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P(X)-modified enaminoketones as novel ligands

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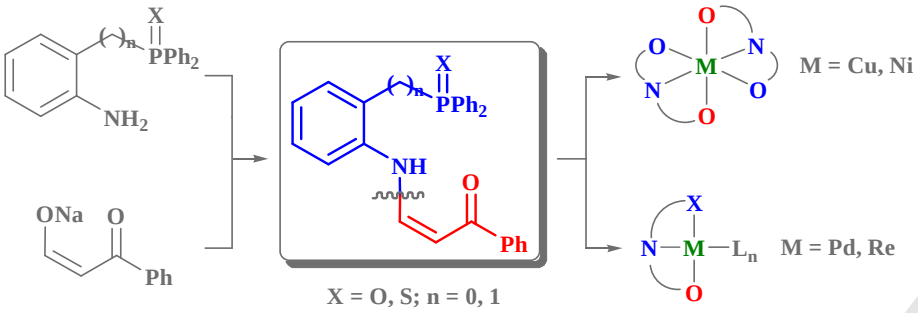

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(Thio)phosphoryl-functionalized enaminoketones: Synthesis, structure, and complexing properties towards transition metal ions

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P(X)-functionalized enaminoketones (X=O, S) **1a,b** have been readily obtained by the condensation of *o*-(thio)phosphorylated anilines with sodium salt of benzoylacetaldehyde. The ligands derived exist in solution in the expected ketamino tautomeric form, but, unlike typical enaminoketones, tend to exist as *cis*-isomers in polar media, favored by the formation of the strong P=O…HN intramolecular hydrogen bond. This six-membered hydrogen-bonded ring is also observed in the solid structure of **1a**, which, nevertheless, features a *trans*-configuration of the enaminoketone fragment. Independent from the isomeric composition, the ligands obtained readily form κ^3-*X,N,O* (X = O, S) complexes with a range of transition metal ions (Re(I), Pd(II), Cu(II), and Ni(II)) adopting in all cases the *cis*-configuration. The structures of the novel compounds are confirmed using multinuclear NMR and IR spectroscopy as well as X-ray crystallography.

Key words: Enaminoketones, Tridentate ligands, Transition metals, X-ray diffraction

1. Introduction

Enaminoketones bearing the N–R^1C=CR^2–CR^3=O conjugated fragment ($R^{1–3}$ = H, Alk, Ar) are extensively studied as useful precursors in organic synthesis,[1] especially for the creation of various heterocycles,[1c,2] and promising candidates in drug development.[2b,3] Furthermore, these readily available monoanionic bidentate chelating ligand systems, capable of forming unsymmetrical metal complexes owing to the presence of different donor centers, are also of unfailing interest in coordination and organometallic chemistry as convenient models for investigation of metal binding modes,[4] high-performance catalysts,[5] CVD precursors[4b,6] and so on.[7] Compared to bidentate ligands, the number of enaminoketones with an additional coordination site, leading on complexation to tridentate structures, is rather limited,[5g,j–l,6,8] being represented for the most part by derivatives of 1,3-diketones. The structural features of these ligands are poorly explored, although they may have a considerable impact on their complexing features.

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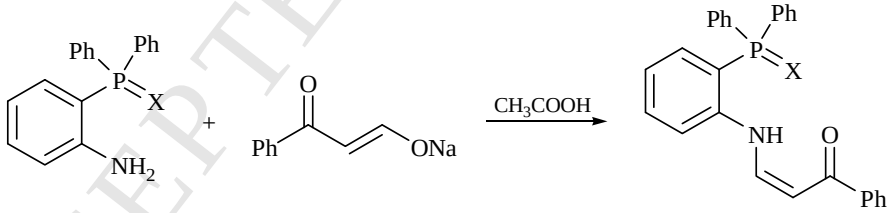
Recently we have shown that *o*-(thio)phosphorylated anilines can be used as convenient basic blocks for the synthesis of oligodentate ligands *via* simple modular assembling with a range of carbonyl derivatives,[9] affording P(X)-modified carbamoylmethylphosphine oxides and sulfides[10] and salicylaldimines[11] which demonstrate interesting coordination behaviour upon interaction with different metal precursors. The complexes obtained feature promising catalytic[11,12] and luminescent properties.[13] Following up this project, it seems interesting to involve *o*-(thio)phosphorylated anilines in the synthesis of P(X)-functionalized enaminoketones using benzoylacetaldehyde as a carbonyl component.

Herein, we report on the synthesis of enaminoketones functionalized with (thio)phosphoryl groups which serve as tridentate monoanionic ligands upon complexation with transition metals. A special emphasis is placed on the structural peculiarities of the novel compounds both in solution and in the solid state.

2. Results and Discussion

2.1. Synthesis and characterization of ligands

Target (thio)phosphorylated enaminoketones **1a,b** have been readily obtained in good yields by the condensation of sodium salt of benzoylacetaldehyde with *o*-(thio)phosphoryl-substituted anilines in aqueous alcohol followed by treatment with acetic acid (Scheme 1). (Thio)phosphorylated anilines, the key precursors, were synthesized according to the earlier published procedures.[10]

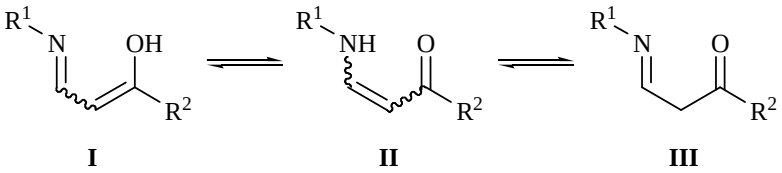


X = O (**1a**) 78%
X= S (**1b**) 58%

Scheme 1. Synthesis of (thio)phosphoryl-functionalized enaminoketones **1a,b**.

As is known, primary and secondary acyclic enaminoketones can undergo prototropic rearrangements resulting in enolimino (**I**), ketamino (**II**), and ketimino (**III**) tautomeric forms (Scheme 2). The spectral (NMR, UV-vis, IR) and X-ray diffraction studies for different enaminoketones suggested that the ketamino form **II** describes the ground state of such derivatives best of all.[2b] In the case of compounds **1a,b**, the absence of an absorption band corresponding to the enol hydroxyl group stretching vibrations in the IR spectra as well as the absence of signals of the OH-group and methylene unit protons in the ^{1}H NMR spectra also give

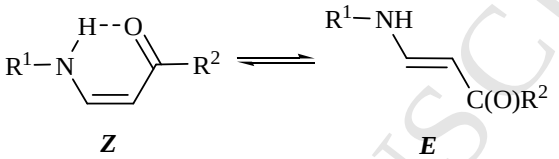
evidence of the ketamino tautomeric form both in solution and in the solid state. Note that the related phosphine-substituted derivative exists in the ketimino tautomeric form.[5g,8a]



I **II** **III**

Scheme 2.

Furthermore, owing to the restricted rotation around the C=C double bond, enaminoketones can exist as two geometric isomers (Scheme 3).



Z ***E***

Scheme 3.

The interconversion between *cis*- and *trans*-forms in solution is facilitated by the conjugation of the system and, in the case of enaminoketones **1a,b**, additionally by the absence of a bulky substituent at the NH–C carbon atom. As a rule, apolar media favor the formation of the *cis*-isomer, which is stabilized by the intramolecular hydrogen bond, while in polar solvents, capable of forming intermolecular hydrogen bonds, a contribution of the *trans*-form enhances. However, the introduction of the ancillary (thio)phosphoryl groups completely changes this tendency (Table 1). According to the NMR spectral data, a mixture of both geometric isomers of enaminoketones **1a,b** is observed in solvents of various polarity ($CDCl_3$, CD_3OD and $(CD_3)_2SO$). This can be readily deduced from the characteristic signal patterns in their ^1H NMR spectra (see Table 1 and the experimental section). Thus, the ^1H NMR spectra of **1a,b** show two doublet signals of the HC–C(O) group proton at 5.71–6.03 and 6.23–6.60 ppm with the corresponding coupling constants of 7.5–8.4 and 12.5–12.8 Hz, which can be related to the *cis*- and *trans*-isomers, respectively. Moreover, a pair of doublet signals is observed also for the NH-protons: at 10.04–10.98 (*trans*-form) and 11.82–12.79 (*cis*-form) ppm. Although the assignment of signals of the second methine proton in the case of *cis*-isomers is complicated by overlapping with the aromatic resonances, the signals of the N–CH fragment proton corresponding to the *trans*-isomer can be readily identified as virtual triplets at *ca*. 8 ppm. Therewith, the high values of $^3J_{HH}$ (11.3–13.3 Hz) evidence for a transoid arrangement of the NH and N–CH protons in all cases. Note that due to a rapid and complete H/D exchange in CD_3OD, the signals of the acidic NH-protons were not detected and those of the N–CH group proton converted into doublets. The ^{31}P NMR spectra of **1a,b** demonstrate two singlet signals. According to the isomer ratios in the ^1H NMR

