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Functionalized phosphorus derivatives of Salpen-like compounds: Synthesis and preliminary complexation studies

Alexandrine Maraval, Germinal Magro, Valérie Maraval, Laure Vendier,
Anne-Marie Caminade *, Jean-Pierre Majoral *

Laboratoire de Chimie de Coordination CNRS, 205 route de Narbonne, 31077 Toulouse Cedex 4, France

Abstract

A new class of Salpen analogues based on phosphorus derivatives where the classical alkylene backbone has been replaced by a N–P–N linkage is described. Such linkage both affords a very good stability in water and an additional (fifth) potentially complexing site. The classical *ortho*-OH groups have been also replaced by various *ortho*-substituents, including diphenylphosphino groups. The synthesis of these compounds is easy and their structure can be varied at will at several levels. Several ways of synthesis can be used to combine the various fragments constituting these Salpen analogues. The structure of one of these fragments, an azide, was determined by X-ray crystallography. A preliminary study of the complexation ability of some of these new ligands was carried out with groups 10 (Ni) and 11 (Au) elements. Depending on the type of substituents and the type of metals used, these compounds can act as mono-, or tetra-dentate ligands.
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1. Introduction

The extraordinary simplicity of the reaction of diamines with salicylaldehyde gave rise to a tremendous amount of work dedicated to the synthesis and study of complexation properties of the corresponding diimine derivatives, the so-called Salen compounds [1]. Indeed, the presence of two covalent and two coordinating sites in these ligands lead in most cases to planar complexes of transition metals, in which two free axial sites on the metal are available, which are particularly useful for catalytic experiments [2–4]. In contrast to the diimine derivatives, the analogous dihydrazone derivatives are relatively rare, despite the known better stability toward hydrolysis of hydrazones compared to imines. Dihydraz-

ides of phosphorus constitute a variety of dihydrazine derivatives which are easily available and react readily with benzaldehydes. In particular we [5,6] and others [7] have shown that the reaction of phosphorus dihydrazides with salicylaldehyde affords the expected Salpen analogues, in which the traditional C–C–C linkage between both imines is replaced by a N–P–N linkage. Beside the complexation ability of the OH and N=CH group, well-known for Salpen derivatives, the presence of phosphorus should bring new complexation properties, using either the lone pair of phosphorus for phosphines derivatives, or the lone pairs of oxygen or sulfur for phosphoryl and thiophosphoryl derivatives. We have already shown that the complexation ability of a P=S group is enhanced when it is included in a P=N–P=S linkage [8], therefore we introduced such linkage in all the compounds we prepared in this paper. Furthermore, salicylaldehyde can be easily replaced by other *ortho*-functionalized benzaldehydes (Fig. 1). In this paper, we

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* Corresponding authors. Tel.: +33 5 61 33 31 25; fax: +33 5 61 55 30 03.
  E-mail addresses: caminade@lcc-toulouse.fr (A.-M. Caminade), majoral@lcc-toulouse.fr (J.-P. Majoral).
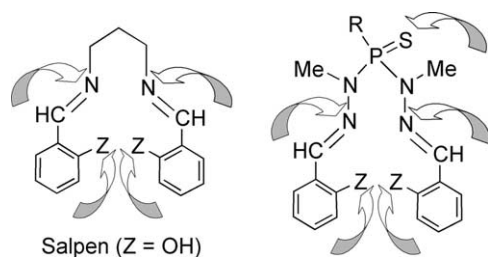
Fig. 1. Potential complexation sites in Salpen and phosphorus Salpen analogues (P-Salpen).

report the synthesis of a number of new phosphorus derivatives of Salpen analogues (P-Salpen), having N–PR(S)–N linkages (R = R$'_3$P=N), and preliminary experiments concerning the complexation properties of some of these compounds.

2. Results and discussion

The synthesis of the phosphorus Salpen analogues necessitates first the synthesis of phosphodihydrazides RP(S)(NMeNH$_2$)$_2$ [9], to be used instead of 1,3-diamines. The P=N–P=S linkage is easily obtained using the Staudinger reaction [10] between a phosphine and a thiophosphoryl azide, thus the R substituent must be N$_3$. The reaction of triphenylphosphine with the azide 1 [11] affords slowly but cleanly the dihydrazide 2 (Scheme 1). The slowness of the reaction (5 days at room temperature) can be ascribed to the absence of strong electron-withdrawing groups on the azide, the PS group being not sufficient [12]. Compound 2 is characterized in ^{31}P NMR by a set of two doublets for the P=N–P=S linkage at $\delta = 12.4$ and 71.0 ppm, respectively, with $^2J_{PP} = 16.7$ Hz.

The next step for obtaining the Salpen analogues 4a–e consists in the condensation of both NH$_2$ groups of 2 with benzaldehyde 3a and various *ortho*-functionalized benzaldehydes: hydroxybenzaldehyde 3b, diphenylphosphino-

benzaldehyde 3c, diphenylthiophosphino benzaldehyde 3d, and helicin 3e (Scheme 1). In all cases, the condensation induces a shielding of the signal corresponding to the P=S group in ^{31}P NMR from 71.0 to ca. 56 ppm, as well as a shielding in ^{13}C NMR of the doublet corresponding to the Me groups from 39.1 ppm to ca. 31 ppm. In all cases excepted for 4e, the condensation affords a single isomer for the C=N bonds, presumably the E isomer in view of the X-ray structure of compound 5d (see later). However, the ^{13}C NMR spectrum of compound 4e displays two signals instead of one for several atoms, approximately in a 1/4 ratio. This splitting is easily detectable on the NMe groups and on several atoms of the helicin function, and the signal of the CH=N group is broadened. These data are indicative of the presence of two isomers for the CH=N groups (E and Z). We have already observed the same phenomenon for helicin linked to the surface of dendrimers [6]. Due to the presence of two β-D-glucoside groups, compound 4e is fairly soluble in water/THF mixtures (v/v); this allowed us to test the stability of this compound. No trace of decomposition is observed even after several weeks in this mixture, illustrating the very good stability toward hydrolysis induced by the phosphorhydrazone linkages compared to imines in classical Salpen [9,13].

