactivity toward various electrophiles has been tested, leading in all cases to the alkylation of the X atom of this linkage, as shown by

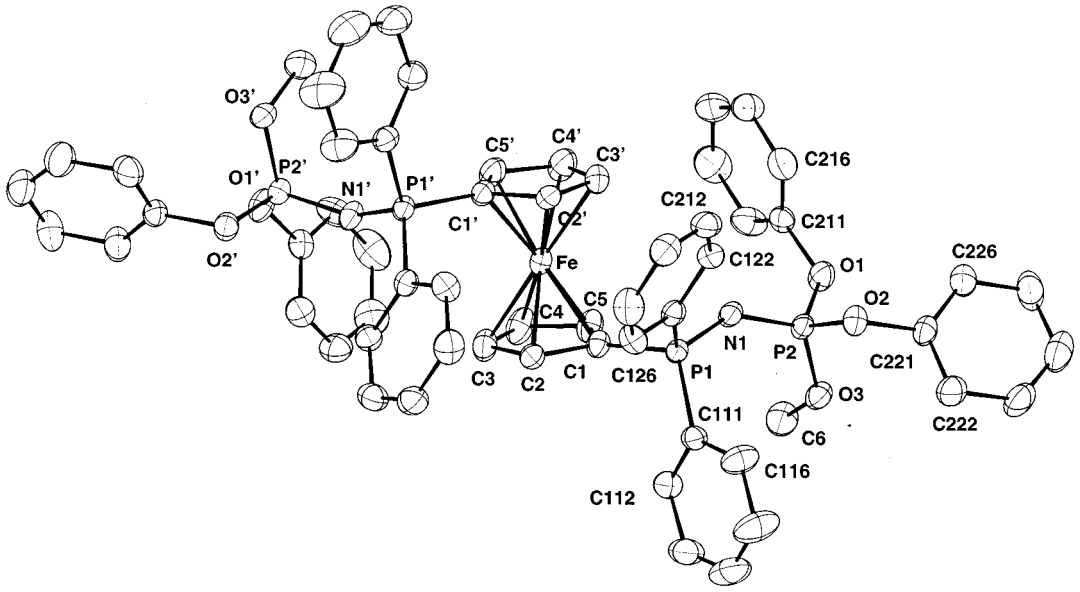
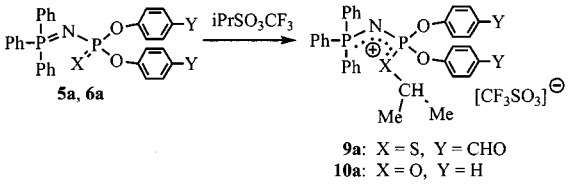
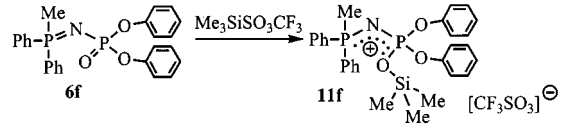


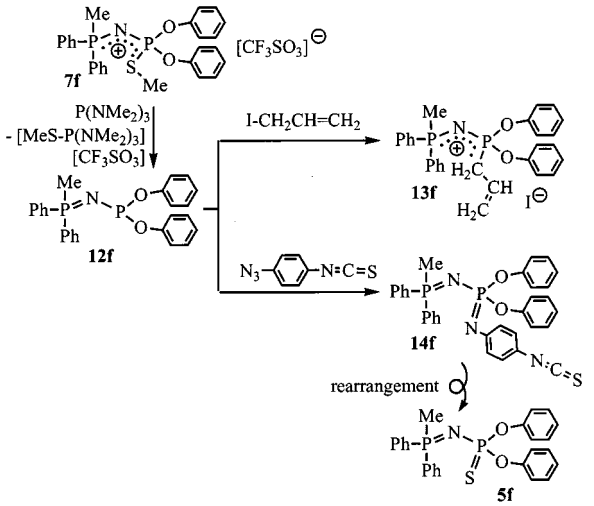
Figure 4. Molecular structure of compound **8g**; the anionic counterion is omitted for clarity



Scheme 4. Alkylation of P=N−P=X lnkage with $iPr_2SO_3CF_3$

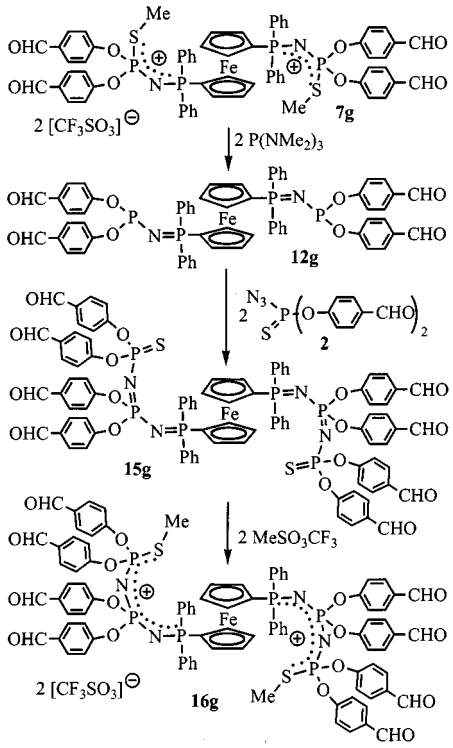


Scheme 5. Alkylation of P=N−P=O linkage with $Me_3SiSO_3CF_3$



Scheme 6. Desulfurization of a P−N−P−S−Me linkage and subsequent reactions

^{31}P-NMR and X-ray diffraction studies. These compounds, particularly $Ph_2MeP{=}N{-}P(S)(OPh)_2$ (**5f**), and $Fe[C_5H_4P\text{-}Ph_2{=}NP(S)(OC_6H_4CHO)_2]_2$ (**5g**) are interesting models to check what type of reactions and reagents could be applied later to dendrimers possessing also P=N−P=S linkages. In this perspective, the desulfurization leading to tricoordinated phosphorus atoms has a great synthetic interest, and has opened the way to a very original field of the chemistry of dendrimers: the grafting of various functional groups and branches in the internal layers of dendrimers after their construction.[5][6]



Scheme 7. Desulfurization of compound **7g** and subsequent reactions

Experimental Section

General: All manipulations were carried out with standard high-vacuum and dry-argon techniques. – ^{1}H-, ^{13}C-, ^{31}P-, and ^{19}F-NMR spectra were recorded with Bruker AC200, AC250 or AMX 400 spectrometers. References for NMR chemical shifts are: $SiMe_4$ for ^{1}H and ^{13}C NMR, 85% H_3PO_4 for ^{31}P NMR, CF_3COOH for ^{19}F NMR. The numbering used for NMR assignments is depicted in Figure 5. – Melting points are uncorrected. – Compounds $N_3P(S)(OC_6H_4CHO)_2$,[11] *t*BuP(C≡CPh)$_2$,[11] Ph(C_4H_6P)[12] and CF_3SO_3*i*Pr,[13] were synthesized according to published procedures. – CF_3SO_3*i*Pr was freshly prepared each time.

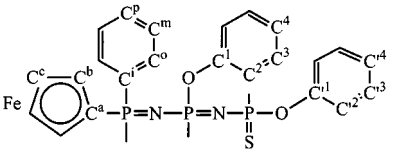


Figure 5. Numbering used for NMR

General Procedure for 5a, 5b, 5d, 5e, 5f, 6a, 6f: To a solution of 3 mmol of compound **2**, **3**, or **4** in THF (10 mL) was added at room temperature a solution of 3 mmol of phosphane **1a,b,d–f** in THF (5 mL). The resulting solution was stirred at room temperature (or at 55°C for **5d**) until the evolution of nitrogen ceases. The solution was concentrated to dryness under vacuum. The residue was washed with ether, then with pentane to afford **5a**, **5b**, **5f**, **6a**, **6f** as powders and **5d**, **5e** as oils.

Synthesis of Compound 5c: The procedure is analogous to the previous one, using CH_3CN instead of THF. Compound **5c** was isolated as an oil.