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spectra, the lower field signals (in the range of 29.9–33.8 for **1a** and 38.5–39.3 ppm for **1b**) were attributed to the *cis*-form, while the higher field ones (35.3–38.3 (**1a**) and 38.9–39.7 (**1b**) ppm) were assigned to the *trans*-form. The high field resonances of the NH-protons of both isomeric forms in the ^{1}H NMR spectra of **1a,b** imply the involvement of these H-atoms in hydrogen bonds in all cases (compare 10–13 ppm for compounds **1a,b** with typical values of 4–8 ppm[2b]). Taking this into account, a difference in the chemical shifts of the phosphorus atoms for the *cis*- and *trans*-forms can be tentatively explained by the different hydrogen bonding patterns, which are likely to involve the (thio)phosphoryl group only in the case of the *trans*-form and carbonyl group in addition to the (thio)phosphoryl one in the case of the *cis*-form (bifurcated hydrogen bond). Thus, the P=O...HN hydrogen-bonded ring seems to be a key structural feature of these systems. Unlike typical enaminoketones, the *cis*-forms of compounds **1a,b** predominate over the expected *trans*-isomers in polar media (Table 1). Presumably, the introduction of the (thio)phosphoryl group, acting as the hydrogen bond donor, leads to the higher polarization of the carbonyl group compared to nonfunctionalized enaminoketones, and this effect is more pronounced for the *cis*-form, which may explain the stability of *cis*-isomers of **1a,b,2** in polar media. As for apolar media, the *trans*-isomer of P(O)-substituted enaminoketone **1a** appeared to be more stable in chloroform and even in benzene,[1] while both geometric isomers of its thiophosphorylated analog **1b** are present in almost equal amounts (Table 1). Interestingly, in the case of P(O)-substituted enaminoketone **2** with the elongated phosphoryl arm, which was synthesized in a similar manner starting from 2-[(diphenylphosphoryl)methyl]aniline,[14] the *cis*-isomer prevail both in polar and apolar media. Apparently, these results, being in contradiction with the known examples, require further investigations.

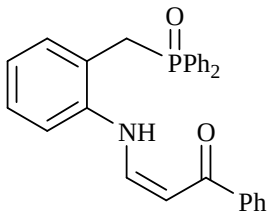

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Table 1. Selected NMR spectral data of compounds **1a,b,2**

Compound	**Solvent**	**^{31}P{^{1}H} NMR:** δ/ppm (content/%)	**^{1}H NMR:** δ/ppm ($^{3}J_{HH}$/Hz)	
			HC–C(O)	NH

[1] The contents of *cis*- and trans-isomers of enaminoketone **1a** in C_6D_6 comprise 15 and 85%, respectively.

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		cis	*trans*	*cis*	*trans*	*cis*	*trans*
1a	$CDCl_3$	31.10 (25)	37.60 (75)	5.99 (8.4)	6.60 (12.8)	12.79 (13.3)	10.94 (12.8)
	$(CD_3)_2SO$	29.85 (70)	35.30 (30)	6.03 (8.4)	6.60 (12.6)	12.45 (12.1)	10.98 (13.2)
	CD_3OD	33.77 (85)	38.34 (15)	5.90 (8.4)	6.47 (12.5)	n/o	n/o
1b	$CDCl_3$	38.93 (45)	39.65 (55)	5.71 (8.2)	6.35 (12.7)	11.82 (11.3)	10.04 (12.7)
	$(CD_3)_2SO$	38.49 (84)	38.85 (16)	5.92 (7.5)	6.42 (12.8)	11.81 (12.3)	9.71 (12.8)
	CD_3OD	39.27 (82)	39.81 (18)	5.74 (8.2)	6.23 (12.8)	n/o	n/o
2	$CDCl_3$	29.42 (73)	35.81 (27)	5.87 (7.6)	6.55 (12.6)	12.41 (11.5)	10.29 (br s)
	$(CD_3)_2SO$	29.09 (60)	33.07 (40)	6.11 (7.8)	6.44 (12.5)	12.37 (12.2)	10.30 (8.9)
	CD_3OD	33.51 (74)	36.77 (26)	6.07 (7.7)	6.55 (12.1)	n/o	n/o

n/o not observed

The IR spectra of solid samples of enaminoketones **1a,b,2** (KBr pellets) show the characteristic absorption bands of the P=X group stretching vibrations at 1184–1197 (X = O) and 637 cm^{-1} (X = S), intensive absorption bands of the C=C and C=O bonds at 1541–1583 and 1617–1654 cm^{-1}, respectively, and the low-intensity absorption bands in the range of 3150–3250 cm^{-1} typical for the NH group stretching vibrations.

The X-ray diffraction data for ligand **1a** showed that the intramolecular hydrogen bond between the P=O and N–H groups, assumed in solution, is indeed realized in the crystalline state (N…O 2.7525(16) Å, NHO 147(1)°), while the enaminoketone moiety adopted the *trans*-configuration (Fig. 1, Tables A. 1 and 2 in supplementary material). This confirms an essential role of the phosphoryl pendant arm in the structural features of these systems. Note that the molecule of **1a** has high planarity: both benzene rings at the ends of the enaminoketone fragment do not significantly deviate from its mean plane (the corresponding dihedral angles are 9.9(2)° and 8.1(2)° for the C(1)–C(6) and C(10)–C(15) rings, respectively. In a crystal, the molecules of **1a** are assembled into a 3D-framework through a series of weak intermolecular interactions. Those include C–H…O, C–H…π, and π…π contacts with the shortest C…O and C…C separations being 3.289(1), 3.758(1), and 3.212(1) Å, respectively.

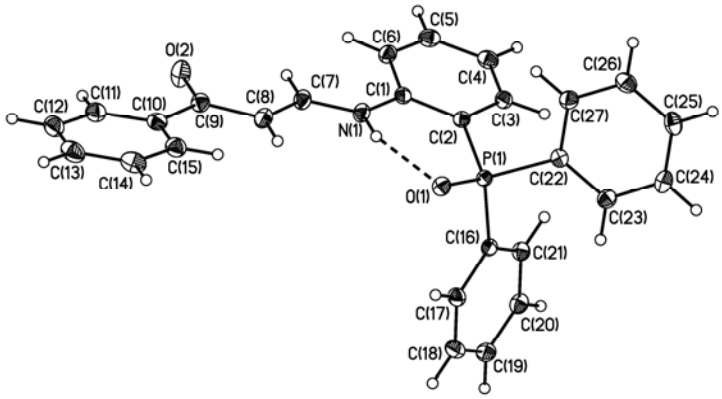

Fig. 1 General view of ligand **1a** in representation of atoms *via* thermal ellipsoids (p = 50%). Dashed line represents the hydrogen bond.

2.2. Synthesis and characterization of complexes

Independent from the isomeric composition, enaminoketones **1a,b,2** readily form complexes with a range of transition metal ions, serving in all cases as tridentate monoanionic ligands, *i.e.*, adopting the *cis*-configuration. Thus, the reaction of **1a,b** and **2** with rhenium pentacarbonyl bromide in toluene solution under reflux in the presence of Et_3N proceeds as the metallation at the amide nitrogen atom accompanied by the coordination of carbonyl and (thio)phosphoryl groups to give κ^3-*X,N,O* (X = O, S) complexes **3a,b** and **4** in high yields (83–88%) (Scheme 4). Of note is the ease of formation of complex **4** bearing fused six- and seven-membered metallocycles. The cyclopalladation of thiophosphoryl-substituted enaminoketone **1b** can be readily accomplished under action of $(PhCN)_2PdCl_2$ in dichloromethane solution at room temperature. The yield of complex **5** (70%) is good enough compared to other hybrid palladium pincer complexes bearing the oxygen donor centers and having two fused six-membered metallocycles.[10] Finally, the interaction of phosphorylated enaminoketones **1a** and **2** with copper and nickel acetates in alcohol solution under reflux afforded κ^3-*O,N,O* complexes **6**–**8** of $(L–H)_2M$ composition in 75–95% yields. Note that the synthesis of Cu(II) complexes **6,7** was accomplished only in the presence of triethylamine, while Ni(II) complex **8** can be smoothly obtained in the absence of a base.

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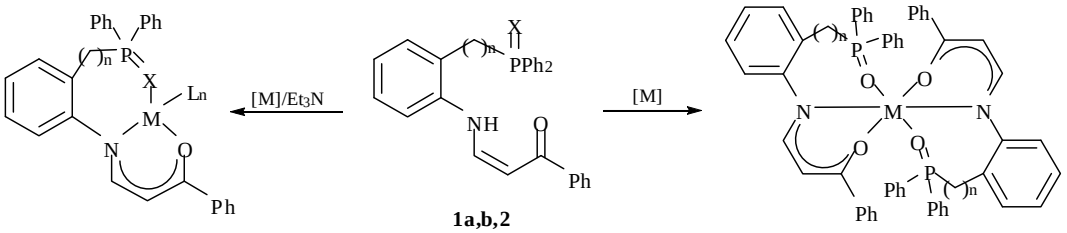

M = Re, Ln=(CO)3:
n = 0, X = O (**3a**) 88%
n = 0, X = S (**3b**) 83%
n = 1, X = O (**4**) 88%
M = Pd, L = Cl:
n = 0, X = S (**5**) 70%

M = Cu:
n = 0, X = O (**6**) 88%
n = 1, X = O (**7**) 95%
M = Ni:
n = 0, X = O (**8**) 75%

Scheme 4. Synthesis of transition metal complexes of (thio)phosphorylated enaminoketones **1a,b,2**.