This method of synthesis is very simple, adaptable, and each component can be varied. For instance, both steps can be inverted, as shown by the condensation of 1 with 3d leading to the azide 5d (Scheme 2). In view of the small number of compounds possessing a λ^4,σ^5-phosphorus azide linkage characterized by X-ray diffraction (only five examples) [14–18], it appeared interesting to obtain single crystals of 5d. The ORTEP drawing of 5d is shown in Fig. 2. The X-ray structure determination (Table 1) gives a N6–N7 bond length value of 1.121(5) Å (Table 2), one of the shortest reported up to now for a λ^4,σ^5-phosphorus azide linkage, close to the value of 1.098 Å known for a triple bond [19]. The N5–N6 bond length (1.228(5) Å) is significantly shorter than a single bond, for instance when compared with
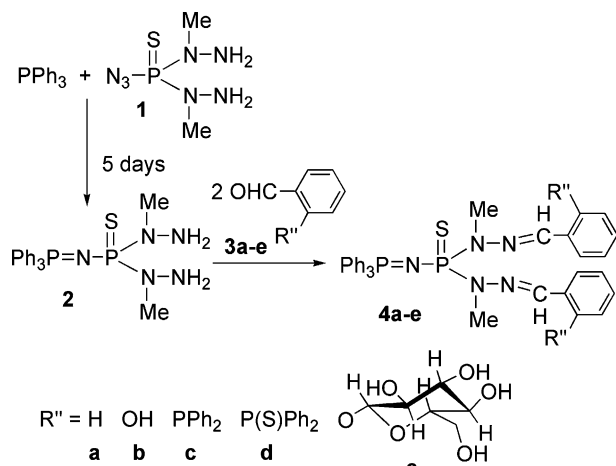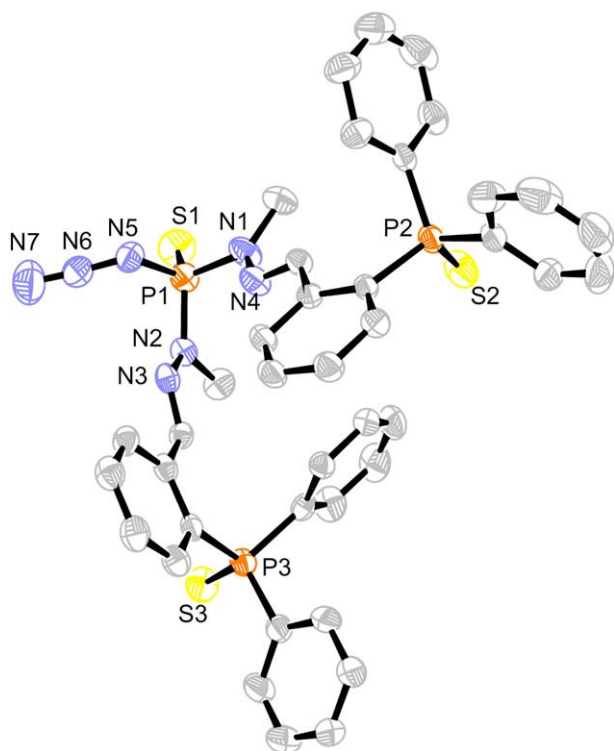

Scheme 1.
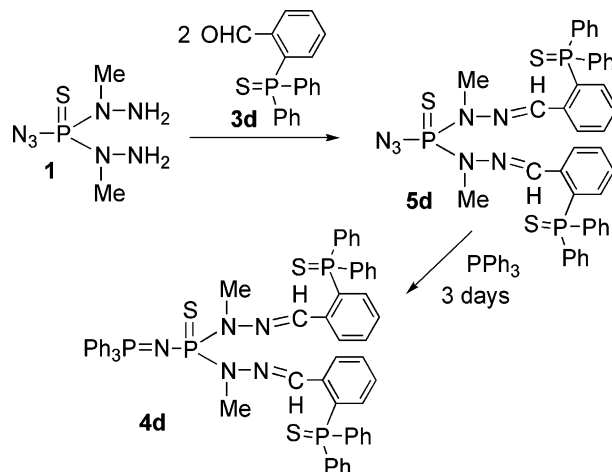
Scheme 2.

Fig. 2. ORTEP diagram for **5d**.

Table 1
Crystal data and structure refinement for **5d** · CH$_2$Cl$_2$

Asymmetric unit	C$_{41}$H$_{38}$Cl$_2$N$_7$P$_3$S$_3$
Formula weight	888.77
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P_1c_1
a (Å)	12.9358(8)
b (Å)	10.3014(7)
C (Å)	16.2095(12)
β (deg)	96.070(6)
V (Å^3)	2147.9(3)
Z	2
ρ_{calc} (g cm^{-3})	1.374
Crystal size (mm)	0.37752 × 0.16324 × 0.0193
Absorption coefficient (mm^{-1})	0.448
$F(000)$	920
θ Range for data collection (°)	3.21–26.37
Limiting indices	$-16 \leqslant h \leqslant 15$, $-12 \leqslant k \leqslant 12$, $-12 \leqslant l \leqslant 20$
Reflections collected/unique	15157/5956 [R_{int} = 0.0411]
Completeness to θ = 26.37 ° (%)	99.8
Absorption correction	Empirical (DIFABS)
Max. and min. transmission	0.988 and 0.856
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5956/2/507
Goodness-of-fit on F^2	0.934
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0414, wR_2 = 0.0943
R indices (all data)	R_1 = 0.0546, wR_2 = 0.1011
Absolute structure parameter	−0.01(7)
Largest diff. peak and hole (e Å^{-3})	0.372 and −0.461

N2–N3 (1.392(4) Å) or N1–N4 (1.380(5) Å). As expected, both CH=N bonds have the *E* configuration. Compound **5d** is then used in a Staudinger reaction with PPh$_3$, to afford again compound **4d** (Scheme 2).

Table 2
Selected bond distances (Å) and bond angles (°) of **5d** (esd in parentheses)

P1–N1	1.658(3)	N1–P1–N2	108.64(16)
P1–N2	1.665(3)	N1–P1–N5	100.7(2)
P1–N5	1.685(4)	N2–P1–N5	102.94(7)
P1–S1	1.9081(16)	N1–P1–S1	113.62(14)
P2–S2	1.9533(15)	N2–P1–S1	113.54(14)
P3–S3	1.9545(15)	N5–P1–S1	116.17(13)
N1–N4	1.380(5)	N7–N6–N5	174.3(5)
N2–N3	1.392(4)		
N5–N6	1.228(5)		
N6–N7	1.121(5)		

Obviously, the synthesis of P-Salpen is not limited to triphenylphosphine, as shown for instance by the use of diphenylphosphinoferrocene (Scheme 3). The Staudinger reaction of the azide **1** is completed in two days, more rapidly than with Ph$_3$P, and affords cleanly the expected compound **6**, characterized by a set of two doublets at 71.6 (P=S) and 15.7 (P=N) ppm ($^2J_{PP}$ = 18.8 Hz). On the other hand, the condensation reaction with helicin is slow and needs 7 days to go to completion. Here again, two isomers are observed for the CH=N bonds in a 1/2 ratio, as shown by ^{13}C NMR.