General Procedure for 5g and 6g: To a solution of 3 mmol of compound **2** or **4** in THF (10 mL) was added at room temperature a solution of 1.5 mmol of 4,4′-bis(diphenylphosphanyl)ferrocene **1g** in THF (10 mL). The resulting solution was stirred at room temperature until the evolution of nitrogen ceased. The solution was concentrated to dryness under vacuum. The residue was washed with ether, then with pentane to give **5g**, **6g** as orange powders. Crystallization at −30°C in CH_2Cl_2 for **5g** and in CH_2Cl_2/pentane (1:1) for **6g** afforded single crystals suitable for X-ray diffraction.

Compound 5a: 97% yield, white powder, m.p. 131°C. – ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 14.9 (d, $^2J_{PP}$ = 30.0 Hz, P=N), 50.1 (d, $^2J_{PP}$ = 30.0 Hz, P=S). – ^{1}H NMR ($CDCl_3$): δ = 7.27–7.78 (m, 23 H, C_6H_4, C_6H_5), 9.90 (s, 2 H, CHO). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 121.8 (d, $^3J_{CP}$ = 5.5 Hz, C^2), 128.0 (dd, $^1J_{CP}$ = 106.5 Hz, $^3J_{CP}$ = 3.8 Hz, C^i), 128.5 (d, $^3J_{CP}$ = 13.0 Hz, C^m), 130.9 (s, C^3), 132.4 (d, $^2J_{CP}$ = 10.5 Hz, C^o), 132.6 (br. s, C^4, C^p), 156.6 (d, $^2J_{CP}$ = 9.6 Hz, C^1), 190.8 (s, CHO). – IR (KBr): $\tilde{\nu}$ = 1701 cm^{-1} (C=O). – $C_{32}H_{25}N_1O_4P_2S$ (581.6): calcd. C 66.09, H 4.33, N 2.41; found C 66.30, H 4.49, N 2.36.

Compound 5b: 95% yield, white powder, m.p. 102°C. – ^{31}P{^{1}H} NMR (CD_3COCD_3): δ = 12.9 (d, $^2J_{PP}$ = 32.0 Hz, P=N), 50.5 (d, $^2J_{PP}$ = 32.0 Hz, P=S). – ^{1}H NMR (CD_3COCD_3): δ = 7.56–8.04 (m, 20 H, C_6H_4), 10.10 (s, 2 H, CHO). – ^{13}C{^{1}H} NMR (CD_3COCD_3): δ = 122.2 (d, $^3J_{CP}$ = 5.0 Hz, C^2), 129.3 (d, $^3J_{CP}$ = 14.0 Hz, C^m), 131.0 (s, C^3), 133.2 (s, C^4), 134.0 (dd, $^1J_{CP}$ = 58.3 Hz, $^3J_{CP}$ = 12.0 Hz, C^i), 134.4 (d, $^2J_{CP}$ = 12.5 Hz, C^o), 139.4 (d, $^4J_{CP}$ = 4.8 Hz, C^p), 156.5 (d, $^2J_{CP}$ = 8.5 Hz, C^1), 190.7 (s, CHO). – IR (KBr): $\tilde{\nu}$ = 1696 cm^{-1} (C=O). – $C_{32}H_{22}Cl_3N_1O_4P_2S$ (684.9): calcd. C 56.09, H 3.21, N 2.04; found C 56.39, H 3.31, N 1.97.

Compound 5c: 94% yield, white viscous oil. – ^{31}P{^{1}H} NMR (CD_3COCD_3): δ = 30.5 (d, $^2J_{PP}$ = 28.0 Hz, P=N), 50.5 (d, $^2J_{PP}$ = 28.0 Hz, P=S). – ^{1}H NMR (CD_3COCD_3): δ = 2.68–3.00 (m, 12 H, CH_2–CH_2), 7.57 (m, 4 H, C_6H_4), 8.97 (m, 4 H, C_6H_4), 10.0 (s, 2 H, CHO). – ^{13}C{^{1}H} NMR (CD_3COCD_3): δ = 21.5 (d, $^1J_{CP}$ = 3.0 Hz, *C*H$_2$P), 22.7 (s, *C*H$_2$CH$_2$P), 118.7 (s, C≡N), 122.1 (d, $^3J_{CP}$ = 4.7 Hz, C^2), 131.1 (br. s, C^3), 133.3 (s, C^4), 156.2 (d, $^2J_{CP}$ = 8.4 Hz, C^1), 191.0 (s, CHO). – IR (THF): $\tilde{\nu}$ = 2210 (C≡N), 1701 (C=O) cm^{-1}. – $C_{23}H_{22}N_4O_4P_2S$ (512.5): calcd. C 53.91, H 4.33, N 10.93; found C 53.67, H 4.43, N 10.81.

Compound 5d: 70% yield, yellow viscous oil. – ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −8.9 (d, $^2J_{PP}$ = 6.0 Hz, P=N), 52.2 (d, $^2J_{PP}$ = 6.0 Hz, P=S). – ^{1}H NMR ($CDCl_3$): δ = 1.30 (d, $^3J_{HP}$ = 21.0 Hz, 9 H, CH_3), 7.24–7.94 (m, 18 H, C_6H_4, C_6H_5), 9.83 (s, 2 H, CHO). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 22.7 (d, $^2J_{CP}$ = 1.9 Hz, CH_3), 34.1 (dd, $^1J_{CP}$ = 103.1 Hz, $^3J_{CP}$ = 7.0 Hz, *C*-CH_3), 76.7 (d, $^1J_{CP}$ = 186.9 Hz, ≡C–P), 106.4 (d, $^2J_{CP}$ = 31.5 Hz, *C*≡C–P), 118.7 (d, $^3J_{CP}$ = 4.4 Hz, C^i), 121.9 (d, $^3J_{CP}$ = 5.1 Hz, C^2), 128.4 (s, C^m), 130.8 (s, C^3), 131.4 (s, C^p), 132.4 (br. s, C^4, C^o), 156.5 (d, $^2J_{CP}$ = 8.3 Hz, C^1), 190.7 (s, CHO). – IR (THF): $\tilde{\nu}$ = 2170 (C≡C), 1701 (C=O) cm^{-1}. – $C_{34}H_{29}N_1O_4P_2S$ (609.6): calcd. C 66.99, H 4.79, N 2.30; found C 66.93, H 4.59, N 2.24.

Compound 5e: 90% yield, white viscous oil. – ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 47.9 (d, $^2J_{PP}$ = 29.0 Hz, P=N), 52.6 (d, $^2J_{PP}$ = 29.0 Hz, P=S). – ^{1}H NMR ($CDCl_3$): δ = 2.34 (md, $^2J_{HP}$ = 136.0 Hz, 2 H, CH_2P), 2.73 (m, 2 H, CH_2CH$_2$P), 6.14 (ddt, $^3J_{HP}$ = 26.7 Hz, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 1.7 Hz, 1 H, C*H*=CH–P), 7.08 (ddt, $^2J_{HP}$ = 45.9 Hz, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.3 Hz, 1 H, =CH–P), 7.27–7.81 (m, 13 H, C_6H_4, C_6H_5), 9.80 (s, 2 H, CHO). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 22.2 (d, $^1J_{CP}$ = 68.9 Hz, CH_2P), 30.5 (d, $^2J_{CP}$ = 9.5 Hz, *C*H$_2$CH$_2$P), 121.4 (d, $^3J_{CP}$ = 4.8 Hz, C^2), 121.6 (d, $^1J_{CP}$ = 90.9 Hz, =CH–P), 128.4 (d, $^3J_{CP}$ = 13.5 Hz, C^m), 128.6 (dd, $^1J_{CP}$ = 110.3 Hz, $^3J_{CP}$ = 9.7 Hz, C^i), 130.2 (d, $^2J_{CP}$ = 11.7 Hz, C^o), 130.7 (s, C^3), 132.1 (s, C^4), 132.2 (s, C^p), 154.9 (d, $^2J_{CP}$ = 23.8 Hz, *C*H=CH-P), 156.1 (d, $^2J_{CP}$ = 9.0 Hz, C^1), 190.4 (s, CHO). – IR (THF): $\tilde{\nu}$ = 1701 cm^{-1} (C=O). – $C_{24}H_{21}N_1O_4P_2S_1$ (481.5): calcd. C 59.87, H 4.40, N 2.91; found C 60.01, H 4.55, N 2.85.