The complexes obtained are yellow (**3a,b,4,8**), red (**5**), and green (**6,7**) crystalline solids, thermally stable up to 150ºC as well as air and moisture resistant. The realization of κ^3-*X,N,O* (X = O, S) coordination was deduced from the multinuclear NMR (^{1}H and ^{31}P) and IR spectral data as well X-ray diffraction analysis. Thus, a shift of the phosphorus resonances in the ^{31}P NMR spectra of Re(I) and Pd(II) complexes **3**–**5** compared to the signals of the free ligands unequivocally confirms the coordination of the (thio)phosphoryl groups. Therewith, the value of $\Delta\delta_P$ and direction of the shift depend on the substituent X in the P=X moiety and nature of metal ion and deuterated solvent (downfield shift by 7.7–11.0 ppm for P(O)-functionalized complexes and upfield or downfield shift by 0.4–2.4 ppm in the case of phosphine sulfide derivatives). Although Cu(II) and Ni(II) complexes **6**–**8** are paramagnetic (no NMR spectra were observed), the coordination of (thio)phosphoryl groups in these particular cases as well as for the other complexes is supported by the lower frequency displacement of absorption bands corresponding to the P=X bond stretching vibrations in the IR spectra, comprising 10–76 cm^{-1} and 33–37 cm^{-1} for phosphoryl- and thiophosphoryl-containing metallocycles, respectively. The absence of both NH-group proton signals in the ^{1}H NMR spectra of compounds **3**–**5** and absorption bands at 3100–3200 cm^{-1} in the IR spectra of all the complexes confirm the occurrence of metallation at the amide nitrogen atom. Furthermore, a strong bathochromic shift of the C=O group stretching vibrations (Δ = 35–65 cm^{-1}) accompanied by the concomitant low-frequency displacement of the C=C bond absorption bands (Δ = 27–71 cm^{-1}) evidences for the coordination of the enaminoketone moiety. The coordination of the N–CH=CH–C=O fragment is also reflected in the ^{1}H NMR spectra of complexes **3**–**5** by the downfield shift of the HC–C(O) and N–CH proton signals with transformation of the latter into doublets (see the experimental section). The ^{13}C NMR spectra of complexes **3**–**5** also fit well the suggested structures. It is worth mentioning that compounds **3a,b** and **4** form stable atropisomers in solution at room temperature (evidenced by separation of the signals of prochiral groupings) like the related Re(I) complexes of P(X)-

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modified (X = O, S) carbamoylmethylphosphine oxides and sulfides.[10] The identity of the complexes derived was also supported by the elemental analysis data.

The single-crystal X-ray diffraction experiments performed for complexes **3a**, **3b**, **5**, and **6** also confirm the realization of κ^3-*X*,*N*,*O*-coordination (X = O, S) of the deprotonated ligand form in all cases (Figs 2–5). The complexation is accompanied by the expected changes in the geometry of P(X)-modified enaminoketones (see Table A. 1 in supplementary material for the selected bond lengths and angles). Thus, the P=O bond lengthens from 1.4995(10) Å in **1a** to 1.514(2) Å in its rhenium complex **3a**, although no elongation is observed for its copper counterpart **6** (*vide infra*). The covalent bonds in the N–CH=CH–C=O fragment of **3a** and **6** become alternatively shorter/longer compared to **1a**, indicating the delocalization of the negative charge over the deprotonated enaminoketone backbone (Table A. 1). In complexes **3b** and **5**, the main bond lengths are also within the normal values. The coordination also affects the molecule planarity: the dihedral angles between the C(1)–C(6) and C(10)–C(15) benzene rings and the enaminoketone moiety increases to 27.5(2)–60.5(5)° and 12.6(6)–29.1(2)°, respectively.

In both of the rhenium complexes **3a** and **3b**, the metal atom has nearly ideal octahedral environment. Palladocycle **5** features the square-planar geometry around the metal center. The copper ion in **6** has a coordination mode of [4+2] formed by two symmetry-equivalent O(2) and N(1) atoms (as there is an inversion center at the position of the metal atom) in a nearly ideal square-planar environment and additionally by two O(1) atoms with the resulting Cu–O line almost perpendicular to this plane (83.4(2)°). Therewith, the Cu–O distances for the oxygen atoms in the equatorial and axial positions are 1.9490(11) and 2.4580(11) Å, respectively. Note that the P=O bond was unexpectedly shorter than that in the free ligand (**1a**) (1.4988(11) and 1.4995(10) Å, respectively), suggesting that the Cu(1)–O(1) bond is weaker than the intramolecular hydrogen bond in **1a**.

The conformations of the resulting metallocycles vary from a flattened envelope (C(O)-containing metallocycle in **3b**) to a distorted boat (P(S)-containing metallocycle in **5)**. Among all the complexes X-rayed in this study, those with palladium and copper were obtained as crystallosolvates with Et_2O and $CHCl_3$ (**5**) and methanol (**6**). In the latter case (Fig. 5), the solvate molecule forms rather strong hydrogen bond with the phosphoryl group (O…O 2.7796(17) Å, OHO 167(1)°) (Table A. 2). This is the strongest intermolecular interaction in the crystals of **3a**, **3b**, **5**, and **6**; others include C–H…O, C–H…π, and π…π (**3a**), or O…π (**3b**), or Cl… π and C–H…Cl (**5**).

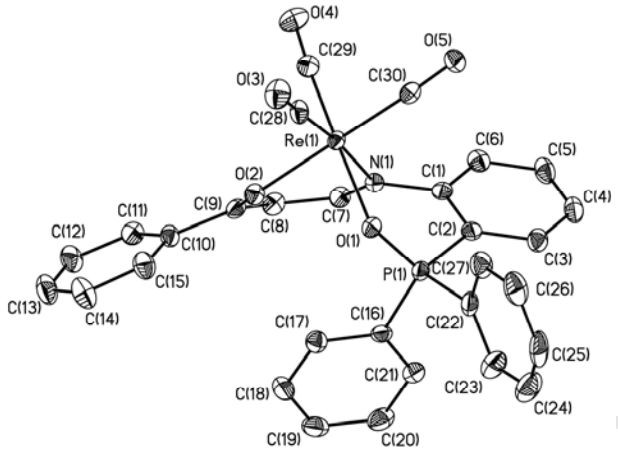

Fig. 2. General view of complex **3a** in representation of atoms by thermal ellipsoids (p = 50%). Hereinafter, the H(C) atoms are omitted for clarity.

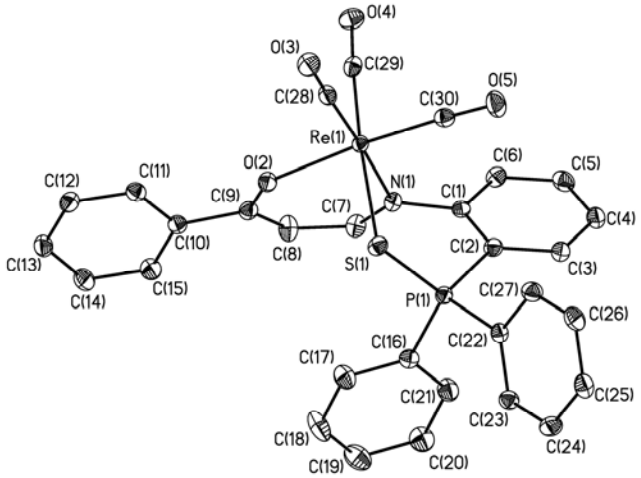

Fig. 3. General view of complex **3b** in representation of atoms by thermal ellipsoids (p = 50%).

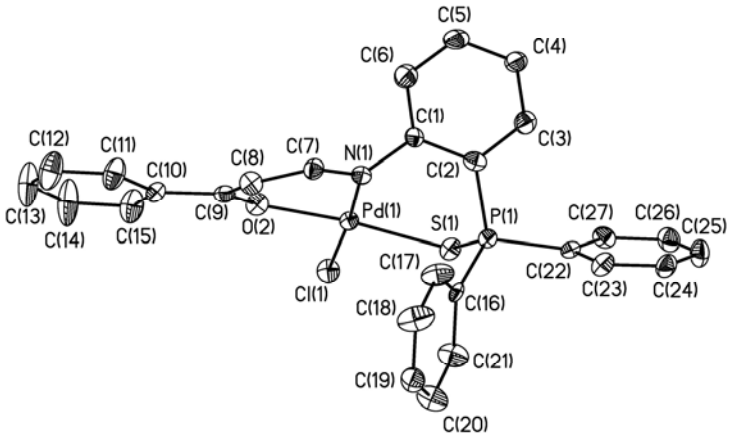

Fig. 4. General view of complex **5** in representation of atoms by thermal ellipsoids (p = 50%). Solvate Et_2O and $CHCl_3$ molecules are not shown.