Having in hand several new Salpen analogues, it was interesting to test the complexation properties of some of them. As shown in Fig. 1, five sites of complexation are potentially available in compounds **4**. Since a previous experiment with a different but related compound [5], and nickel acetate afforded a complex in which nickel was linked to four sites (2N and 2O), we tried the same experiment with compound **4b**. Surprisingly, no reaction occurred with nickel acetate, presumably because of the steric hindrance induced by the PPh$_3$ group. In order to avoid this problem, we tried in this case also to invert the order of the reactions, i.e., to use the preformed Ni(Salen)$_2$ · 2H$_2$O complex [20] in a condensation reaction with **2**. After 5 days at 60 °C, the dark green paramagnetic solution of **8** and **2** becomes a yellow diamagnetic solution of **9b** (Scheme 4). The color change is very characteristic of a modification of the geometry around nickel, from octahedral in **8** to square planar in **9b**. The reaction is also
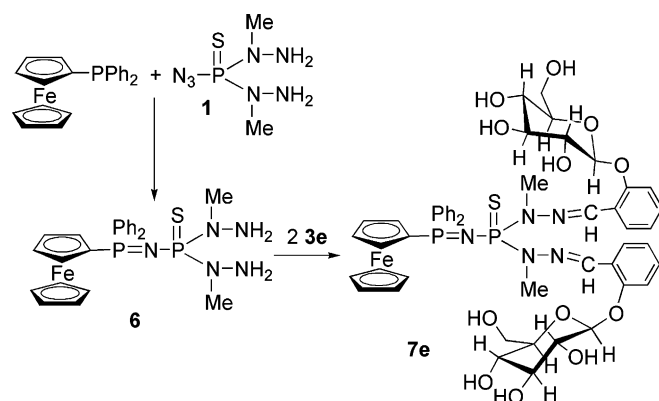
Scheme 3.
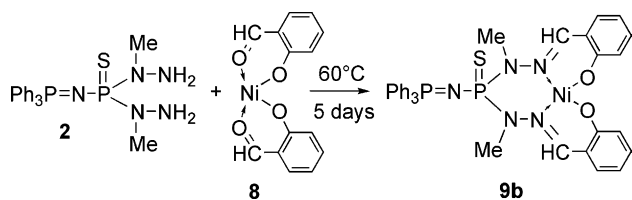
Scheme 4.
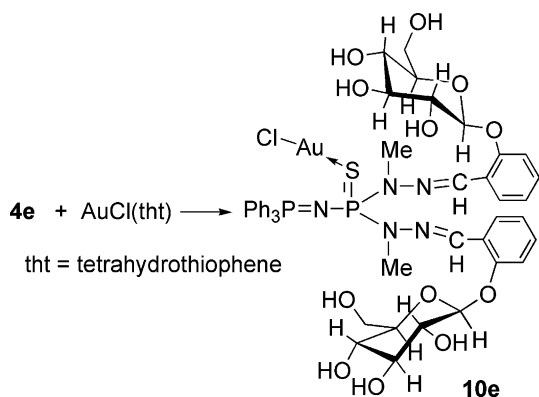
Scheme 5.

characterized in ^{31}P NMR by the shielding of the signal corresponding to the P=S group from 71.0 ppm in **2** to 56.5 ppm in **9b**. The later value is close but slightly different from that of the corresponding free ligand **4b** (56.9 ppm), but the coupling constant differs significantly ($^2J_{PP}$ = 28.2 Hz for **4b** and 19.8 Hz for **9b**). Beside multinucleus NMR, complex **9b** is also characterized by FAB mass spectrometry, which confirms in particular the absence of dimers; only the expected 1[**2**]/1[**8**] condensation occurred.

The ^{31}P NMR data and the color of the solution indicate that the P=S group is not involved in the complexation of nickel in **9b**, only the O and N atoms are used. In order to check the ability of the P=S group of compounds **4** for complexation, we used compound **4e**. The P=S group of this compound is the sole site usable for complexation, since the phenol group is protected by a β-glycoside group, which should sterically hinder the nitrogen atoms. The reaction of AuCl(tht) (tht = tetrahydrothiophene) with **4e** occurs readily on the P=S group (Scheme 5). The complexation induces as expected [8] a shielding of the signal corresponding to P=S in ^{31}P NMR from 57.0 for **4e** to 49.2 for **10e**. A deshielding of the signal corresponding to the Ph$_3$P=N group from 11.2 for **4e** to 18.3 for **10e** is also observed. Both phenomenon are indicative of a partial electronic transfer along the P=N–P=S linkage.

3. Conclusion

We have described the easy synthesis of new Salpen analogues, in which a N–PR(S)–N linkage (R = R'$_3$P= N)

replaces the traditional C–C–C linkage. The presence of hydrazone groups induces a high stability of these derivatives toward hydrolysis, in contrast to classical Salpen. In view of the large number of *ortho*-functionalized benzaldehydes available, these compounds can be easily tailored to afford precisely the compound desired for specific complexations. We have shown that these P-Salpen can act as mono-, or tetra-dentate ligands. Preliminary tests have shown that metals pertaining to several columns and rows of the periodic table can be complexed. Thus, this new family of ligands should open the way to the obtaining of a variety of complexes, potentially usable as catalysts.

4. Experimental

4.1. General

All manipulations were carried out with standard high vacuum and dry-argon techniques. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker AC 200, AC 250, DPX 300 or AMX 400 spectrometers. References for NMR chemical shifts are 85% H$_3$PO$_4$ for ^{31}P NMR, SiMe$_4$ for ^{1}H and ^{13}C NMR. The attribution of ^{13}C NMR signals has been done using J_{mod} experiments. The numbering used for ^{13}C NMR is C$_{i,o,m,p}$ for the PPh$_3$ part (*ipso, ortho, meta, para* to P), C$_{i',o',m',p'}$ for the PPh$_2$ part when it exists (compounds **4c**, **4d**), C^1 for the substituted C$_6$H$_4$ carbon linked to the hydrazone, C^2 for the substituted C$_6$H$_4$ in *ortho*-position, then C^{3,4,5,6} for the others C$_6$H$_4$ carbons, C$_g^1$ for the glucoside carbon linked to two O, then C$_g^{2,3,4,5}$. Mass spectrometry (FAB) was carried out with Finnoganmat TSQ 700. Solvents were dried and distilled prior to use (THF and ether over sodium/benzophenone, pentane and CH$_2$Cl$_2$ over phosphorus pentoxide) and degazed when phosphines are used. Compounds **1** [11], **6** [20] and AuCl(tht) [21] were prepared as described previously.

Caution. In our hands, the N$_3$ derivatives appear stable, however, many azides are explosives, thus maximum care must be taken.

4.2. Ph$_3$P=NP(S)[NMe-NH$_2$]$_2$ (**2**)

Powdered triphenylphosphine (0.166 g, 0.633 mmol) and azide **1** (0.123 g, 0.633 mmol) were dissolved in dichloromethane (3 mL) and stirred for 5 days at room temperature. Then, the solvent was removed under vacuum, and the resulting powder was washed three times with pentane, to afford compound **2** as a white powder in 98% yield.