Compound 5f: 88% yield, white viscous oil. – ^{31}P {^{1}H} NMR (THF): δ = 15.5 (d, $^2J_{PP}$ = 32.1 Hz, P=N), 53.0 (d, $^2J_{PP}$ = 32.1 Hz, P=S). – ^{1}H NMR ($CDCl_3$): δ = 2.20 (d, $^3J_{HP}$ = 13.3 Hz, 3 H, CH_3), 7.00–7.65 (m, 20 H, C_6H_5). – ^{13}C {^{1}H} NMR ($CDCl_3$): δ 14.6 (d, $^2J_{CP}$ = 67.9 Hz, CH_3), 121.7 (d, $^3J_{CP}$ = 4.3 Hz, C^2), 124.2 (s, C^4), 128.8 (d, $^3J_{CP}$ = 13.1 Hz, C^m), 129.1 (s, C^3), 130.6 (dd, $^1J_{CP}$ = 108.0 Hz, $^3J_{CP}$ = 5.1 Hz, C^i), 131.1 (d, $^2J_{CP}$ = 10.9 Hz, C^o), 132.3 (d, $^4J_{CP}$ = 3.5 Hz, C^p), 152.1 (d, $^2J_{CP}$ = 8.7 Hz, C^1). – $C_{25}H_{23}NO_2P_2S$ (463.5): calcd. C 64.79, H 5.00, N 3.02; found C 64.98, H 4.95, N, 2.97.

Compound 5g: 97% yield, orange powder, m.p. 211°C. – ^{31}P {^{1}H} NMR ($CDCl_3$): δ = 16.1 (d, $^2J_{PP}$ = 32.0 Hz, P=N), 49.2 (d, $^2J_{PP}$ = 32.0 Hz, P=S). – ^{1}H NMR ($CDCl_3$): δ = 4.35 (dd, $^3J_{HH}$ = 1.8 Hz, $^3J_{HP}$ = 3.7 Hz, 4 H, C^{b}H), 4.55 (dd, $^3J_{HH}$ = 1.8 Hz, $^3J_{HP}$ = 3.5 Hz, 4 H, C^{c}H), 7.24–7.82 (m, 36 H, C_6H_4, C_6H_5), 9.90 (s, 4 H, CHO). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 71.8 (dd, $^1J_{CP}$ = 122.0 Hz, $^3J_{CP}$ = 3.4 Hz, C^a), 74.1 (d, $^2J_{CP}$ = 13.4 Hz, C^b), 74.1 (d, $^3J_{CP}$ = 11.3 Hz, C^c), 121.6 (d, $^3J_{CP}$ = 5.8 Hz, C^2), 128.3 (d, $^3J_{CP}$ = 13.4 Hz, C^m), 129.1 (dd, $^1J_{CP}$ = 108.6 Hz, $^3J_{CP}$ = 4.0 Hz, C^i), 131.1 (s, C^3), 131.8 (d, $^2J_{CP}$ = 10.9 Hz, C^o), 132.5 (s, C^4), 132.6 (d, $^4J_{CP}$ = 2.3 Hz, C^p), 156.7 (d, $^2J_{CP}$ = 9.3 Hz, C^1), 190.8 (s, CHO). – IR (KBr): $\tilde{\nu}$ = 1699 cm^{-1} (C=O). – $C_{62}H_{48}FeN_2O_8P_4S_2$ (1193.0): calcd. C 62.42, H 4.06, N 2.35; found C 62.60, H 4.19, N 2.25.

Compound 6a: 97% yield, white powder, m.p. 145°C. – ^{31}P {^1H} NMR ($CDCl_3$): δ = −7.9 (d, $^2J_{PP}$ = 32.0 Hz, P=O), 13.7 (d, $^2J_{PP}$ = 32.0 Hz, P=N). – ^1H NMR ($CDCl_3$): δ = 7.01−7.62 (m, 25 H, C_6H_5). – ^{13}C {^1H} NMR ($CDCl_3$): δ = 120.4 (d, $^3J_{CP}$ = 4.4 Hz, C^2), 123.4 (s, C^4), 128.4 (d, $^3J_{CP}$ = 12.9 Hz, C^m), 128.8 (s, C^3), 129.1 (dd, $^1J_{CP}$ = 107.3 Hz, $^3J_{CP}$ = 3.6 Hz, C^i), 132.1 (s, C^p), 132.3 (d, $^2J_{CP}$ = 11.6 Hz, C^o), 152.1 (d, $^2J_{CP}$ = 7.7 Hz, C^1). – $C_{30}H_{25}N_1O_3P_2$ (509.5): calcd. C 70.73, H 4.95, N 2.75; found C 70.90, H 5.03, N 2.68.

Compound 6f: 96% yield, white powder, m.p. 72°C. – ^{31}P {^1H} NMR ($CDCl_3$): δ = −6.2 (d, $^2J_{PP}$ = 31.0 Hz, P=O), 15.2 (d, $^2J_{PP}$ = 31.0 Hz, P=N). – ^1H NMR ($CDCl_3$): δ = 2.07 (d, $^2J_{HP}$ = 13.3 Hz, 3 H, CH_3), 7.02−7.58 (m, 20 H, C_6H_5). – ^{13}C {^1H} NMR ($CDCl_3$): δ = 15.4 (d, $^1J_{CP}$ = 67.9 Hz, CH_3), 120.4 (d, $^3J_{CP}$ = 5.2 Hz, C^2), 123.4 (s, C^4), 128.5 (d, $^3J_{CP}$ = 12.9 Hz, C^m), 128.9 (s, C^3), 130.2 (dd, $^1J_{CP}$ = 107.7 Hz, $^3J_{CP}$ = 5.5 Hz, C^i), 130.5 (d, $^2J_{CP}$ = 10.7 Hz, C^o), 132.0 (s, C^p), 152.0 (d, $^2J_{CP}$ = 7.9 Hz, C^1). – $C_{25}H_{23}N_1O_3P_2$ (447.4): calcd. C 67.11, H 5.18, N 3.13; found C 67.33, H 5.22, N 2.98.

Compound (6g): 96% yield, orange powder, m.p. 174°C. – ^{31}P {^1H} NMR ($CDCl_3$): δ = −8.6 (d, $^2J_{PP}$ = 37.0 Hz, P=O), 14.5 (d, $^2J_{PP}$ = 37.0 Hz, P=N). – ^1H NMR ($CDCl_3$): δ = 4.21 (br. s, 4 H, C^bH), 4.56 (br. s, 4 H, C^cH), 7.02−7.46 (m, 40 H, C_6H_5). – ^{13}C {^1H} NMR ($CDCl_3$): δ = 72.0 (dd, $^1J_{CP}$ = 120.7 Hz, $^3J_{CP}$ = 3.4 Hz, C^a), 73.7 (d, $^2J_{CP}$ = 13.7 Hz, C^b), 75.0 (d, $^3J_{CP}$ = 11.0 Hz, C^c), 120.2 (d, $^3J_{CP}$ = 5.2 Hz, C^2), 123.4 (s, C^4), 128.2 (d, $^3J_{CP}$ = 13.1 Hz, C^m), 128.8 (dd, $^1J_{CP}$ = 50.0 Hz, $^3J_{CP}$ = 4.2 Hz, C^i), 129.0 (s, C^3), 131.5 (d, $^2J_{CP}$ = 11.4 Hz, C^o), 132.0 (d, $^4J_{CP}$ = 1.9 Hz, C^p), 152.3 (d, $^2J_{CP}$ = 7.7 Hz, C^1). – $C_{58}H_{48}FeN_2O_6P_4$ (1048.8): calcd. C 66.42, H 4.61, N 2.67; found C 66.63, H 4.73, N 2.53.

General Procedure for 7a-f, 8a, 8f: To a solution of 1 mmol of compounds **5a**−**f**, **6a**, **6f** in CH_2Cl_2 (10 mL) was added at room temperature 1.05 mmol (slight excess) of $MeSO_3CF_3$. The solution was stirred for 15 min, then concentrated to dryness. The residue was washed twice with ether/pentane (1:1) to afford **7a**−**f**, **8a**, **8f** as oils.