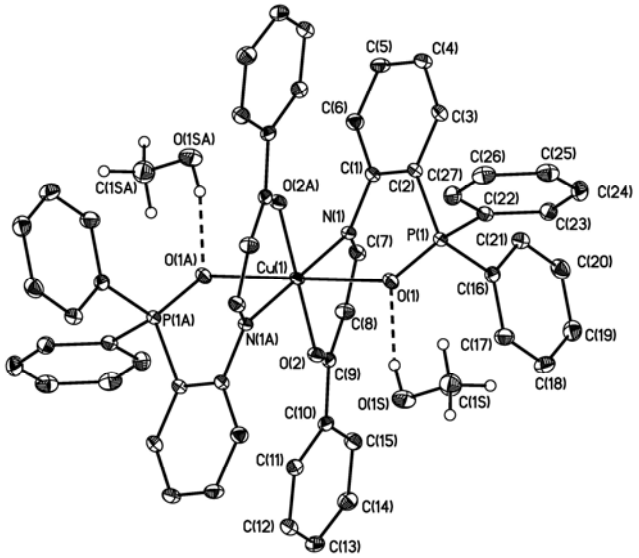

Fig. 5. General view of complex **6** in representation of atoms by thermal ellipsoids (p = 50%). Dashed line represents the hydrogen bond.

3. Conclusions

Simple condensation of *o*-(thio)phosphorylated anilines with sodium enolate of benzoylacetaldehyde afforded novel oligodentate ligands, namely, P(X)-functionalized enaminoketones (X=O, S). The compounds obtained show interesting structural behavior both in solution and in the solid state and readily form stable complexes with a range of transition metal ions (Re(I), Pd(II), Cu(II), and Ni(II)), adopting in all cases *X*,*N*,*O*-coordination mode (X = O, S).

4. Experimental

4.1. General remarks

All manipulations were carried out without taking precautions to exclude air and moisture. Dichloromethane was distilled from P_2O_5. 2-(Diphenylphosphoryl)aniline and its thioanalog were obtained from 2-diphenylphosphinoaniline according to the literature procedures.[10] 2-[(Diphenyl)phosphorylmethyl]aniline was derived by the reduction of the nitro-substituted predecessor easily available, in turn, by the Arbuzov reaction between o-nitrobenzyl bromide and Ph_2POEt.[14] Benzoylacetaldehyde sodium salt was synthesized by the Claisen condensation of acetophenone with ethyl formate under action of sodium ethoxide analogous to the procedure described in ref.[15] All other chemicals and solvents were used as purchased.

NMR spectra were recorded on Bruker Avance-300 and Bruker Avance-400 spectrometers, and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^{1}H and ^{13}C) or externally to H_3PO_4 (^{31}P). For simplicity, the integral

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intensities of the proton signals for the *trans*- and *cis*-isomers of ligands **1a,b,2** in the description of the ^{1}H NMR spectral data are given irrespective of the real contents of the isomers, which, in turn, can be found in Table 1. The ^{13}C NMR spectra were registered using the *J*MODECHO mode; the signals for the C atoms bearing odd and even numbers of protons have opposite polarities. The numeration of carbon atoms of the central benzene ring in the descriptions of ^{1}H and ^{13}C NMR spectral data for ligands **1a,b,2** and complexes **3**–**5** is in agreement with IUPAC nomenclature for the ligands. The same principle of numbering was used to describe the solid-state molecular structures characterized by X-ray crystallography.

Column chromatography was carried out using Merck silica gel 60 (230–400 mesh ASTM). IR spectra were recorded on a Nicolet Magna-IR750 FT-spectrometer, resolution 2 cm^{-1}, 128 scans. The assignment of absorption bands in the IR spectra was made according to ref.[16] Melting points were determined with a MPA 120 EZMelt Automated Melting Point Apparatus and were uncorrected.

*4.2. General procedure for the synthesis of (thio)phosphorylated enaminoketones **1a,b***

A solution of sodium enolate of benzoylacetaldehyde (1.30 g, 7.65 mmol) in 20 mL of water was added to a stirred solution of the corresponding aniline (7.65 mmol) in 30 mL of H_2O/C_2H_5OH (1:1) mixture. The resulting reaction mixture was treated with acetic acid (1.38 g, 23.0 mmol), and the desired product was extracted with dichloromethane. The organic phase was separated, dried over anhydrous Na_2SO_4, evaporated to dryness, and purified by silica gel column chromatography (eluent $CHCl_3$ (**1a**), CH_2Cl_2/hexane (20:1) (**1b**)) to give enaminoketones **1a,b** as yellow crystalline solids.

*4.2.1. 3-{[2-(Diphenylphosphoryl)phenyl]amino}-1-phenylprop-2-en-1-one **1a***

Yield: 2.52 g (78%). Mp: 201–202°C. ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$, δ/ppm): 31.10 (25%, *cis*), 37.60 (75%, *trans*). ^{1}H NMR (300.13 MHz, $CDCl_3$, δ/ppm, *J*/Hz): δ 5.99 (d, 1H, HC–C(O) (*cis*), $^{3}J_{HH}$ = 8.4), 6.60 (d, 1H, HC–C(O) (*trans*), $^{3}J_{HH}$ = 12.8), 6.98–7.10 (m, 3H, H_{Ar} (1H (*cis*) + 2H (*trans*))), 7.15–7.26 (m, 2H, H_{Ar} (*cis*)), 7.28–7.34 (m, 1H, H_{Ar} (*cis*)), 7.43–7.59 (m, 10H, H_{Ar} (6H (*cis*) +4H (*trans*))), 7.63–7.73 (m, 16H, H_{Ar} (10H (*trans*) + 6H (*cis*))), 7.77–7.83 (m, 3H, H_{Ar} (2H (*cis*) + 1H (*trans*))), 7.97–8.02 (m, 4H, H_{Ar} (2H (*cis*) + 2H (*trans*))), 8.30 (vt, 1H, N–CH (*trans*), $^{3}J_{HH}$ = 12.8), 10.94 (d, 1H, NH (*trans*), $^{3}J_{HH}$ = 12.8), 12.79 (d, 1H, NH (*cis*), $^{3}J_{HH}$ = 13.3 Hz). IR (KBr, ν/cm^{-1}): 514(m), 544(s), 665(w), 697(m), 711(w), 724(m), 744(m), 755(w), 783(w), 813(w), 890(w), 981(w), 1000(vw), 1023(w), 1038(w), 1065(vw), 1074(vw), 1094(vw), 1117(m), 1129(w), 1145(w), 1158(w), 1167(w), 1177(w), 1197(m) (ν(P=O)), 1223(w), 1265(s), 1293(m), 1308(m), 1437(m), 1455(m), 1526(w), 1553(s) (ν(C=C)), 1583(m), 1606(m), 1654(s) (ν(C=O)), 3052(w), 3152(w), 3203(w), 3254(br, vw) (both ν(NH)). Anal. Calcd for $C_{27}H_{22}NO_2P$: C, 76.58; H, 5.24; N, 3.31. Found: C, 76.56; H, 5.31; N, 3.22%.

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*4.2.2. 3-{[2-(Diphenylthiophosphoryl)phenyl]amino}-1-phenylprop-2-en-1-one **1b***