^{31}P {^{1}H} NMR (CH$_2$Cl$_2$): δ = 12.4 (d, $^2J_{PP}$ = 16.7 Hz, P=N), 71.0 (d, $^2J_{PP}$ = 16.7 Hz, P=S). ^{1}H NMR (CDCl$_3$): δ = 2.71 (d, $^3J_{HP}$ = 11.9 Hz, 6H, CH$_3$), 3.52 (br s, 4H, NH$_2$), 7.43–7.57 (m, 9H, H-C$_m$, H-C$_p$), 7.76 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 12.9 Hz, 6H, H-C$_o$). ^{13}C {^{1}H} NMR (CDCl$_3$): δ = 39.1 (d, $^2J_{CP}$ = 7.3 Hz, CH$_3$), 128.4 (d, $^3J_{CP}$ = 13.1 Hz, C$_m$), 129.7 (dd, $^1J_{CP}$ = 103.5 Hz, $^3J_{CP}$ = 2.7 Hz, C$_i$), 132.2 (d, $^4J_{CP}$ = 2.9 Hz, C$_p$), 132.6 (d, $^2J_{CP}$ = 10.3 Hz, C$_o$). Anal. Calc. for C$_{20}$H$_{25}$N$_5$P$_2$S (429.5):

C, 55.94; H, 5.87; N, 16.31. Found: C, 55.81; H, 5.83; N, 16.19%.

4.3. *o-Ph$_2$P(S)(C$_6$H$_4$-CHO) (3d)*

Powdered S$_8$ (0.400 g, 1.56 mmol) was added to a solution of (2-formyl-phenyl)(diphenyl)phosphine **3c** (0.450 g, 1.55 mmol) in THF (20 mL). The resulting mixture was stirred for 5 h at room temperature, then centrifuged. The resulting solution was evaporated to dryness to afford oil, which was purified by column chromatography on silica (eluent: Et$_2$O/pentane 3/7). Compound **3d** was obtained as pale yellow oil in 90% yield.

^{31}P {^{1}H} NMR (CDCl$_3$): $\delta = 40.4$ (s, P(S)Ph$_2$). ^{1}H NMR (CDCl$_3$): $\delta = 7.01$ (ddd, $^3J_{HH} = 7.6$ Hz, $^3J_{HP} = 14.6$ Hz, $^4J_{HH} = 1.0$ Hz, 1H, H-C^3), 7.36–7.55 (m, 6H, H-C^4, H-C^5, H-C$'_m$), 7.59 (br t, $^3J_{HH} = 7.5$ Hz, 2H, H-C$'_p$), 7.80 (ddd, $^3J_{HH} = 7.7$ Hz, $^3J_{HP} = 13.6$ Hz, $^4J_{HH} = 1.4$ Hz, 4H, H-C$'_o$), 7.95 (ddd, $^3J_{HH} = 7.5$ Hz, $^4J_{HP} = 4.2$ Hz, $^4J_{HH} = 1.3$ Hz, 1H, H-C^6), 10.73 (s, 1H, CHO). ^{13}C {^{1}H} NMR (CDCl$_3$): $\delta = 125.4$ (s, C^5), 128.7 (d, $^3J_{CP} = 12.0$ Hz, C$'_m$), 129.6 (d, $^3J_{CP} = 8.8$ Hz, C^4 or C^6), 130.9 (s, C^1), 131.9 (d, $^4J_{CP} = 2.8$ Hz, C$'_p$), 132.2 (d, $^2J_{CP} = 11.5$ Hz, C$'_o$), 132.3 (d, $^2J_{CP} = 8.0$ Hz, C^3), 132.7 (d, $^2J_{CP} = 9.1$ Hz, C^4 or C^6), 136.5 (d, $^1J_{CP} = 92.9$ Hz, C^2), 136.7 (d, $^1J_{CP} = 84.3$ Hz, C$'_i$). Anal. Calc. for C$_{19}$H$_{15}$OPS (322.4): C, 70.79; H, 4.69. Found: C, 71.15; H, 4.77%.

4.4. *Ph$_3$P=NP(S)[NMe–N=CH(C$_6$H$_5$)]$_2$ (4a)*

Benzaldehyde **3a** (0.035 mL, 0.391 mmol) was added dropwise to a solution of **2** (0.08 g, 0.186 mmol) in dichloromethane (5 mL) at room temperature. The resulting solution was stirred overnight, then evaporated to dryness. Then, the resulting powder was washed three times with CH$_2$Cl$_2$/pentane (1/50). Compound **4a** was obtained as a white powder in 98% yield.

^{31}P {^{1}H} NMR (CH$_2$Cl$_2$): $\delta = 11.2$ (d, $^2J_{PP} = 26.7$ Hz, P=N), 56.8 (d, $^2J_{PP} = 26.7$ Hz, P=S). ^{1}H NMR (CDCl$_3$): $\delta = 3.22$ (d, $^3J_{HP} = 9.8$ Hz, 6H, CH$_3$), 7.18–7.22 (m, 6H, H-C^2, H-C^4), 7.30 (br s, 2H, HC=N), 7.38–7.48 (m, 10H, H-C^3, H-C$_m$), 7.53 (ttd, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.6$ Hz, $^5J_{HP} = 1.6$ Hz, 3H, H-C$_p$), 7.86 (ddd, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 1.2$ Hz, $^3J_{HP} = 13.2$ Hz, 6H, H-C$_o$). ^{13}C {^{1}H} NMR (CDCl$_3$): $\delta = 32.5$ (d, $^2J_{CP} = 9.8$ Hz, CH$_3$), 126.3 (s, C^2), 127.5 (s, C^4), 128.2 (s, C^3), 128.4 (d, $^3J_{CP} = 13.8$ Hz, C$_m$), 129.9 (dd, $^1J_{CP} = 106.0$ Hz, $^3J_{CP} = 4.0$ Hz, C$_i$), 132.1 (br s, C$_p$), 133.0 (d, $^2J_{CP} = 9.9$ Hz, C$_o$), 134.6 (d, $^3J_{CP} = 14.2$ Hz, HC=N), 136,8 (s, C^1). Anal. Calc. for C$_{34}$H$_{33}$N$_5$P$_2$S (605.7): C, 67.42; H, 5.49; N, 11.56. Found: C, 67.50; H, 5.57; N, 11.49%.

4.5. *Ph$_3$P=NP(S)[NMe–N=CH(C$_6$H$_4$)-o-OH]$_2$ (4b)*

Salicylaldehyde **3b** (0.128 mL, 1.2 mmol) was added dropwise to a solution of **2** (0.250 g, 0.582 mmol) in dichlo-

romethane (5 mL) at room temperature. The resulting solution was stirred overnight, then evaporated to dryness. Then, the resulting powder was washed three times with pentane. Compound **4b** was obtained as a white powder in 98% yield.