General Procedure for 7g, 8g, and 16g: To a solution of 1 mmol of compound **5g**, **6g** or **15g** in CH_2Cl_2 (10 mL) was added at room temperature 2.1 mmol (slight excess) of $MeSO_3CF_3$. The solution was stirred for 15 min, then concentrated to dryness. The residue was washed twice with ether/pentane (1:1) to afford **7g**, **8g** or **16g** as a powder. Crystallization at −30°C in CH_2Cl_2/pentane (1:1) afforded single crystals of **7g** and **8g** suitable for X-ray diffraction.

Compound 7a: 95% yield, orange viscous oil. – ^{31}P {^1H} NMR ($CDCl_3$): δ = 22.8 (d, $^2J_{PP}$ = 20.0 Hz, P=N), 23.4 (d, $^2J_{PP}$ = 20.0 Hz, P−S−Me). – ^{31}P NMR ($CDCl_3$): δ = 22.8 (m, P=N), 23.4 (qd, $^2J_{PP} \approx {}^3J_{HP} \approx$ 19 Hz, P−S−Me). – ^1H NMR ($CDCl_3$): δ = 2.59 (d, $^3J_{HP}$ = 19.0 Hz, 3 H, CH_3-S), 7.24−7.92 (m, 23 H, C_6H_4, C_6H_5), 9.96 (s, 2 H, CHO). – ^{13}C {^1H} NMR ($CDCl_3$): (CF_3SO_3 not detected) δ = 13.7 (d, $^2J_{CP}$ = 5.5 Hz, CH_3−S), 121.3 (d, $^3J_{CP}$ = 5.5 Hz, C^2), 124.0 (d, $^1J_{CP}$ = 110.9 Hz, C^i), 130.2 (d, $^3J_{CP}$ = 13.1 Hz, C^m), 131.9 (d, $^2J_{CP}$ = 11.0 Hz, C^o), 132.0 (s, C^3), 134.6 (br. s, C^4, C^p), 153.1 (d, $^2J_{CP}$ = 10.1 Hz, C^1), 190.6 (s, CHO). – ^{19}F NMR ($CDCl_3$): δ = −2.2 (s, CF_3SO_3). – IR (KBr): $\tilde{\nu}$ = 1699 (C=O) cm^{-1}. – $C_{34}H_{28}F_3N_1O_7P_2S_2$ (745.7): calcd. C 54.76, H 3.78, N 1.88; found C 54.83, H 3.82, N 1.85.

Compound 7b: 91% yield, red viscous oil. – ^{31}P {^1H} NMR (CD_3COCD_3): δ = 26.2 (d, $^2J_{PP}$ = 23.0 Hz, P=N), 31.4 (d, $^2J_{PP}$ = 23.0 Hz, P−S−Me). – ^{31}P NMR (CD_3COCD_3): δ = 26.2 (m, P=N), 31.4 (qd, $^2J_{PP} \approx {}^3J_{HP} \approx$ 20 Hz, P−S−Me). – ^1H NMR (CD_3COCD_3): δ = 2.95 (d, $^3J_{HP}$ = 18.5 Hz, 3 H, CH_3-S), 7.74−8.19 (m, 20 H, C_6H_4), 10.18 (s, 2 H, CHO). – ^{13}C {^1H} NMR (CD_3COCD_3): δ = 13.6 (d, $^2J_{CP}$ = 4.6 Hz, CH_3−S), 121.4 (q, $^1J_{CF}$ = 319.9 Hz, CF_3SO_3), 122.0 (d, $^3J_{CP}$ = 4.5 Hz, C^2), 123.1 (br. d, $^1J_{CP}$ = 109 Hz, C^i), 130.3 (d, $^3J_{CP}$ = 14.1 Hz, C^m), 132.1 (s, C^3), 134.4 (d, $^2J_{CP}$ = 14.0 Hz, C^o), 135.3 (s, C^4), 141.0 (s, C^p), 153.3 (d, $^2J_{CP}$ = 9.6 Hz, C^1), 190.9 (s, CHO). – ^{19}F NMR (CD_3COCD_3): δ = 2.7 (s, CF_3SO_3). – IR (KBr): $\tilde{\nu}$ = 1698 (C=O) cm^{-1}. – $C_{34}H_{25}Cl_3F_3N_1O_7P_2S_2$ (849.0): calcd. C 48.07, H 2.94, N 1.64; found C 48.13, H 3.00, N 1.58.

Compound 7c: 92% yield, orange viscous oil. – ^{31}P {^1H} NMR (CD_3COCD_3): δ = 28.9 (d, $^2J_{PP}$ = 10.0 Hz, P−S−Me), 45.7 (d, $^2J_{PP}$ = 10.0 Hz, P=N). – ^{31}P NMR (CD_3COCD_3): δ = 28.9 (qd, $^2J_{PP}$ = 10.0 Hz, $^3J_{HP}$ = 19.0 Hz, P−S−Me), 45.7 (m, P=N). – ^1H NMR (CD_3COCD_3): δ = 2.83 (d, $^3J_{HP}$ = 19.0 Hz, 3 H, CH_3-S), 2.84−2.98 (m, 12 H, CH_2−CH_2), 7.78−8.17 (d, $^3J_{HH}$ = 12.0 Hz, 8 H, C_6H_4), 10.09 (s, 2 H, CHO). – ^{13}C {^1H} NMR (CD_3COCD_3): δ = 13.6 (d, $^2J_{CP}$ = 5.3 Hz, CH_3-S), 21.1 (s, CH_2P), 22.4 (s, CH_2CH_2P), 118.7 (s, C≡N), 121.2 (q, $^1J_{CF}$ = 320.7 Hz, CF_3SO_3), 121.9 (d, $^3J_{CP}$ = 4.8 Hz, C^2), 132.1 (s, C^3), 135.3 (s, C^4), 153.6 (d, $^2J_{CP}$ = 11.0 Hz, C^1), 191.1 (s, CHO). – ^{19}F NMR (CD_3COCD_3): δ = 2.5 (s, CF_3SO_3). – IR (THF): $\tilde{\nu}$ = 2211 (CN), 1700 (C=O) cm^{-1}. – MS [FAB$^+$ (MNBA/CH_2Cl_2)]; *m/z* (%): 527 (100) [$M^+ - CF_3SO_3$]. – $C_{25}H_{25}F_3N_4O_7P_2S_2$ (676.6): calcd. C 44.38, H 3.72, N 8.28; found C 44.47, H 3.73, N 8.24.

Compound 7d: 79% yield, orange viscous oil. – ^{31}P {^1H} NMR ($CDCl_3$): δ = −4.7 (d, $^2J_{PP}$ = 5.5 Hz, P=N), 28.5 (d, $^2J_{PP}$ = 5.5 Hz, P-S-Me). – ^{31}P NMR ($CDCl_3$): δ = −4.7 (dec d, $^2J_{PP}$ = 5.2 Hz, $^3J_{HP}$ = 24.0 Hz, P=N), 28.5 (br. q, $^3J_{HP}$ = 18.5 Hz, P−S−Me). – ^1H NMR ($CDCl_3$): δ = 1.25 (d, $^3J_{HP}$ = 22.5 Hz, 9 H, C−CH_3), 2.79 (d, $^3J_{HP}$ = 18.5 Hz, 3 H, CH_3−S), 7.38−7.95 (m, 18 H, C_6H_4, C_6H_5), 9.85 (s, 2 H, CHO). – ^{13}C {^1H} NMR ($CDCl_3$): δ = 13.5 (d, $^2J_{CP}$ = 5.1 Hz, CH_3−S), 22.3 (d, $^2J_{CP}$ = 2.3 Hz, C−CH_3), 35.0 (dd, $^1J_{CP}$ = 94.9 Hz, $^3J_{CP}$ = 6.0 Hz, C−CH_3), 73.2 (d, $^1J_{CP}$ = 201.7 Hz, ≡C−P), 110.5 (d, $^2J_{CP}$ = 36.0 Hz, C≡C-P), 116.7 (d, $^3J_{CP}$ = 4.6 Hz, C^i), 120.7 (q, $^1J_{CF}$ = 320.8 Hz, CF_3SO_3), 121.3 (d, $^3J_{CP}$ = 4.9 Hz, C^2), 129.0 (s, C^m), 132.0 (s, C^3), 132.6 (s, C^p), 132.8 (d, $^4J_{CP}$ = 1.7 Hz, C^o), 134.6 (d, $^5J_{CP}$ = 1.3 Hz, C^4), 152.9 (d, $^2J_{CP}$ = 10.8 Hz, C^1), 190.3 (s, CHO). – ^{19}F NMR ($CDCl_3$): δ = −2.0 (s, CF_3SO_3). – IR (THF): $\tilde{\nu}$ = 2170 (C≡C), 1699 (C=O) cm^{-1}. – $C_{36}H_{32}F_3N_1O_7P_2S_2$ (773.8): calcd. C 55.88, H 4.17, N 1.81; found C 55.95, H 4.19, N 1.77.