Yield: 1.95 g (58%). Mp: 148–150°C. $^{31}P\{^{1}H\}$ NMR (161.98 MHz, $CDCl_3$, δ/ppm): 38.93 (45%, *cis*), 39.65 (55%, *trans*). ^{1}H NMR (400.13 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 5.71 (d, 1H, HC–C(O) (*cis*), $^{3}J_{HH}$ = 8.2), 6.35 (d, 1H, HC–C(O) (*trans*), $^{3}J_{HH}$ = 12.7), 6.76 (dd, 1H, H(C3) (*trans*), $^{3}J_{HH}$ = 7.7, $^{3}J_{HP}$ = 14.7), 6.91 (dd, 1H, N–CH (*cis*), $^{3}J_{HH}$ = 8.2, $^{3}J_{HH}$ = 11.3), 6.97 (t, 1H, H_{Ar} (*trans*), $^{3}J_{HH}$ = 7.5), 7.03–7.04 (m, 2H, H_{Ar} (*cis*)), 7.20 (dd, 1H, H(C6) (*trans*), $^{3}J_{HH}$ = 7.8, $^{4}J_{HP}$ = 5.2), 7.34–7.56 (m, 21H, H_{Ar} (11H (*cis*) + 10H (*trans*))), 7.68 (dd, 4H, *o*-H in $P(S)Ph_2$ (*trans*), $^{3}J_{HH}$ = 7.7, $^{3}J_{HP}$ = 13.8), 7.80 (d, 2H, *o*-H in C(O)Ph (*cis*), $^{3}J_{HH}$ = 7.7), 7.85 (dd, 4H, *o*-H in $P(S)Ph_2$ (*cis*), $^{3}J_{HH}$ = 7.4, $^{3}J_{HP}$ = 13.7), 7.88 (d, 2H, *o*-H in C(O)Ph (*trans*), $^{3}J_{HH}$ = 7.5), 7.99 (vt, 1H, N–CH (*trans*), $^{3}J_{HH}$ = 12.7), 10.04 (d, 1H, NH (*trans*), $^{3}J_{HH}$ = 12.7), 11.82 (d, 1H, NH (*cis*), $^{3}J_{HH}$ = 11.3). IR (KBr, ν/cm^{-1}): 520(m), 614(w), 637(m) (ν(P=S)), 688(m), 713(m), 718(m), 739(w), 760(m), 819(vw), 992(w), 1021(m), 1040(w), 1065(w), 1094(m), 1145(w), 1179(w), 1210(m), 1232(s), 1274(m), 1278(m), 1351(w), 1437(s), 1454(s), 1482(w), 1499(w), 1541(s) (ν(C=C)), 1567(m), 1580(s), 1597(w), 1617(m) and 1627(s) (both ν(C=O)), 2851(vw), 2920(w), 3063(w), 3153(br, vw) (ν(NH)). Anal. Calcd for $C_{27}H_{22}NOPS$: C, 73.78; H, 5.05; N, 3.19. Found: C, 73.69; H, 5.04; N, 3.14%.

*4.3. Synthesis of 3-({2-[(diphenylphosphoryl)methyl]phenyl}amino)-1-phenylprop-2-en-1-one **2***

A solution of 2-[diphenylphosphoryl)methyl]aniline (2.53 g, 8.24 mmol) in chloroform (20 mL) was saturated with HCl. The solvent was removed in *vacuo* to give crude 2-[(diphenylphosphoryl)methyl]anilinium chloride in quantitative yield. A solution of benzoylacetaldehyde sodium salt (1.40 g, 8.24 mmol) in 20 mL of water was added to a stirred solution of the above salt in 30 mL of H_2O/C_2H_5OH (1:1) mixture. The resulting precipitate was filtered off and purified by silica gel column chromatography (eluent: $CHCl_3$/acetone (20:1)) to give 2.88 g of **2** as a yellow crystalline solid. Yield: 80%. Mp: 210–212°C. $^{31}P\{^{1}H\}$ NMR (161.98 MHz, $CDCl_3$, δ/ppm): 29.42 (73%, *cis*), 35.81 (27%, *trans*). ^{1}H NMR (400.13 MHz, $CDCl_3$, δ/ppm, *J*/Hz): δ 3.71 (d, 2H, CH_2 (*trans*), $^{2}J_{HP}$ = 13.2), 3.77 (d, 2H, CH_2 (*cis*), $^{2}J_{HP}$ = 13.3), 5.87 (d, 1H, HC–C(O) (*cis*), $^{3}J_{HH}$ = 7.6), 6.55 (d, 1H, HC–C(O) (*trans*), $^{3}J_{HH}$ = 12.6), 6.71 (d, 1H, H(C6) (*trans*), $^{3}J_{HH}$ = 7.3), 6.84 (t, 1H, H(C4) (*trans*), $^{3}J_{HH}$ = 7.4), 6.99–7.08 (m, 3H, H_{Ar} (*cis*)), 7.18–7.28 (m, 3H, H_{Ar} (*trans*)), 7.35–7.57 (m, 19H, H_{Ar} (11H (*cis*) + 8H (*trans*))), 7.71 (dd, 4H, *o*-H in $P(O)Ph_2$ (*trans*), $^{3}J_{HH}$ = 7.6, $^{3}J_{HP}$ = 11.6), 7.79 (dd, 4H, *o*-H in $P(O)Ph_2$ (*cis*), $^{3}J_{HH}$ = 7.7, $^{3}J_{HP}$ = 11.5), 7.94–7.97 (m, 4H, H_{Ar} (2H (*cis*) + 2H (*trans*))), 8.11 (vt, 1H, N–CH (*trans*), $^{3}J_{HH}$ = 12.6), 10.29 (br s, 1H, NH (*trans*)), 12.41 (d, 1H, NH (*cis*), $^{3}J_{HH}$ = 11.5). IR (KBr, ν/cm^{-1}): 513(w), 523(w), 594(w), 694(m), 721(m), 741(w), 745(m), 751(m), 771(w), 850(w), 859(w), 1020(w), 1043(w), 1071(w), 1105(w), 1120(w), 1184(m) (ν(P=O)), 1240(m), 1285(m),

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1359(w), 1437(m), 1465(m), 1491(w), 1507(w), 1559(m), 1589(m) (ν(C=C)), 1604(w), 1631(s) (ν(C=O)), 2941(w), 3053(w), 3209(br, vw) (ν(NH)). Anal. Calcd for $C_{28}H_{24}NO_2P$: C, 76.87; H, 5.53; N, 3.20. Found: C, 76.94; H, 5.45; N, 3.16%.

*4.4. General procedure for the synthesis of Re(I) complexes **3a,b,4***

A solution of $Re(CO)_5Br$ (60 mg, 0.148 mmol), triethylamine (21 μL, 0.148 mmol), and the corresponding ligand (0.148 mmol) in 10 mL of toluene was refluxed for 1.5 h. After cooling to room temperature, the solvent was removed in *vacuo*, and the residue was purified by silica gel column chromatography (eluent CH_2Cl_2 (**3a,b**), $CHCl_3$ (**4**)) to give complexes **3a,b,4** as yellow crystalline solids.

4.4.1. [κ^3-*O,N,O*-(L–H)Re(I)] ***3a***

Yield: 90 mg (88%). Mp: >260°C (decomp.). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, δ/ppm): 42.13. ^1H NMR (400.13 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 5.38 (d, 1H, HC–C(O), $^3J_{HH}$ = 6.6), 7.00 (d, 1H, N–CH, $^3J_{HH}$ = 6.6), 7.02 (dd, 1H, H(C3), $^3J_{HH}$ = 7.4, $^3J_{HP}$ = 13.7), 7.14 (dt, 2H, *m*-H in P(O)Ph, $^3J_{HH}$ = 7.7, $^4J_{HP}$ = 3.5), 7.22 (dt, 1H, H(C4), $^3J_{HH}$ = 7.4, $^4J_{HP}$ = 3.1), 7.27–7.33 (m, 3H, H_{Ar}), 7.36–7.47 (m, 4H, H_{Ar}), 7.56 (dt, 2H, *m*-H in P(O)Ph, $^3J_{HH}$=7.8, $^4J_{HP}$ = 3.4), 7.66–7.71 (m, 4H, H_{Ar}), 7.82 (d, 2H, *o*-H in C(O)Ph, $^3J_{HH}$=7.6). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 95.48 (s, HC–C(O)), 120.65 (d, C6, $^3J_{CP}$ = 6.9), 124.77 (d, C4, $^3J_{CP}$ = 13.1), 127.03 (d, *ipso*-C in P(O)Ph, $^1J_{CP}$ = 112.4), 127.14 (s, *m*-C in C(O)Ph), 127.33 (d, C2, $^1J_{CP}$ = 105.5), 128.06 (s, *o*-C in C(O)Ph), 128.38 (d, *ipso*-C in P(O)Ph, $^1J_{CP}$ = 114.1), 128.53 (d, *m*-C in P(O)Ph, $^3J_{CP}$ = 13.1), 128.98 (d, *m*-C in P(O)Ph, $^3J_{CP}$ = 12.7), 130.38 (s, *p*-C in C(O)Ph), 131.41 (d, *o*-C in P(O)Ph, $^2J_{CP}$ = 10.7), 132.03 (d, C3, $^2J_{CP}$ = 11.0), 132.26 (d, *p*-C in P(O)Ph, $^4J_{CP}$ = 3.1), 132.50 (d, *o*-C in P(O)Ph, $^2J_{CP}$ = 10.7), 133.33 (d, *p*-C in P(O)Ph, $^4J_{CP}$ = 2.7), 134.57 (d, C5, $^4J_{CP}$ = 2.1), 138.80 (s, *ipso*-C in C(O)Ph), 158.87 (s, N–CH), 160.19 (d, C1, $^2J_{CP}$ = 2.7), 177.29 (s, C=O), 196.99 (s, CO), 197.89 (s, 2CO). IR (KBr, ν/cm^{-1}): 529(w), 545(m), 563(m), 691(m), 712(m), 731(m), 746(w), 758(w), 767(w), 838(w), 945(w), 999(w), 1026(w), 1068(m), 1088(w), 1121(m) and 1131(m) (both ν(P=O)), 1184(w), 1260(w), 1278(w), 1308(w), 1340(s), 1409(s), 1441(m), 1452(m), 1460(m), 1484(m), 1514(s) (ν(C=C)), 1562(m), 1570(m), 1590(m) (C=O), 1864(vs) (ν(CO)), 1892(vs) (ν(CO)), 2011(vs) (ν(CO)), 3076(vw). Anal. Calcd for $C_{30}H_{21}NO_5PRe$: C, 52.02; H, 3.06; N, 2.02. Found: C, 52.17; H, 2.96; N, 1.81%.