^{31}P {^{1}H} NMR (CH$_2$Cl$_2$): $\delta = 15.2$ (d, $^2J_{PP} = 28.4$ Hz, P=N), 56.9 (d, $^2J_{PP} = 28.4$ Hz, P=S). ^{31}P {^{1}H} (CDCl$_3$): $\delta = 16.2$ (d, $^2J_{PP} = 28.2$ Hz, P=N), 56.9 (d, $^2J_{PP} = 28.2$ Hz, P=S). ^{1}H NMR (CDCl$_3$): $\delta = 3.20$ (d, $^3J_{HP} = 8.2$ Hz, 6H, CH$_3$), 6.78–7.10 (m, 8H, H-C^3, H-C^4, H-C^5, H-C^6), 7.35–7.82 (m, 17H, HC=N, H-Ar), 11.63 (s, 2H, OH). ^{13}C {^{1}H} NMR (CDCl$_3$): $\delta = 31.4$ (d, $^2J_{CP} = 8.4$ Hz, CH$_3$), 116.4 (s, C^3), 118.6 (s, C^5), 119.4 (s, C^1), 128.4 (d, $^3J_{CP} = 13.1$ Hz, C$_m$), 128.6 (dd, $^1J_{CP} = 106.0$ Hz, $^3J_{CP} = 4.3$ Hz, C$_i$), 129.0 (s, C^4), 129.3 (s, C^6), 132.3 (d, $^4J_{CP} = 2.7$ Hz, C$_p$), 132.7 (d, $^2J_{CP} = 11.0$ Hz, C$_o$), 138.3 (d, $^3J_{CP} = 13.8$ Hz, HC=N), 157.2 (s, C^2). Anal. Calc. for C$_{34}$H$_{33}$N$_5$O$_2$P$_2$S (637.7): C, 64.04; H, 5.22; N, 11.98. Found: C, 63.91; H, 5.15; N, 11.86%.

4.6. *Ph$_3$P=NP(S)[NMe–N=CH(C$_6$H$_4$)-o-PPh$_2$]$_2$ (4c)*

A solution of (2-formyl-phenyl)(diphenyl)phosphine **3c** (0.305 g, 1.051 mmol) in dichloromethane (4 mL) was added dropwise to a solution of **2** (0.215 g, 0.501 mmol) in dichloromethane (5 mL) at room temperature and stirred overnight. Then the solvent was evaporated and the resulting powder was washed three times with CH$_2$Cl$_2$/pentane (1/30). Compound **4c** was obtained as pale yellow powder in 95% yield.

^{31}P {^{1}H} NMR (CH$_2$Cl$_2$): $\delta = -14.4$ (s, PPh$_2$), 11.3 (d, $^2J_{PP} = 27.5$ Hz, P=N), 56.9 (d, $^2J_{PP} = 27.5$ Hz, P=S). ^{1}H NMR (CDCl$_3$): $\delta = 2.97$ (d, $^3J_{HP} = 9.1$ Hz, 6H, CH$_3$), 6.84 (dd, $^3J_{HH} = 8.8$ Hz, $^3J_{HP} = 5.0$ Hz, 2H, H-C^3), 7.07–7.16 (m, 4H, H-C^4, H-C^5), 7.24–7.39 (m, 28H, HC=N, H-C$_m$, H-C$'_o$, H-C$'_m$, H-C$'_p$), 7.48 (br t, $^3J_{HH} = 7.6$ Hz, 3H, H-C$_p$), 7.81 (dd, $^3J_{HH} = 7.3$ Hz, $^3J_{HP} = 13.1$ Hz, 6H, H-C$_o$), 7.91 ("t", J = 4.8 Hz, 2H, H-C^6). ^{13}C {^{1}H} NMR (CDCl$_3$): $\delta = 32.4$ (d, $^2J_{CP} = 10.1$ Hz, CH$_3$), 125.6 (br s, C$'_p$), 127.5 (s, C^6 or C^5), 128.1 (s, C^5 or C^6), 128.4 (d, $^3J_{CP} = 16.5$ Hz, C$'_m$), 128.5 (d, $^3J_{CP} = 11.9$ Hz, C$_m$), 129.6 (dd, $^1J_{CP} = 105.9$ Hz, $^3J_{CP} = 2.9$ Hz, C$_i$), 132.0 (br s, C^4, C$_p$), 132.8 (d, $^2J_{CP} = 10.8$ Hz, C$_o$), 132.9 (d, $^3J_{CP} = 13.5$ Hz, HC=N), 133.6 (s, C^3), 133.8 (br s, C^1), 133.8 (d, $^2J_{CP} = 19.5$ Hz, C$'_o$), 136.1 (d, $^1J_{CP} = 9.0$ Hz, C$'_i$), 139.9 (d, $^1J_{CP} = 17.7$ Hz, C^2). Anal. Calc. for C$_{58}$H$_{51}$N$_5$P$_4$S (974.0): C, 71.52; H, 5.28; N, 7.19. Found: C, 71.47; H, 5.34; N, 7.23%.

4.7. *Ph$_3$P=NP(S)[NMe–N=CH(C$_6$H$_4$)-o-P(S)Ph$_2$]$_2$ (4d)*

Way from 3d. A solution of (2-formyl-phenyl)-(diphenyl)thiophosphine **3d** (0.188 g, 0.583 mmol) in dichloromethane (4 mL) was added dropwise to a solution of **2** (0.114 g, 0.235 mmol) in dichloromethane (5 mL) at room temperature and stirred overnight. Then the solvent was evaporated and the resulting powder was

washed three times with CH_2Cl_2/pentane (1/50). Compound **4d** was obtained as white powder in 95% yield.

Way from 5d. Powdered triphenylphosphine (0.01 g, 0.038 mmol) and azide **5d** (0.031 g, 0.038 mmol) were dissolved in dichloromethane (3 mL) and stirred for 3 days at room temperature. Then, the solvent was removed under vacuum, and the resulting powder was washed three times with pentane, to afford compound **4d** as a white powder in 98% yield.