Compound 7e: 91% yield, red-orange viscous oil. – ^{31}P {^1H} NMR ($CDCl_3$): δ = 24.6 (d, $^2J_{PP}$ = 12.0 Hz, P−S−Me), 53.7 (d, $^2J_{PP}$ = 12.0 Hz, P=N). – ^{31}P NMR ($CDCl_3$): δ = 24.6 (qd, $^2J_{PP} = {}^3J_{HP}$ = 18.0 Hz, P−S−Me), 53.7 (m, P=N). – ^1H NMR ($CDCl_3$): δ = 2.33 (m, 2 H, CH_2P), 2.91 (m, 2 H, CH_2CH_2P), 2.60 (d, $^3J_{HP}$ = 18.0 Hz, 3 H, CH_3−S), 6.17 (ddt, $^3J_{HP}$ = 29.2 Hz, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 2.2 Hz, 1 H, CH=CH-P), 7.24−7.97 (m, 14 H, C_6H_4, C_6H_5, =CH−P), 9.93 (s, 2 H, CHO). – ^{13}C {^1H} NMR ($CDCl_3$): δ = 13.5 (d, $^2J_{CP}$ = 5.4 Hz, CH_3S), 24.3 (d, $^1J_{CP}$ = 71.2 Hz, CH_2P), 30.9 (d, $^2J_{CP}$ = 11.0 Hz, CH_2CH_2P) 118.6 (d, $^1J_{CP}$ = 90.8 Hz, = CH-P), 121.1 (q, $^1J_{CF}$ = 320.5 Hz, CF_3SO_3), 121.2 (d, $^3J_{CP}$ = 4.7 Hz, C^2), 124.9 (dd, $^1J_{CP}$ = 110.1 Hz, $^3J_{CP}$ = 7.4 Hz, C^i), 124.9 (d, $^3J_{CP}$ = 14.1 Hz, C^m), 130.2 (d, $^2J_{CP}$ = 12.5 Hz, C^o), 132.0 (s, C^3), 132.2 (d, $^4J_{CP}$ = 3.2 Hz, C^p), 134.5 (s, C^4), 153.1 (d, $^2J_{CP}$ = 11.3 Hz, C^1), 160.6 (d, $^2J_{CP}$ = 26.3 Hz, CH=CH-P), 190.4 (s, CHO). – ^{19}F NMR ($CDCl_3$): δ = −2.1 (s, CF_3SO_3). – IR (THF): $\tilde{\nu}$ = 1698 (C=O) cm^{-1}. – MS [FAB$^+$ (MNBA/CH_2Cl_2)]; *m/z* (%): 496 (100) [$M^+ - CF_3SO_3$]. – $C_{26}H_{24}F_3N_1O_7P_2S_2$ (645.6): calcd. C 48.37, H 3.75, N 2.17; found C 48.56, H 3.75, N 2.15.

Compound 7f: 92% yield, orange powder. – ^{31}P {^1H} NMR ($CDCl_3$): δ = 23.2 (d, $^2J_{PP}$ = 20 Hz, P=N or P−S−Me), 24.2 (d, $^2J_{PP}$ = 20 Hz, P−S−Me or P=N). – ^1H NMR ($CDCl_3$): δ = 2.18

(d, $^2J_{HP}$ = 13.2 Hz, 3 H, CH_3P), 2.59 (d, $^3J_{HP}$ = 18.5 Hz, 3 H, CH_3−S), 6.85−7.65 (m, 20 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 13.6 (d, $^2J_{CP}$ = 5.1 Hz, CH_3S), 14.2 (d, $^1J_{CP}$ = 67.8 Hz, CH_3P), 119.8 (d, $^3J_{CP}$ = 4.8 Hz, C^2), 120.6 (q, $^1J_{CF}$ = 320.0 Hz, CF_3SO_3), 126.2 (dd, $^1J_{CP}$ = 108.0 Hz, $^3J_{CP}$ = 4.7 Hz, C^i), 126.5 (s, C^4), 128.9 (d, $^3J_{CP}$ = 13.0 Hz, C^m), 130.0 (s, C^3), 131.1 (d, $^2J_{CP}$ = 14.5 Hz, C^o), 133.1 (br. s, C^p), 148.9 (d, $^2J_{CP}$ = 8.7 Hz, C^1). − ^{19}F NMR ($CDCl_3$): δ = −2.1 (s, CF_3SO_3). − $C_{27}H_{26}F_3N_1O_5P_2S_2$ (627.6): calcd. C 51.67, H 4.17, N 2.23; found C 51.85, H 4.20, N 2.28.

Compound 7g: 95% yield, orange powder, m.p. 196°C. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 23.9 (d, $^2J_{PP}$ = 23.0 Hz, P−S−Me), 25.4 (d, $^2J_{PP}$ = 23.0 Hz, P=N). − ^{31}P NMR ($CDCl_3$): δ = 23.9 (qd, $^2J_{PP} \approx {}^2J_{HP} \approx$ 20 Hz, P−S−Me), 25.4 (m, P=N). − ^1H NMR ($CDCl_3$): δ = 2.20 (d, $^3J_{HP}$ = 18.5 Hz, 6 H, CH_3−S), 3.65 (br. s, 4 H, C^bH), 4.02 (br. s, 4 H, C^cH), 6.90−7.70 (m, 36 H, C_6H_4, C_6H_5), 9.71 (s, 4 H, CHO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 12.6 (d, $^2J_{CP}$ = 5.5 Hz, CH_3−S), 67.8 (dd, $^1J_{CP}$ = 125.2 Hz, $^3J_{CP}$ = 6.3 Hz, C^a), 72.6 (d, $^2J_{CP}$ = 14.4 Hz, C^b), 74.8 (d, $^3J_{CP}$ = 11.5 Hz, C^c), 120.3 (d, $^3J_{CP}$ = 5.0 Hz, C^2), 124.3 (dd, $^1J_{CP}$ = 107.5 Hz, $^3J_{CP}$ = 3.7 Hz, C^i), 128.6 (d, $^3J_{CP}$ = 13.5 Hz, C^m), 130.6 (d, $^2J_{CP}$ = 12.1 Hz, C^o), 131.0 (s, C^3), 133.6 (d, $^4J_{CP}$ = 2.7 Hz, C^p), 133.9 (d, $^5J_{CP}$ = 1.3 Hz, C^4), 152.2 (d, $^2J_{CP}$ = 11.0 Hz, C^1), 189.9 (s, CHO); CF_3SO_3 signal not detected. − ^{19}F NMR ($CDCl_3$): δ = −2.6 (s, CF_3SO_3). − IR (KBr): $\tilde{\nu}$ = 1705 (C=O) cm^{-1}. − MS [FAB^+ (MNBA/CH_2Cl_2)]; *m/z* (%): 584 (100) [(M^{2+} − Fe − 2 CF_3SO_3)/2]. − $C_{66}H_{54}F_6FeN_2O_{14}P_4S_4$ (1521.2): calcd. C 52.11, H 3.58, N 1.84; found C 52.11, H 3.60, N 1.82.