*4.4.2. Complex **3b***

Yield: 90 mg (83%). Mp: >232°C (decomp.). $^{31}P\{^1H\}$ NMR (161.98 MHz, $(CD_3)_2SO$, δ/ppm): 38.88. ^1H NMR (400.13 MHz, $(CD_3)_2SO$, δ/ppm, *J*/Hz): 5.10 (d, 1H, HC–C(O), $^3J_{HH}$ = 6.6), 6.80 (d, 1H, N–CH, $^3J_{HH}$ = 6.6), 6.96 (dd, 1H, H(C3), $^3J_{HH}$ = 7.6, $^3J_{HP}$ = 14.2), 7.27 (dt, 2H, *m*-H in P(S)Ph, $^3J_{HH}$ = 7.8, $^4J_{HP}$ = 3.6), 7.35–7.56 (m, 8H, H_{Ar}), 7.64 (d, 2H, *o*-H in C(O)Ph, $^3J_{HH}$ = 7.7), 7.69–7.72 (m, 4H, H_{Ar}), 7.77–7.86 (m, 2H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$,

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δ/ppm, *J*/Hz): 95.19 (s, HC–C(O)), 122.33 (d, C6, $^{3}J_{CP}$ = 6.9), 124.84 (d, C4, $^{3}J_{CP}$ = 12.5), 126.37 (d, *ipso*-C in P(S)Ph_2, $^{1}J_{CP}$ = 85.8), 127.11 (s, *m*-C in C(O)Ph), 127.98 (s, *o*-C in C(O)Ph), 128.67 (d, C2, $^{1}J_{CP}$ = 86.5), 128.79 (d, *m*-C in P(S)Ph, $^{3}J_{CP}$ = 13.8), 129.00 (d, *m*-C in P(S)Ph, $^{3}J_{CP}$ = 12.5), 130.26 (s, *p*-C in C(O)Ph), 131.81 (d, C3, $^{2}J_{CP}$ = 6.2), 131.93 (d, *o*-C in P(S)Ph, $^{2}J_{PC}$ = 11.1), 132.16 (d, *p*-C in P(S)Ph, $^{4}J_{CP}$ = 3.0), 133.00 (d, *p*-C in P(S)Ph, $^{4}J_{CP}$ = 2.7), 133.23 (d, *o*-C in P(S)Ph, $^{2}J_{CP}$ = 10.4), 134.73 (s, C5), 138.98 (s, *ipso*-C in C(O)Ph), 159.00 (d, C1, $^{2}J_{CP}$ = 2.6), 159.98 (s, N–CH), 177.81 (s, C=O), 194.05 (s, CO), 194.35 (s, CO), 195.56 (s, CO). IR (KBr, ν/cm^{-1}): 485(w), 513(w), 525(w), 600(m) (ν(P=S)), 620(w), 651(w), 690(m), 707(m), 749(w), 768(w), 838(w), 998(w), 1024(w), 1070(w), 1100(w), 1107(w), 1125(w), 1158(w), 1185(w), 1254(w),1310(w), 1339(s), 1411(s), 1438(m), 1454(s), 1484(m), 1514(s) (ν(C=C)), 1563(m), 1571(m), 1592(m) (ν(C=O)), 1891(vs) (ν(CO)), 1903(vs) (ν(CO)), 2011(vs) (ν(CO)), 2922(vw), 3056(vw). Anal. Calcd for $C_{30}H_{21}NO_4PReS{\cdot}0.25\ CH_2Cl_2$: C, 49.77; H, 2.97 N, 1.92. Found: C, 49.88; H, 2.62; N, 1.80%.

*4.4.3. Complex **4***

Yield: 92 mg (88%). Mp: >248°C (decomp.). $^{31}P\{^{1}H\}$ NMR (161.98 MHz, $CDCl_3$, δ/ppm): 37.21. ^{1}H NMR (400.13 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 3.39 (dd, 1H, CH_2, $^{2}J_{HH}$ = 15.4, $^{2}J_{HP}$ = 6.6), 3.80 (dd, 1H, CH_2, $^{2}J_{HH}$ = 15.4, $^{2}J_{HP}$ = 20.1), 5.90 (d, 1H, HC–C(O), $^{3}J_{HH}$ = 6.7), 7.04 (t, 1H, H(C4), $^{3}J_{HH}$ = 7.4), 7.11 (d, 1H, H(C6), $^{3}J_{HH}$ = 7.6), 7.17 (d, 1H, H(C3), $^{3}J_{HH}$ = 7.4), 7.30–7.34 (m, 3H, H_{Ar}), 7.41–7.52 (m, 7H, H_{Ar}), 7.54–7.64 (m, 3H, H_{Ar}), 7.82 (dd, 2H, *o*-H in P(O)Ph, $^{3}J_{HH}$ = 8.4, $^{3}J_{HP}$ = 11.9), 7.99 (d, 2H, *o*-H in C(O)Ph, $^{3}J_{HH}$ = 7.7). $^{13}C\{^{1}H\}$ NMR (100.61 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 35.80 (d, CH_2, $^{1}J_{CP}$ = 62.7), 93.92 (s, HC–C(O)), 123.74 (d, C6, $^{4}J_{CP}$ = 2.3), 124.35 (d, C2, $^{2}J_{CP}$ = 8.3), 125.63 (s, C5), 126.13 (d, *ipso*-C in P(O)Ph, $^{1}J_{CP}$ = 101.2), 127.05 (s, *m*-C in C(O)Ph), 128.08 (s, *o*-C in C(O)Ph), 128.73 (d, C4, $^{4}J_{CP}$ = 3.0), 128.88 (d, *m*-C in P(O)Ph, $^{3}J_{CP}$ = 12.1), 129.12 (d, *m*-C in P(O)Ph, $^{3}J_{CP}$ = 12.1), 130.02 (d, *ipso*-C in P(O)Ph, $^{1}J_{CP}$ = 109.5), 130.03 (s, *p*-C in C(O)Ph), 130.32 (d, *o*-C in P(O)Ph, $^{2}J_{CP}$ = 10.6), 130.63 (d, C3, $^{3}J_{CP}$ = 7.6), 131.66 (d, *o*-C in P(O)Ph, $^{2}J_{CP}$ = 9.8), 132.67 (d, *p*-C in P(O)Ph, $^{4}J_{CP}$ = 2.3), 132.25 (d, *p*-C in P(O)Ph, $^{4}J_{CP}$ = 3.0), 139.42 (s, *ipso*-C in C(O)Ph), 157.37 (d, C1, $^{3}J_{CP}$ = 4.5), 158.16 (s, N–CH), 175.06 (s, C=O), 196.28 (s, CO), 199.02 (s, CO), 199.08 (s, CO). IR (KBr, ν/cm^{-1}): 497(w), 536(w), 563(w), 692(m), 707(w), 715(w), 747(m), 759(w), 819(w), 997(w), 1025(w), 1073(w), 1098(w), 1121(m), 1142(m) and 1160(m) (both ν(P=O)), 1248(w), 1361(m), 1401(m), 1415(m), 1439(m), 1456(m), 1481(s), 1518(s) (ν(C=C)), 1571(m), 1593(m) (ν(C=O)), 1862(vs) (ν(CO)), 1875(vs) (ν(CO)), 1888(vs) (ν(CO)), 1900(s) (ν(CO)), 2007(vs) (ν(CO)), 2914(vw), 3060(vw). Anal. Calcd for $C_{31}H_{23}NO_5PRe$:·C, 52.69; H, 3.28 N, 1.98. Found: C, 52.64; H, 3.20; N, 1.91%.