^{31}P {^1H} NMR (CH_2Cl_2): $\delta = 11.4$ (d, $^2J_{PP} = 28.8$ Hz, P=N), 41.1 (s, P(S)Ph$_2$), 55.8 (d, $^2J_{PP} = 28.8$ Hz, P=S). ^1H NMR (CDCl$_3$): $\delta = 2.55$ (d, $^3J_{HP} = 8.9$ Hz, 6H, CH$_3$), 6.95 (dd, $^3J_{HH} = 7.8$ Hz, $^3J_{HP} = 15.0$ Hz, 2H, H-C^3), 7.12 (br t, $^3J_{HH} = 7.2$ Hz, 2H, H-C^4), 7.27 (t, $^3J_{HH} = 7.2$ Hz, 2H, H-C^5), 7.33–7.45 (m, 17H, H-C$_p$, H-C$_m$, H-C$'_m$), 7.53 (br t, $^3J_{HH} = 7.5$ Hz, 4H, H-C$'_p$), 7.72–7.86 (m, 14H, H-C$'_p$, H-C$_o$), 7.89 (s, 2H, HC=N), 7.95 (dd, $^3J_{HH} = 7.5$ Hz, $^4J_{HP} = 7.5$ Hz, 2H, H-C^6). ^{13}C {^1H} NMR (CDCl$_3$): $\delta = 32.8$ (d, $^2J_{CP} = 9.7$ Hz, CH$_3$), 127.1 (d, $^3J_{CP} = 12.7$ Hz, C^4), 127.4 (d, $^3J_{CP} = 9.5$ Hz, C^6), 128.9 (d, $^3J_{CP} = 13.0$ Hz, C$_m$), 129.0 (d, $^3J_{CP} = 12.4$ Hz, C$'_m$), 129.1 (d, $^3J_{CP} = 12.4$ Hz, C$'_m$), 130.1 (dd, $^1J_{CP} = 106.8$ Hz, $^3J_{CP} = 3.1$ Hz, C$_i$), 130.7 (d, $^1J_{CP} = 82.8$ Hz, C^2), 131.9 (d, $^4J_{CP} = 2.4$ Hz, C$_p$), 132.0 (d, $^4J_{CP} = 2.5$ Hz, C$'_p$), 132.7 (br s, C^5, C^3), 132.7 (d, $^1J_{CP} = 84.0$ Hz, C$'_i$), 132.7 (d, $^2J_{CP} = 10.6$ Hz, C$'_o$), 132.9 (d, $^2J_{CP} = 10.6$ Hz, C$_o$), 133.0 (d, $^1J_{CP} = 84.0$ Hz, C$'_i$), 133.3 (d, $^2J_{CP} = 11.0$ Hz, C$_o$), 133.9 (dd, $^3J_{CP} = 14.5$ Hz, $^3J_{CP} = 8.7$ Hz, HC=N), 139.7 (d, $^2J_{CP} = 6.7$ Hz, C^1). Anal. Calc. for $C_{58}H_{51}N_5P_4S_3$ (1038.2): C, 67.10; H, 4.95; N, 6.75. Found: C, 67.21; H, 4.93; N, 6.68%.

4.8. Ph₃P=NP(S)[NMe–N=CH(C₆H₄)-o-(O-β-D-glucoside)]₂ (4e)

Powdered **2** (0.10 g, 0.232 mmol) and helicin **3e** (0.132 g, 0.465 mmol) are dissolved in DMF (5 mL) at room temperature, and stirred overnight. The resulting solution was then evaporated to dryness, and the powder was washed with CH_2Cl_2/pentane (1/30). Compound **4e** was obtained as a yellow powder in 99% yield.

^{31}P {^1H} NMR (DMF): $\delta = 11.2$ (d, $^2J_{PP} = 28.5$ Hz, P=N), 57.0 (d, $^2J_{PP} = 28.5$ Hz, P=S). ^{31}P {^1H} NMR (THF-d_8): $\delta = 13.2$ (d, $^2J_{PP} = 28.4$ Hz, P=N), 60.3 (d, $^2J_{PP} = 28.4$ Hz, P=S). ^1H NMR (THF-d_8): $\delta = 3.34$ (d, $^3J_{HP} = 9.1$ Hz, 3H, CH$_3$), 3.36 (d, $^3J_{HP} = 9.1$ Hz, 3H, CH$_3$), 3.30–4.00 (m, 12H, CH$_2$, *H*COH), 4.77–5.18 (m, 10H, H-C^1_g, -OH), 6.93 ("t", $^3J_{HH} = 7.4$ Hz, 2H, H-C^5), 7.19–7.33 (m, 4H, H-C^3, H-C^4), 7.54–8.10 (m, 19H, HC=N, H-Ar). ^{13}C {^1H} NMR (THF-d_8): $\delta = 33.8$ (d, $^2J_{CP} = 13.0$ Hz, CH$_3$) and 34.0 (d, $^2J_{CP} = 11.3$ Hz, CH$_3$), 64.0 (s, CH$_2$OH), 72.1 (s, C^4_g), 75.9 and 76.1 (2s, C^5_g), 79.0 (s, C^2_g or C^3_g), 79.4 and 79.6 (2s, C^3_g or C^2_g), 104.3 and 104.5 (2s, C^1_g), 119.7 and 119.8 (2s, C^3), 124.5 (s, C^5), 127.8 (s, C^6), 129.8 (s, C^1), 130.0 (s, C^4), 130.3 (d, $^3J_{CP} = 13.3$ Hz, C$_m$), 132.4 (br d, $^3J_{CP} = 13$ Hz, CH=N), 132.8 (dd, $^1J_{CP} = 106.1$ Hz, $^3J_{CP} = 4.0$ Hz, C$_i$), 134.0 (s, C$_p$),

135.2 (d, $^2J_{CP} = 11.8$ Hz, C$_o$), 157.6 (s, C^2). Anal. Calc. for $C_{46}H_{53}N_5O_{12}P_2S$ (962.0): C, 57.44; H, 5.55; N, 7.28. Found: C, 57.23; H, 5.68; N, 7.14%.

4.9. N₃-P(S)[NMe–N=CH(C₆H₄)-o-P(S)Ph₂]₂ (5d)

A solution of (2-formyl-phenyl)(diphenyl) thiophosphine **3d** (0.290 g, 0.900 mmol) in dichloromethane (4 mL) was added dropwise to a solution of **1** (0.080 g, 0.410 mmol) in dichloromethane (5 mL) at room temperature and stirred overnight. The resulting solution was then evaporated under vacuum. The product was purified by silica gel chromatography using CH_2Cl_2 as eluent. The pure product was obtained as a white powder in 80% yield. Crystals suitable for X-ray diffraction were obtained in a mixture CH_2Cl_2/hexane 1:4 by slow evaporation at room temperature.