Compound 8a: 96% yield, colorless viscous oil. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −10.0 (d, $^2J_{PP}$ = 34.8 Hz, P−O−Me), 21.8 (d, $^2J_{PP}$ = 34.8 Hz, P=N). − ^{31}P NMR ($CDCl_3$): δ = −10.0 (qd, $^2J_{PP}$ = 34.0 Hz, $^3J_{HP}$ = 12.2 Hz, P−O−Me), 21.8 (m, P=N). − ^1H NMR ($CDCl_3$): δ = 4.01 (d, $^3J_{HP}$ = 12.5 Hz, 3 H, CH_3−O), 6.86−7.61 (m, 25 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 57.4 (d, $^2J_{CP}$ = 7.7 Hz, CH_3−O), 119.4 (d, $^3J_{CP}$ = 4.8 Hz, C^2), 120.4 (q, $^1J_{CF}$ = 321.2 Hz, CF_3SO_3), 124.5 (dd, $^1J_{CP}$ = 109.1 Hz, $^3J_{CP}$ = 3.6 Hz, C^i), 126.3 (s, C^4), 129.1 (d, $^3J_{CP}$ = 13.3 Hz, C^m), 129.9 (s, C^3), 131.5 (d, $^2J_{CP}$ = 11.2 Hz, C^o), 133.8 (s, C^p), 148.7 (d, $^2J_{CP}$ = 9.2 Hz, C^1). − ^{19}F NMR ($CDCl_3$): δ = −2.1 (s, CF_3SO_3). − $C_{32}H_{28}F_3N_1O_6P_2S_1$ (673.6): calcd. C 57.06, H 4.19, N 2.08; found C 57.10, H 4.19, N 2.03.

Compound 8f: 96% yield, colorless viscous oil. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −9.3 (d, $^2J_{PP}$ = 32.5 Hz, P−O−Me), 24.2 (d, $^2J_{PP}$ = 32.5 Hz, P=N). − ^{31}P NMR ($CDCl_3$): δ = −9.3 (qd, $^2J_{PP}$ = 31.6 Hz, $^3J_{HP}$ = 12.3 Hz, P−O−Me), 24.2 (m, P=N). − ^1H NMR ($CDCl_3$): δ = 2.08 (d, $^2J_{HP}$ = 13.2 Hz, 3 H, CH_3P), 4.04 (d, $^3J_{HP}$ = 12.5 Hz, 3 H, CH_3O), 6.96−7.51 (m, 20 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 14.5 (d, $^1J_{CP}$ = 67.9 Hz, CH_3P), 57.2 (d, $^2J_{CP}$ = 9.0 Hz, CH_3O), 119.5 (d, $^3J_{CP}$ = 4.7 Hz, C^2), 120.4 (q, $^1J_{CF}$ = 319.4 Hz, CF_3SO_3), 126.0 (dd, $^1J_{CP}$ = 107.9 Hz, $^3J_{CP}$ = 4.6 Hz, C^i), 126.4 (s, C^4), 129.1 (d, $^3J_{CP}$ = 12.9 Hz, C^m), 130.0 (s, C^3), 130.1 (d, $^2J_{CP}$ = 14.7 Hz, C^o), 133.3 (s, C^p), 148.9 (d, $^2J_{CP}$ = 8.6 Hz, C^1). − ^{19}F NMR ($CDCl_3$): δ = −2.1 (s, CF_3SO_3). − $C_{27}H_{26}F_3N_1O_6P_2S$ (611.5): calcd. C 53.03, H 4.29, N 2.29; found C 53.08, H 4.29, N 2.27.

Compound 8g: 96% yield, orange powder, m.p. 169°C. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −9.7 (d, $^2J_{PP}$ = 34.5 Hz, P−O−Me), 25.2 (d, $^2J_{PP}$ = 34.5 Hz, P=N). − ^{31}P NMR ($CDCl_3$): δ = −9.7 (dq, $^2J_{PP}$ = 34.5 Hz, $^3J_{HP}$ = 12.9 Hz, P−O−Me), 25.2 (m, P=N). − ^1H NMR ($CDCl_3$): δ = 4.03 (br. s, 4 H, C^bH), 4.13 (d, $^3J_{HP}$ = 12.4 Hz, 6 H, CH_3−O), 4.39 (br. s, 4 H, C^cH), 7.00−7.64 (m, 40 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): (CF_3SO_3 not detected) δ = 58.1 (d, $^2J_{CP}$ = 9.1 Hz, CH_3−O), 68.5 (dd, $^1J_{CP}$ = 126.8 Hz, $^3J_{CP}$ = 4.7 Hz, C^a), 73.6 (d, $^2J_{CP}$ = 15.1 Hz, C^b), 76.2 (d, $^3J_{CP}$ = 11.8 Hz, C^c), 119.7 (d, $^3J_{CP}$ = 4.3 Hz, C^2), 126.3 (dd, $^1J_{CP}$ = 107.9 Hz, $^3J_{CP}$ = 4.7 Hz, C^i), 126.8 (s, C^4), 129.4 (d, $^3J_{CP}$ = 13.8 Hz, C^m), 130.5 (s, C^3), 131.4 (d, $^2J_{CP}$ = 11.8 Hz, C^o), 134.1 (s, C^p), 149.4 (d, $^2J_{CP}$ = 9.2 Hz, C^1). − ^{19}F NMR ($CDCl_3$): δ = −2.0 (s, CF_3SO_3). − MS [FAB^+ (MNBA/CH_2Cl_2)]; *m/z* (%): 512 (100) [(M^{2+} − Fe − 2 CF_3SO_3)/2]. − $C_{62}H_{54}F_6FeN_2O_{12}P_4S_2$ (1377.0): calcd. C 54.06, H 3.92, N 2.03; found C 54.10, H 3.95, N 2.00.

General Procedure for 9a, 10a: To a solution of 1 mmol of compound **5a** or **6a** in CH_2Cl_2 (10 mL) was added at room temperature a solution of 1.05 mmol (slight excess) of *i*$PrSO_3CF_3$ generated in situ in CCl_4 at 0°C. The resulting solution was allowed to reach room temperature under stirring for 30 min, then concentrated to dryness. The residue was washed twice with ether/pentane (1:1) to afford **9a** or **10a** as oils.

Compound 9a: 90% yield, red viscous oil. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 21.5 (d, $^2J_{PP}$ = 17.3 Hz, P−S−*i*Pr), 22.4 (d, $^2J_{PP}$ = 17.3 Hz, P=N). − ^1H NMR ($CDCl_3$): δ = 1.43 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, CH_3), 3.83 (septd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 13.6 Hz, 1 H, C*H*Me_2), 7.01−7.96 (m, 23 H, C_6H_4, C_6H_5), 9.91 (s, 2 H, CHO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 24.7 (d, $^3J_{CP}$ = 7.4 Hz, CH_3), 42.6 (d, $^2J_{CP}$ = 5.3 Hz, *C*HMe_2), 120.5 (q, $^1J_{CF}$ = 321.4 Hz, CF_3SO_3), 121.1 (d, $^3J_{CP}$ = 5.1 Hz, C^2), 124.0 (dd, $^1J_{CP}$ = 103.6 Hz, $^3J_{CP}$ = 7.2 Hz, C^i), 129.6 (d, $^3J_{CP}$ = 13.3 Hz, C^m), 131.8 (d, $^2J_{CP}$ = 10.7 Hz, C^o), 131.9 (s, C^3), 134.4 (br. s, C^4, C^p), 153.1 (d, $^2J_{CP}$ = 11.7 Hz, C^1), 190.5 (s, CHO). − ^{19}F NMR ($CDCl_3$): δ = −2.0 (s, CF_3SO_3). − IR (KBr): $\tilde{\nu}$ = 1700 (C=O) cm^{-1}. − $C_{36}H_{32}F_3N_1O_7P_2S_2$ (773.8): calcd. C 55.88, H 4.17, N 1.81; found C 55.83, H 4.09, N 1.86.