*4.5. Synthesis of Pd(II) complex **5***

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A solution of $(PhCN)_2PdCl_2$ (66 mg, 0.172 mmol) in 5 mL of dichloromethane was slowly dropwise added to a solution of **1b** (76 mg, 0.172 mmol) and triethylamine (24 μL, 0.172 mmol) in 5 mL of CH_2Cl_2. The resulting reaction mixture was left under ambient conditions for 12 h, then the solvent was removed in *vacuo*, and the residue was purified by silica gel column chromatography (eluent CH_2Cl_2) to give 52 mg of complex **5** as a red crystalline solid. Yield: 70 mg (70%). Mp: >178°C (decomp.). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, δ/ppm): 36.58. ^1H NMR (400.13 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 5.76 (d, 1H, HC–C(O), $^3J_{HH}$ = 7.2), 6.53 (d, 1H, N–CH, $^3J_{HH}$ = 7.2), 6.84 (dd, 1H, H(C3), $^3J_{HH}$ = 7.7, $^3J_{HP}$ = 15.1), 6.95 (dd, 1H, H(C6), $^3J_{HH}$ = 7.8, $^4J_{HP}$ = 6.1), 7.17 (m, 1H, H_{Ar}), 7.31–7.34 and 7.39–7.43 (both m, 2H + 1H, H_{Ar}), 7.52–7.59 (m, 5H, H_{Ar}), 7.63–7.72 (m, 6H, H_{Ar}), 7.89 (d, 2H, *o*-H_{Ar} in C(O)Ph, $^3J_{HH}$ = 7.8). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 97.98 (s, HC–C(O)), 120.97 (d, C2, $^1J_{CP}$ = 83.8), 124.75 (d, C4, $^3J_{CP}$ = 12.5), 125.56 (d, *ipso*-C in $P(S)Ph_2$, $^1J_{CP}$ = 87.6), 126.42 (d, C6, $^3J_{CP}$ = 7.6), 127.80 (s, *m*-C in C(O)Ph), 128.12 (s, *o*-C in C(O)Ph), 129.32 (d, *m*-C in $P(S)Ph_2$, $^3J_{CP}$ = 13.2), 130.78 (d, C3, $^2J_{CP}$ = 7.9), 131.14 (s, *p*-C in C(O)Ph), 132.70 (d, *o*-C in $P(S)Ph_2$, $^2J_{CP}$ = 11.0), 133.40 (d, *p*-C in $P(S)Ph_2$, $^4J_{CP}$ = 3.0), 134.58 (d, C5, $^4J_{CP}$ = 2.3), 135.81 (s, *ipso*-C in C(O)Ph), 153.52 (d, C1, $^2J_{CP}$ = 3.0), 154.94 (s, N–CH), 176.20 (s, C=O). IR (KBr, ν/cm^{-1}): 502(m), 518(m), 541(w), 604(m) (ν(P=S)), 622(w), 690(m), 707(s), 748(m), 768(w), 844(w), 970(w), 998(w), 1025(w), 1072(w), 1104(m), 1134(w), 1163(w), 1183(w), 1231(m), 1261(m), 1274(w), 1332(s), 1403(s), 1437(s), 1450(s), 1461(s), 1483(m), 1513(s) (ν(C=C)), 1554(s), 1587(m) (ν(C=O)), 2852(vw), 2921(vw), 3055(w). Anal. Calcd for $C_{27}H_{21}ClNOPPdS$: C, 55.88; H, 3.65; N, 2.41. Found: C, 55.87; H, 3.67; N, 2.30%.

4.6. General procedure for the synthesis of Cu(II) complexes ***6,7***

A solution of $Cu(OAc)_2·H_2O$ (22 mg, 0.110 mmol), triethylamine (31 μL, 0.220 mmol), and the corresponding ligand (0.220 mmol) in 12 mL of methanol was refluxed for 1.5 h. After cooling to room temperature, the solvent was removed under reduced pressure. The resulting residue was washed with hot ethanol (10 mL) and diethyl ether (5 mL) and dried in *vacuo* to give complexes **6,7** as green crystalline solids.

4.6.1. [κ^3-*O,N,O*-$(L–H)_2Cu(II)$] ***6***

Yield: 90 mg (88%). Mp: >255°C (decomp.). IR (KBr, ν/cm^{-1}): 543(m), 554(m), 703(m), 710(m), 721(m), 748(w), 760(w), 773(w), 836(w), 998(w), 1025(w), 1072(w), 1100(w), 1118(w), 1126(m), 1157(w), 1174(m) and 1187(m) (ν(P=O)), 1235(w), 1274(w), 1309(w), 1350(m), 1419(s), 1436(m), 1457(s), 1485(m), 1517(s) (ν(C=C)), 1568(sh, m), 1571(m), 1592(m) (ν(C=O)), 2923(vw), 3054(w). Anal. Calcd for $C_{54}H_{42}CuN_2O_4P_2·H_2O$: C, 70.01; H, 4.79; N, 3.02. Found: C, 69.50; H, 4.89; N, 2.95%.

4.6.2. [κ^3-*O,N,O*-$(L–H)_2Cu(II)$] ***7***

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Yield: 104 mg (95%). Mp: >150°C (decomp.). IR (KBr, ν/cm^{-1}): 499(w), 508(w), 537(w), 694(m), 714(m), 746(m), 824(w), 999(w), 1023(w), 1072(w), 1103(w), 1120(m), 1143(w), 1174(m) and 1183(m) (ν(P=O)), 1240(w), 1279(w), 1308(w), 1358(m), 1420(m), 1437(m), 1457(m), 1480(s), 1520(s) (ν(C=C)), 1569(m), 1591(m) (ν(C=O)), 1630(w), 2943(vw), 3023(vw), 3056(w). Anal. Calcd for $C_{56}H_{46}CuN_2O_4P_2 \cdot 3H_2O$: C, 67.90; H, 5.29; N, 2.83. Found: C, 67.92; H, 5.30; N, 2.93%.

*4.7. Synthesis of Ni(II) complex **8***

A solution of $Ni(OAc)_2 \cdot 4H_2O$ (27 mg, 0.109 mmol) and **1a** (92 mg, 0.218 mmol) in 12 mL of EtOH was refluxed for 4.5 h. After cooling to room temperature, the resulting precipitate of complex **8** was filtered off, washed with ethanol (2×3 mL) and diethyl ether (2×3 mL), and dried in *vacuo* to give 74 mg of complex **8** as a yellow crystalline solid. Yield: 75%. Mp: >281°C (decomp.). IR (nujol, ν/cm^{-1}): 537(w), 561(m), 691(m), 703(m), 725(m), 741(w), 746(), 758(), 770(w), 830(w), 981(), 998(vw), 1023(w), 1071(w), 1098(w), 1117(w), 1128(m), 1152(m) and 1164(sh, m) (both ν(P=O)), 1246(w), 1275(w), 1346(m), 1427(s), 1439(m), 1456(s), 1465(s), 1483(m), 1506(m) (ν(C=C)), 1561(m), 1571(m), 1595(m) (ν(C=O)), 3053(w). Anal. Calcd for $C_{54}H_{42}N_2NiO_4P_2$: C, 71.78; H, 4.69; N, 3.10. Found: C, 71.81; H, 4.80; N, 3.04%.

4.8. X-ray crystallography

Single crystals suitable for X-ray experiments were obtained by recrystallization from EtOAc/EtOH (**1a**) and MeOH (**6**) or slow diffusion of hexane (**3a,b**) or ether (**5**) into chloroform solutions. X-ray diffraction experiments were carried out with an APEX2 DUO CCD diffractometer for compounds **1a** and **6** and with a SMART APEX2 CCD diffractometer for all others, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans) at 100K. The structures were solved by direct method and refined by full-matrix least-squares method against F^2 in anisotropic approximation for non-hydrogen atoms. Hydrogen atom of NH group in **1a** and that of OH group of a solvate methanol molecule in **6** were found in difference Fourier synthesis; the H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model. Crystal data and structure refinement parameters for **1a**, **3a**, **3b**, **5**, and **6** are given in Table 2. All calculations were performed using the SHELXTL software.[17]

Table 2. Crystal data and structure refinement parameters for **1a**, **3a**, **3b**, **5**, and **6**.

	1a	**3a**	**3b**	**5**	**6**
Empirical formula	$C_{27}H_{22}NO_2P$	$C_{30}H_{21}NO_5PRe$	$C_{30}H_{21}NO_4PReS$	$C_{59}H_{53}Cl_5N_2O_3P_2Pd_2S_2$	$C_{56}H_{50}CuN_2O_6P_2$
Formula weight	423.43	692.65	708.71	1354.14	972.46
T, K	100	100	100	100	100

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Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1	Fdd2	P-1
Z	4	4	2	8	1
a, Å	10.3025(4)	11.1347(4)	9.6378(3)	31.998(5)	8.2787(6)
b, Å	8.3782(3)	17.9830(7)	10.0867(3)	39.689(7)	10.9732(8)
c, Å	24.5325(10)	13.0777(5)	14.8057(5)	9.1926(15)	13.1079(10)
α, °	90.00	90.00	74.7460(10)	90.00	79.643(2)
β, °	100.4940(10)	94.8740(10)	82.5520(10)	90.00	80.973(2)
γ, °	90.00	90.00	71.1970(10)	90.00	83.683(2)
V, $Å^3$	2082.14(14)	2609.15(17)	1312.92(7)	11674(3)	1152.75(15)
D_{calc} (g cm^{-1})	1.351	1.763	1.793	1.541	1.401
Linear absorption, μ (cm^{-1})	1.57	47.6	48.06	10.17	5.99
F(000)	888	1352	692	5472	507
$2\theta_{max}$, °	58	58	58	54	57
Reflections measured	20834	28787	15843	29676	14407
Independent reflections	5528	6931	6971	6372	6127
Observed reflections [$I > 2\sigma(I)$]	4643	5817	6585	4605	5193
Parameters	280	343	343	359	305
R1	0.0395	0.0281	0.0191	0.0511	0.0350
wR2	0.1154	0.0629	0.0448	0.0835	0.0936
GOF	1.008	1.007	1.001	1.002	1.001
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e $Å^{-3}$)	0.615/-0.249	1.196/-0.991	1.164/-1.027	1.144/-0.914	0.545/-0.514

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Appendix A. Supplementary material

CCDC 956539–956543 contain the supplementary crystallographic data for **1a**, **3a**, **3b**, **5**, and **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Appendix B. Supplementary material

Supplementary material includes selected bond lengths and angles as well as hydrogen bond parameters for the compounds obtained.