^{31}P {^1H} NMR (CDCl$_3$): $\delta = 41.1$ (s, PPh$_2$), 66.0 (s, N$_3$-P); ^1H NMR (CDCl$_3$): $\delta = 2.62$ (d, $^3J_{HP} = 10.3$ Hz, 6H, CH$_3$), 6.89 (dd, $^3J_{HH} = 6.7$ Hz, $^3J_{HP} = 14.8$ Hz, 2H, H-C^3), 7.22 (br t, $^3J_{HH} = 6.8$ Hz, 2H, H-C^4), 7.41–7.53 (m, 14H, H-C$'_p$, H-C$'_m$, H-C^5), 7.80 (m, 8H, H-C$'_o$), 8.04 (dd, $^3J_{HH} = 6.8$ Hz, $^3J_{HP} = 4.5$ Hz, 2H, H-C^6), 8.35 (s, 2H, CH=N); ^{13}C {^1H} NMR (CDCl$_3$): $\delta = 31.6$ (d, $^2J_{CP} = 11.0$ Hz, CH$_3$), 127.6 (d, $^3J_{CP} = 9.4$ Hz, C^4), 128.3 (d, $^3J_{CP} = 12.1$ Hz, C^6), 128.7 (d, $^3J_{CP} = 11.5$ Hz, C$'_m$), 131.9 (s, C$'_p$), 132.0 (d, $^1J_{CP} = 75.7$ Hz, C$'_i$), 132.0 (d, $^1J_{CP} = 88.5$ Hz, C^2), 132.4 (d, $^2J_{CP} = 11.3$ Hz, C$'_o$), 132.4 (s, C^3, C^5), 137.4 (d, $^2J_{CP} = 6.3$ Hz, C^1), 138.7 (dd, $^3J_{CP} = 8.4$ Hz, $^3J_{CP} = 15.2$ Hz, CH=N). IR (KBr): 2149 cm^{-1} ($\bar{v}$ N$_3$). Anal. Calc. for $C_{40}H_{36}N_7P_3S_3$ (803.9): C, 59.77; H, 4.51; N, 12.20. Found: C, 59.72; H, 4.48; N, 12.23%.

4.10. CpFeC₅H₄PPh₂=NP(S)[NMe-NH₂]₂ (6)

Powdered diphenylphosphinoferrocene (0.066 g, 0.178 mmol) and azide **1** (0.035 g, 0.178 mmol) were dissolved in dichloromethane (5 mL) and stirred for 2 days at room temperature. Then, the solvent was removed under vacuum, and the resulting powder was washed three times with CH_2Cl_2/pentane, to afford compound **6** as a yellow powder in 83% yield.

^{31}P {^1H} NMR (CH_2Cl_2): $\delta = 15.7$ (d, $^2J_{PP} = 18.8$ Hz, P=N), 71.6 (d, $^2J_{PP} = 18.8$ Hz, P=S). ^1H NMR (CDCl$_3$): $\delta = 2.74$ (d, $^3J_{HP} = 11.8$ Hz, 6H, CH$_3$), 3.52 (br s, 4H, NH$_2$), 3.98 (s, 5H, C$_5H_5$), 4.47 (dd, $^3J_{HP} = 3.8$ Hz, $^3J_{HH} = 1.9$ Hz, 2H, C$_5H_4$), 4.65 (dd, $^3J_{HP} = 3.8$ Hz, $^3J_{HH} = 1.9$ Hz, 2H, C$_5H_4$), 7.40–7.74 (m, 10H, H-Ar). ^{13}C {^1H} NMR (CDCl$_3$): $\delta = 39.1$ (d, $^2J_{CP} = 5.8$ Hz, CH$_3$), 69.1 (dd, $^1J_{CP} = 103$ Hz, $^3J_{CP} = 4.3$ Hz, C^1 $_5H_4$), 69.5 (s, C$_5H_5$), 72.1 (d, $^3J_{CP} = 11.6$ Hz, C$^{3,4}_5H_4$), 72.7 (d, $^2J_{CP} = 13.3$ Hz, C$^{2,5}_5H_4$), 128.1 (d, $^3J_{CP} = 13.3$ Hz, C$_m$), 131.4 (dd, $^1J_{CP} = 106.0$ Hz, $^3J_{CP} = 4.3$ Hz, C$_i$), 132.02 (s, C$_p$), 132.04 (d, $^2J_{CP} = 10.6$ Hz, C$_o$). Anal. Calc. for $C_{24}H_{29}N_5P_2SFe$ (537.4): C, 53.64; H, 5.44; N, 13.03. Found: C, 53.78; H, 5.43; N, 13.09%.

4.11. $CpFeC_5H_4PPh_2=NP(S)[NMe-N=CH(C_6H_4)-o-(O-\beta-\text{D}s\text{-glucoside})]_2$ (7e)

Powdered **6** (0.015 g, 0.0279 mmol) and helicin **3e** (0.016 g, 0.0558 mmol) are dissolved in DMF (1 mL) at room temperature, and stirred for 7 days. The resulting solution was then evaporated to dryness, and the powder was washed with THF/pentane. Compound **4e** was obtained as a yellow powder in 95% yield.

^{31}P {^1H} NMR (THF-d_8): $\delta = 17.2$ (d, $^2J_{PP} = 34.3$ Hz, P=N), 62.1 (d, $^2J_{PP} = 34.3$ Hz, P=S). ^1H NMR (THF-d_8): $\delta = 3.39$ (d, $^3J_{HP} = 8.7$ Hz, 6H, CH$_3$), 3.40–4.06 (m, 12H, CH$_2$, HCOH), 4.22 (s, 5H, C$_5$H$_5$), 4.64–5.10 (m, 14H, C$_5$H$_4$, H-C$_g^1$, –OH), 6.92 (m, 2H, H-C^5), 7.22 (m, 4H, H-C^3, H-C^4), 7.48–8.04 (m, 14H, HC=N, H-Ar). ^{13}C {^1H} NMR (THF-d_8): $\delta = 34.3$ (d, $^2J_{CP} = 11.5$ Hz, CH$_3$) and 34.4 (d, $^2J_{CP} = 11.5$ Hz, CH$_3$), 63.8 (s, CH$_2$OH), 71.8 (s, C$_5$H$_5$), 72.2 and 72.3 (s, C$_g^4$), 73.8 (d, $^3J_{CP} = 13.0$ Hz, C$_5^{3,4}$H$_4$), 75.4 (d, $^2J_{CP} = 14.0$ Hz, C$_5^{2,5}$H$_4$), 75.9 and 76.0 (2s, C$_g^5$), 79.1 (s, C$_g^2$ or C$_g^3$), 79.4 and 79.6 (2s, C$_g^3$ or C$_g^2$), 104.5 and 104.7 (2s, C$_g^1$), 119.5 and 119.7 (2s, C^3), 124.3 and 124.4 (2s, C^5), 127.7 (s, C^6), 128.1 (s, C^1), 129.8 (s, C^4), 130.0 (d, $^3J_{CP} = 13.0$ Hz, C$_m$), 130.5 (dd, $^1J_{CP} = 105.0$ Hz, $^3J_{CP} = 4.3$ Hz, C$_i$), 132.2 (br d, $^3J_{CP} = 13$ Hz, CH=N), 133.6 (s, C$_p$), 134.6 (d, $^2J_{CP} = 13.3$ Hz, C$_o$), 157.6 (s, C^2). Anal. Calc. for C$_{50}$H$_{57}$N$_5$O$_{12}$P$_2$SFe (1069.9): C, 56.13; H, 5.37; N, 6.55. Found: C, 56.32; H, 5.46; N, 6.48%.