Compound 10a: 91% yield, colorless viscous oil. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −12.1 (d, $^2J_{PP}$ = 21.5 Hz, P−O−*i*Pr), 21.7 (d, $^2J_{PP}$ = 21.5 Hz, P=N). − ^1H NMR ($CDCl_3$): δ = 1.33 (d, $^3J_{HH}$ = 6.2 Hz, 6 H, CH_3), 5.04 (septd, $^3J_{HH}$ = 6.2 Hz, $^3J_{HP}$ = 12.6 Hz, 1 H, C*H*Me_2), 6.91−7.69 (m, 25 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 23.1 (d, $^3J_{CP}$ = 5.2 Hz, CH_3), 79.7 (d, $^2J_{CP}$ = 9.2 Hz, *C*HMe_2), 119.7 (d, $^3J_{CP}$ = 5.4 Hz, C^2), 120.8 (q, $^1J_{CF}$ = 321 Hz, CF_3SO_3), 125.0 (dd, $^1J_{CP}$ = 108.9 Hz, $^3J_{CP}$ = 3.7 Hz, C^i), 126. 6 (s, C^4), 129.5 (d, $^3J_{CP}$ = 13.1 Hz, C^m), 130.2 (s, C^3), 131.9 (d, $^2J_{CP}$ = 12.0 Hz, C^o), 134.2 (s, C^p), 149.3 (d, $^2J_{CP}$ = 9.4 Hz, C^1). − ^{19}F NMR ($CDCl_3$): δ = −2.3 (s, CF_3SO_3). − $C_{34}H_{32}N_1O_6F_3P_2S$ (701.7): calcd. C 58.20, H 4.60, N 2.00; found C 58.32, H 4.69, N 2.05.

Synthesis of Compound 11f: To a solution of 1 mmol of compound **6f** (450 mg) in CH_2Cl_2 (10 mL) was added at room temperature 1.05 mmol (slight excess) of $Me_3SiSO_3CF_3$. The solution was stirred for 15 min, then concentrated to dryness. The residue was not washed, it was directly used for NMR characterization. − 90% yield, colourless viscous oil. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −18.6 (d, $^2J_{PP}$ = 33.1 Hz, P−O−Si), 23.2 (d, $^2J_{PP}$ = 33.1 Hz, P=N). − ^1H NMR ($CDCl_3$): δ = 0.25 (br. s, 9 H, CH_3Si), 2.12 (d, $^2J_{HP}$ = 12.9 Hz, 3 H, CH_3P), 7.02−7.62 (m, 20 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 0.0 (s, CH_3Si), 14.6 (d, $^1J_{CP}$ = 73.7 Hz, CH_3P), 119.6 (s, C^2), 119.8 (q, $^1J_{CF}$ = 319.4 Hz, CF_3SO_3), 126.3 (dd, $^1J_{CP}$ = 112.7 Hz, $^3J_{CP}$ = 4.9 Hz, C^i), 126.4 (s, C^4), 129.2 (d, $^3J_{CP}$ = 13.9 Hz, C^m), 130.1 (s, C^3), 130.3 (d, $^2J_{CP}$ = 14.5 Hz, C^o), 133.6 (s, C^p), 149.2 (d, $^2J_{CP}$ = 7.6 Hz, C^1). − ^{19}F NMR ($CDCl_3$): δ = −1.9 (s, CF_3SO_3).

General Procedure for 12f, and 12g: To a solution of 1 mmol of compound **7f**, or 0.5 mmol of compound **7g** in CH_2Cl_2 (10 mL) was added at room temperature 1.1 mmol (slight excess) of $P(NMe_2)_3$. The solution was stirred for 1 hour, then concentrated to dryness. The residue was extracted with toluene (10 mL) and the solution was filtered under argon to give **12f** or **12g** which were

used without further purification, due to their high sensitivity toward air and moisture.

Compound 12f: Not isolated. − $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ = 9.9 (d, $^2J_{PP}$ = 32 Hz, P=N), 143.9 (d, $^2J_{PP}$ = 32 Hz, P^{III}).

Compound 12g: Not isolated. − $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ = 12.8 (d, $^2J_{PP}$ = 63 Hz, P=N), 144.4 (d, $^2J_{PP}$ = 63 Hz, P^{III}).

Synthesis of Compound 13f: To a solution of 0.5 mmol of compound **12f** in toluene (10 mL) was added at room temperature 1 mmol (100% excess) of allyl iodide. The solution was stirred for 1 h. The phosphonium salt **13f** precipitated progressively. This precipitate was recovered by filtration, and washed with pentane to afford **13f** as a powder. − 85% yield, white powder. − $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ = 27.3 (d, $^2J_{PP}$ = 20.3 Hz, P=N), 28.9 (d, $^2J_{PP}$ = 20.3 Hz, P-allyl). − ^{31}P NMR (CD_3COCD_3): δ = 27.3 (m, P=N), 28.9 (dt, $^2J_{PP} \approx {}^2J_{PH} \approx$ 20 Hz, P-allyl). − ^1H NMR (CD_3COCD_3): δ = 2.57 (d, $^2J_{HP}$ = 13.4 Hz, 3 H, CH_3P), 3.87 (dddd, $^2J_{HP}$ = 20.1 Hz, $^3J_{HHA}$ = 7.3 Hz, $^4J_{HHB} \approx {}^4J_{HHC} \approx$ 1.1 Hz, 2 H, CH_2), 5.52 (dddt, $^3J_{HBHA}$ = 10.2 Hz, $^4J_{HBP}$ = 5.1 Hz, $^2J_{HBHC} \approx {}^4J_{HBCH2} \approx$ 1.2 Hz, 1 H, H_B), 5.64 (dddt, $^3J_{HCHA}$ = 16.8 Hz, $^4J_{HCP}$ = 6.1 Hz, $^2J_{HCHB} \approx {}^4J_{HCCH2} \approx$ 1.3 Hz, 1 H, H_C), 6.03 (dddt, $^3J_{HAHC}$ = 16.8 Hz, $^3J_{HAHB}$ = 10.2 Hz, $^3J_{HACH2} \approx {}^3J_{HAP} \approx$ 7.3 Hz, 1 H, H_A), 7.20−7.90 (m, 20 H, C_6H_5). − $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ = 15.8 (d, $^1J_{CP}$ = 68.0 Hz, CH_3P), 33.2 (d, $^1J_{CP}$ = 133.6 Hz, -CH_2-), 121.6 (d, $^3J_{CP}$ = 4.2 Hz, C^2), 123.3 (d, $^3J_{CP}$ = 16.2 Hz, CH_2=), 125.4 (d, $^2J_{CP}$ = 12.9 Hz, CH_A), 126.9 (s, C^4), 128.2 (dd, $^1J_{CP}$ = 108.0 Hz, $^3J_{CP}$ = 4.5 Hz, C^i), 129.7 (d, $^2J_{CP}$ = 12.2 Hz, C^m), 130.9 (s, C^3), 131.4 (d, $^3J_{CP}$ = 12.0 Hz, C^o), 133.7 (d, $^4J_{CP}$ = 2.7 Hz, C^p), 149.9 (d, $^2J_{CP}$ = 11.6 Hz, C^1). − $C_{28}H_{28}INO_2P_2$ (599.4): C 56.11, H 4.71, N 2.34; found C 55.98, H 4.63, N 2.27.

Synthesis of Compound 14f: A solution of 0.5 mmol of compound **12f** in toluene (10 mL) was added at room temperature to 0.5 mmol of 4-azidophenyl isothiocyanate. Evolution of nitrogen occurred rapidly. After 1 h, the solution was concentrated to dryness, and the residue was washed twice with THF/pentane (1:5) to afford compound **14f** as a viscous oil. This compound is not stable when left in solution. − 91% Yield, orange viscous oil. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −7.7 (d, $^2J_{PP}$ = 16 Hz, N=P−O), 15.3 (d, $^2J_{PP}$ = 16 Hz, N=P−C). − ^1H NMR ($CDCl_3$): δ = 1.95 (d, $^3J_{HP}$ = 13.3 Hz, 3 H, CH_3), 6.80−7.80 (m, 24 H, C_6H_5, C_6H_4). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 15.0 (d, $^1J_{CP}$ = 69 Hz, CH_3), 121.0 (d, $^3J_{CP}$ = 4.7 Hz, C^2), 123.3 (d, $^3J_{CP}$ = 21.0 Hz, C'^o), 124.2 (s, C^4), 126.3 (s, C'^m), 126.9 (s, C'^p), 128.7 (d, $^3J_{CP}$ = 13.5 Hz, C^m), 129.3 (s, C^3), 130.6 (dd, $^1J_{CP}$ = 107 Hz, $^3J_{CP}$ = 5 Hz, C^i), 130.8 (d, $^2J_{CP}$ = 10.3 Hz, C^o), 132.3 (br. s, C^p), 133.7 (s, C=S), 149.8 (br. s, C'^i), 151.7 (d, $^2J_{CP}$ = 8.6 Hz, C^1). − $C_{32}H_{27}N_3O_2P_2S$ (579.6): C 54.40, H 3.85, N 5.95; found C 54.29, H 3.80, N 5.84.