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Condensation of (thio)phosphorylanilines with PhC(O)CH=CHONa afforded novel ligands.

P(X)-functionalized enaminoketones (X=O, S) show interesting structural behavior.

The ligands obtained readily form κ^3-*X*,*N*,*O*-complexes (X=O, S) with transition metals.

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(Thio)phosphoryl-functionalized enaminoketones: Synthesis, structure, and complexing properties towards transition metal ions

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Supplementary material

Table A. 1. Selected bond lengths (Å) and angles (°) for compounds **1a**, **3a**, **3b**, **5**, and **6**.

1a			
P(1)–O(1)	1.4995(10)	N(1)–C(7)–C(8)	124.90(13)
P(1)–C(2)	1.8069(13)	C(7)–N(1)–H(1N)	116.9
N(1)–C(1)	1.4020(17)	N(1)–C(7)–H(7C)	117.6
N(1)–C(7)	1.3491(17)	C(8)–C(7)–H(7C)	117.6
C(7)–C(8)	1.361(2)	C(7)–C(8)–H(8C)	120.6
C(8)–C(9)	1.4544(19)	C(7)–C(8)–C(9)	118.82(13)
O(2)–C(9)	1.2408(18)	C(9)–C(8)–H(8C)	120.6
C(9)–C(10)	1.5003(19)	O(2)–C(9)–C(8)	121.90(13)
O(1)–P(1)–C(2)	112.96(6)	C(8)–C(9)–C(10)	119.24(12)
N(1)–C(1)–C(2)	119.24(12)	O(2)–C(9)–C(10)	118.85(13)
C(7)–N(1)–C(1)	126.62(12)	C(15)–C(10)–C(9)	123.13(13)
C(1)–N(1)–H(1N)	116.5		
3°			
Re(1)–C(28)	1.930(3)	N(1)–Re(1)–O(1)	82.33(9)
Re(1)–C(29)	1.889(4)	O(2)–Re(1)–N(1)	82.15(9)
Re(1)–C(30)	1.884(3)	C(28)–Re(1)–N(1)	173.73(13)
Re(1)–O(1)	2.173(2)	C(29)–Re(1)–O(1)	176.46(12)
Re(1)–O(2)	2.130(2)	C(30)–Re(1)–O(2)	177.90(12)
Re(1)–N(1)	2.151(3)	O(1)–P(1)–C(2)	113.05(14)
P(1)–O(1)	1.514(2)	C(2)–C(1)–N(1)	117.6(3)
P(1)–C(2)	1.799(3)	C(7)–N(1)–C(1)	117.8(3)
N(1)–C(1)	1.430(4)	N(1)–C(7)–C(8)	125.8(3)
N(1)–C(7)	1.313(4)	N(1)–C(7)–H(7C)	117.1
C(7)–C(8)	1.392(5)	C(8)–C(7)–H(7C)	117.1

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C(8)–C(9)	1.386(5)	C(7)–C(8)–H(8C)	118.0
O(2)–C(9)	1.291(4)	C(9)–C(8)–C(7)	124.1(3)
C(9)–C(10)	1.494(5)	C(9)–C(8)–H(8C)	118.0
C(30)–Re(1)–C(28)	88.47(14)	O(2)–C(9)–C(8)	124.6(3)
C(30)–Re(1)–C(29)	85.31(15)	C(8)–C(9)–C(10)	120.4(3)
C(29)–Re(1)–C(28)	90.77(15)	O(2)–C(9)–C(10)	114.9(3)
O(2)–Re(1)–O(1)	85.45(8)		
3b			
Re(1)–C(28)	1.925(2)	N(1)–Re(1)–S(1)	85.44(5)
Re(1)–C(29)	1.905(2)	O(2)–Re(1)–N(1)	84.33(6)
Re(1)–C(30)	1.901(2)	C(28)–Re(1)–N(1)	176.91(8)
Re(1)–S(1)	2.5396(6)	C(29)–Re(1)–S(1)	176.38(7)
Re(1)–O(2)	2.1269(15)	C(30)–Re(1)–O(2)	174.15(8)
Re(1)–N(1)	2.1584(18)	C(2)–P(1)–S(1)	116.45(8)
P(1)–S(1)	2.0075(8)	C(2)–C(1)–N(1)	117.95(19)
P(1)–C(2)	1.816(2)	C(7)–N(1)–C(1)	118.30(18)
N(1)–C(1)	1.421(3)	N(1)–C(7)–C(8)	126.3(2)
N(1)–C(7)	1.320(3)	N(1)–C(7)–H(7C)	116.9
C(7)–C(8)	1.397(3)	C(8)–C(7)–H(7C)	117.3
C(8)–C(9)	1.395(3)	C(7)–C(8)–H(8C)	117.3
O(2)–C(9)	1.280(3)	C(9)–C(8)–C(7)	125.4(2)
C(9)–C(10)	1.496(3)	C(9)–C(8)–H(8C)	117.3
C(30)–Re(1)–C(28)	87.14(9)	O(2)–C(9)–C(8)	125.3(2)
C(30)–Re(1)–C(29)	89.94(9)	C(8)–C(9)–C(10)	119.4(2)
C(29)–Re(1)–C(28)	88.88(9)	O(2)–C(9)–C(10)	115.25(19)
O(2)–Re(1)–S(1)	87.12(5)		
5			
Pd(1)–O(2)	2.003(4)	S(1)–Pd(1)–Cl(1)	84.28(6)
Pd(1)–N(1)	2.042(5)	O(2)–Pd(1)–Cl(1)	85.85(12)
Pd(1)–S(1)	2.2921(16)	C(2)–P(1)–S(1)	109.8(2)
Pd(1)–Cl(1)	2.3093(16)	C(2)–C(1)–N(1)	121.3(5)
P(1)–S(1)	2.009(2)	C(7)–N(1)–C(1)	115.1(5)
P(1)–C(2)	1.787(6)	N(1)–C(7)–C(8)	129.4(6)
C(1)–N(1)	1.425(7)	N(1)–C(7)–H(7C)	115.3
N(1)–C(7)	1.318(7)	C(8)–C(7)–H(7C)	115.3
C(7)–C(8)	1.390(7)	C(7)–C(8)–H(8C)	117.9
C(8)–C(9)	1.392(8)	C(7)–C(8)–C(9)	124.1(6)
O(2)–C(9)	1.287(7)	C(9)–C(8)–H(8C)	117.9
C(9)–C(10)	1.490(8)	O(2)–C(9)–C(8)	123.0(5)

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N(1)–Pd(1)–O(2)	90.28(18)	C(8)–C(9)–C(10)	121.5(5)
N(1)–Pd(1)–S(1)	99.60(14)	O(2)–C(9)–C(10)	115.4(5)
N(1)–Pd(1)–Cl(1)	176.04(14)		
6			
Cu(1)–O(2)	1.9490(11)	C(9)–O(2)–Cu(1)	125.23(10)
Cu(1)–N(1)	1.9934(13)	O(1)–P(1)–C(2)	115.34(7)
Cu(1)–O(1)	2.4580(11)	C(2)–C(1)–N(1)	118.21(13)
P(1)–O(1)	1.4988(11)	C(7)–N(1)–C(1)	117.15(13)
P(1)–C(2)	1.8114(16)	N(1)–C(7)–C(8)	125.72(15)
N(1)–C(1)	1.4215(19)	N(1)–C(7)–H(7C)	117.1
N(1)–C(7)	1.319(2)	C(8)–C(7)–H(7C)	117.1
C(7)–C(8)	1.403(2)	C(7)-C(8)–H(8C)	118.4
C(8)–C(9)	1.395(2)	C(9)–C(8)–C(7)	123.28(15)
O(2)–C(9)	1.2801(19)	C(9)–C(8)–H(8C)	118.4
C(9)–C(10)	1.503(2)	O(2)–C(9)–C(8)	125.04(14)
O(2)–Cu(1)–N(1)	90.19(5)	C(8)–C(9)–C(10)	119.95(14)
C(7)–N(1)–Cu(1)	121.79(11)	O(2)–C(9)–C(10)	115.01(13)
C(1)–N(1)–Cu(1)	120.77(10)		

Table A. 2. Hydrogen bond geometry for compounds **1a** and **6** (Å, °).

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
1a				
N(1)–H(1N)...O(1)	0.91	1.94	2.7525(16)	147
6				
O(1S)–H(1SO)...O(1)	0.85	1.95	2.7796(17)	167

Symmetry transformations used to generate equivalent atoms: x,y,z