4.12. $Ph_3P=NP(S)[NMe-N=CH(C_6H_4)-o-O]_2[Ni]$ (9b)

Powdered **2** (0.133 g, 0.31 mmol) and Ni(sal)$_2 \cdot 2$H$_2$O **8** (0.105 g, 0.31 mmol) and THF (5 mL) are mixed in a sealed Schlenck and heated at 60 °C for 5 days under stirring. Upon heating, the suspension became a green solution, which turned into a dark yellow solution with time. The solvent was evaporated to dryness, and the resulting powder was extracted with dichloromethane. The solution was evaporated and compound **9b** was obtained as yellow powder 99% yield.

^{31}P {^1H} NMR (THF): $\delta = 13.9$ (d, $^2J_{PP} = 21.4$ Hz, P=N), 56.5 (d, $^2J_{PP} = 21.4$ Hz, P=S). ^{31}P {^1H} NMR (CDCl$_3$): $\delta = 14.5$ (d, $^2J_{PP} = 19.8$ Hz, P=N), 55.6 (d, $^2J_{PP} = 19.8$ Hz, P=S). ^1H NMR (CDCl$_3$): $\delta = 3.50$ (d, $^3J_{HP} = 10.2$ Hz, 6H, CH$_3$), 6.47 ("t", $^3J_{HH} = 6.9$ Hz, 2H, H-C^5), 6.80 (d, $^3J_{HH} = 7.4$ Hz, 2H, H-C^3), 6.98 (d, $^3J_{HH} = 8.5$ Hz, 2H, H-C^6), 7.20 ("t", $^3J_{HH} = 7.0$ Hz, 2H, H-C^4), 7.48–7.61 (m, 11H, HC=N, H-C$_m$, H-C$_p$), 7.73 (dd, $^3J_{HH} = 7.3$ Hz, $^3J_{HP} = 13.0$ Hz, 6H, H-C$_o$). ^{13}C {^1H} NMR (CDCl$_3$): $\delta = 44.5$ (br s, CH$_3$), 115.4 (s, C^3), 118.3 (s, C^5), 123.0 (br s, C^1), 128.8 (d, $^3J_{CP} = 11.8$ Hz, C$_m$), 128.9 (dd, $^1J_{CP} = 106.4$ Hz, $^3J_{CP} = 3.8$ Hz, C$_i$), 131.7 (d, $^4J_{CP} = 2.7$ Hz, C$_p$), 132.8 (s, C^4), 132.8 (d, $^2J_{CP} = 11.7$ Hz, C$_o$), 134.8 (s, C^6), 164.7 (s, C^2), 166.5 (d, $^3J_{CP} = 5.6$ Hz, HC=N). Mass (FAB): $m/z = 694$ [MH]$^+$. Anal. Calc. for C$_{34}$H$_{31}$N$_5$NiO$_2$P$_2$S (694.3): C, 58.81; H, 4.50; N, 10.09. Found: C, 58.67; H, 4.55; N, 10.01%.

4.13. $Ph_3P=NP(S)[NMe-N=CH(C_6H_4)-o-(O-\beta-\text{D}-glucoside})]_2[AuCl]$ (10e)

A solution of AuCl(tht) (0.030 g, 0.094 mmol) in CH$_2$Cl$_2$ (3 mL) was added dropwise to a solution of **4e** (0.090 g, 0.094 mmol) in THF (2 mL), and stirred overnight at room temperature. The solvent was evaporated to afford a solid, which was washed three times with CH$_2$Cl$_2$/pentane/Et$_2$O, to afford compound **10e** as a white powder in 85% yield.

^{31}P {^1H} NMR (THF-d_8): $\delta = 18.3$ (d, $^2J_{PP} = 18.9$ Hz, P=N), 49.2 (d, $^2J_{PP} = 18.9$ Hz, P=S). ^1H NMR (THF-d_8): $\delta = 3.49$ (d, $^3J_{HP} = 9.8$ Hz, 6H, CH$_3$), 3.52–3.97 (m, 12H, CH$_2$, HCOH), 4.67–5.03 (m, 10H, H-C$_g^1$, -OH), 7.01 (m, 2H, H-C^5), 7.35 (m, 4H, H-C$_g^3$, H-C$_g^4$), 7.63–8.24 (m, 19 H, HC=N, H-Ar). ^{13}C {^1H} NMR (THF-d_8): $\delta = 34.5$ (d, $^2J_{CP} = 13.6$ Hz, CH$_3$), 34.6 (d, $^2J_{CP} = 13.6$ Hz, CH$_3$), 63.67 and 63.74 (2s, CH$_2$OH), 72.13 and 72.18 (2s, C$_g^4$), 75.85 and 75.91 (2s, C$_g^5$), 79.1 (s, C$_g^2$ or C$_g^3$), 79.38 and 79.44 (2s, C$_g^3$ or C$_g^2$), 104.54 and 104.78 (2s, C$_g^1$), 119.7 and 120.1 (2s, C^3), 124.39 and 124.49 (2s, C^5), 127.5 (s, C^6), 128.10 and 128.16 (2s, C^1), 130.2 (dd, $^1J_{CP} = 104.6$ Hz, $^3J_{CP} = 4.0$ Hz, C$_i$), 130.7 (d, $^3J_{CP} = 12.1$ Hz, C$_m$), 131.2 (s, C^4), 134.7 (s, C$_p$), 135.0 (d, $^2J_{CP} = 106.0$ Hz, C$_o$), 136.7 (d, $^3J_{CP} = 15.8$ Hz, CH=N), 158.0 (s, C^2). Anal. Calc. for C$_{46}$H$_{53}$AuClN$_5$O$_{12}$P$_2$S (1194.4): C, 46.26; H, 4.47; N, 5.86. Found: C, 46.03; H, 4.52; N, 5.78%.

5. X-ray structure analysis

Data collection were collected at low temperature (180(2) K) on an Xcalibur Oxford Diffraction diffractometer using a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device. The final unit cell parameters have been obtained by means of least-squares refinement performed on a set of 5000 well measured reflections, and crystal decay has been monitored during the data collections, no significant fluctuations of intensities have been observed. The structures have been solved by Direct Methods using SIR92 [22], and refined by means of least-squares procedures on a F^2 with the aid of the program SHELXL97 [23] include in the software package WINGX version 1.63 [24]. The atomic scattering factors were taken from International tables for X-ray crystallography [25]. All hydrogen atoms were located on a difference Fourier maps, and refined by using a riding model. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. Drawing of molecule is performed with the program ORTEP32 [26] with 50% probability displacement ellipsoids for non-hydrogen atoms.

Appendix A. Supporting information available

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 287345 for compound **5d**. Copies of this information may be obtained free of charge from: The Director CCDC 12 Union Road, Cambridge, CB2 1EZ UK, fax (int. code): +44 1223 336 033, or e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.a-c.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.12.022.

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