Synthesis of Compound 15g: To a solution of 0.5 mmol of compound **12g** in toluene (10 mL) was added at room temperature a solution of 1 mmol of the azide **2** in toluene (10 mL). Evolution of nitrogen occurred rapidly. After 1 h, the solution was concentrated to dryness, and the residue was washed with dichloromethane/pentane (1:5) to afford compound **15g** as a powder. 95% yield, orange powder, m.p. 237°C. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −14.3 (dd, $^2J_{PP}$ = 63.5 Hz, $^2J_{PP}$ = 23.2 Hz, N−P=N), 17.9 (d, $^2J_{PP}$ = 23.2 Hz, C−P=N), 45.9 (d, $^2J_{PP}$ = 63.5 Hz, P=S). − ^1H NMR ($CDCl_3$): δ = 4.14 (br. s, 4 H, C^bH), 4.53 (br. s, 4 H, C^cH), 7.02−7.69 (m, 52 H, C_6H_4, C_6H_5), 9.86 (s, 8 H, CHO). − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 70.7 (dd, $^1J_{CP}$ = 126.8 Hz, $^3J_{CP}$ = 4.6 Hz, C^a), 73.6 (d, $^2J_{CP}$ = 13.8 Hz, C^b), 75.5 (d, $^3J_{CP}$ = 11.3 Hz, C^c), 121.0 (d, $^3J_{CP}$ = 4.5 Hz, C^2), 121.5 (d, $^3J_{CP}$ = 4.5 Hz, C'^2), 128.5 (dd, $^1J_{CP}$ = 108.5 Hz, $^3J_{CP}$ = 4.3 Hz, C^i), 128.6 (d, $^3J_{CP}$ = 13.5 Hz, C^m), 130.9 (s, C^3), 131.1 (s, C'^3), 131.8 (d, $^2J_{CP}$ = 11.6 Hz, C^o), 132.4 (s, C'^4), 132.9 (d, $^4J_{CP}$ = 5.0 Hz, C^p), 133.0 (s, C^4), 155.6 (d, $^2J_{CP}$ = 9.1 Hz, C^1), 156.5 (d, $^2J_{CP}$ = 9.1 Hz, C'^1), 190.5 (s, CHO), 190.7 (s, CHO). − IR (KBr): $\tilde{\nu}$ = 1699 cm^{-1} (C=O). − $C_{90}H_{68}FeN_4O_{16}P_6S_2$ (1767.4): calcd. C 61.16, H 3.88, N 3.17; found C 61.25, H 3.95, N 3.14.

Synthesis of Compound 16g: To a solution of 0.4 mmol of compound **15g** in CH_2Cl_2 (10 mL) was added at room temperature 0.81 mmol (slight excess) of $MeSO_3CF_3$. The solution was stirred for 30 min, then concentrated to dryness. The residue was washed twice with ether/pentane (1:1) to afford compound **16g** as a powder. − 96% yield, orange powder. − $^{31}P\{^1H\}$ NMR (CD_3COCD_3): δ = −16.9 (dd, $^2J_{PP}$ = 51 Hz, $^2J_{PP}$ = 29 Hz, N−P=N), 20.0 (d, $^2J_{PP}$ = 51 Hz, P−S−Me), 21.5 (d, $^2J_{PP}$ = 29 Hz, C−P=N). − ^1H NMR (CD_3COCD_3): δ = 2.73 (d, $^3J_{PP}$ = 18.4 Hz, 6 H, CH_3−S), 4.00 (br. s, 4 H, C^bH), 4.40 (br. s, 4 H, C^cH), 7.18−8.00 (m, 52 H, C_6H_4, C_6H_5), 10.0 (s, 8 H, CHO). − $^{13}C\{^1H\}$ NMR (CD_3COCD_3): δ = 13.3 (d, $^2J_{CP}$ = 4.6 Hz, CH_3), 70.4 (dd, $^1J_{CP}$ = 126.4 Hz, $^3J_{CP}$ = 6.8 Hz, C^a), 73.9 (d, $^2J_{CP}$ = 14.1 Hz, C^b), 76.0 (d, $^3J_{CP}$ = 11.4 Hz, C^c), 121.5 (d, $^3J_{CP}$ = 4.9 Hz, C^2 or C'^2), 121.6 (d, $^3J_{CP}$ = 4.9 Hz, C'^2 or C^2), 121.7 (q, $^1J_{CF}$ = 321.1 Hz, CF_3SO_3), 127.5 (dd, $^1J_{CP}$ = 108.0 Hz, $^3J_{CP}$ = 4.0 Hz, C^i), 129.7 (d, $^3J_{CP}$ = 13.6 Hz, C^m), 132.0 (d, $^2J_{CP}$ = 11.1 Hz, C^o), 132.1 (s, C'^3, C^3), 134.3 (br. s, C^p), 134.7 (s, C'^4), 135.3 (s, C^4), 153.5 (d, $^2J_{CP}$ = 9.9 Hz, C^1), 154.6 (d, $^2J_{CP}$ = 9.5 Hz, C'^1), 191.0 (s, CHO). − IR (KBr): $\tilde{\nu}$ = 1699 cm^{-1} (C=O). − $C_{94}H_{74}F_6FeN_4O_{22}P_6S_4$ (2095.6): calcd. C 53.87, H 3.56, N 2.67; found C 54.01, H 3.61, N 2.64.

X-ray Structure Determination for Compounds 5g ($C_{62}H_{48}FeN_2O_8P_4S_2$), 6g ($C_{58}H_{48}FeN_2O_6P_4$), 7g {$[C_{64}H_{54}N_2O_8P_4S_2Fe][CF_3SO_3]_2$ 3/2CH_2Cl_2}, and 8g {$[C_{60}H_{54}N_2O_6P_4Fe][CF_3SO_3]_2$}: The data were collected on a Stoe Imaging Plate Diffraction System (I.P.D.S) equipped with an Oxford Cryosystems Cooler Device, for the four compounds. The structures were solved by direct methods (SIR92)[14] and refined by least-squares procedures on F_o. All hydrogen atoms were located on a difference Fourier map, but they were introduced in calculation in idealized positions [d(C−H) = 0.96 Å], their atomic coordinates were recalculated after each cycle of refinement. They were given isotropic thermal parameters 20% higher than those of the carbon atoms to which they were connected. All non-hydrogen atoms were anisotropically refined. Models were easily located and refined for **5g**, **6g** and **8g**; concerning the structure **7g**, the molecule appears as relatively disordered. Moreover, around the molecules of solvent (CH_2Cl_2) the electron density seems to be spread and diffuse. Finally, the difference Fourier synthesis still shows some residual electron density in these regions, which could not be fitted to any model. Least-squares refinement was carried out by minimizing the function $\Sigma w(||F_o| - |F_c||)^2$, where F_o and F_c are the observed and calculated structure factors. A weighting scheme was used in the last refinement cycles, where weights are calculated from the following expression: w = [weight] × [1 − Δ(F)/6 × σ(F)]^2.[15] Models reached convergence with R = $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and Rw = $[\Sigma w(||F_o| - |F_c||)^2/\Sigma w(|F_o|)^2]^{1/2}$. The calculations were performed with CRYSTALS programs[16] running on a PC. The drawing of the molecules was realized with the aid of CAMERON[17] and the atomic scattering factors were taken from International Tables for X-Ray Crystallography.[18] Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103861 (**5g**), -103862 (**6g**), -103863 (**7g**), -103864 (**8g**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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