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4-Diphenylphosphinosydnone imines as bidentate ligands

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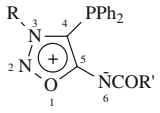
ABSTRACT

The synthesis and characterization of new 3-substituted-4-diphenylphosphinosydnone imines (1,2,3-oxadiazolium-imines-5) are reported.



(R= ^{n}Bu, NMe_2 ; R'= Me, ^{t}Bu, Ph, CF_3)

These compounds react with $[PdCl_2(MeCN)_2]$ in MeCN to afford monomeric *cis*-P,N-coordinated palladium complexes.

1. Introduction

The synthesis and application of phosphorus ligands, especially for the cases where the phosphorus ligand contains another coordinating functionality, are of considerable interest [1]. By introducing the second donor atom (N, S, O, Se, As, P) into the ligand it is possible to obtain bidentate ligands with donor centers of different donor capability and steric properties. The use of a heterocyclic moiety as a part of the ligand system has attracted great attention in recent years. In this paper we report the synthesis of new type of bidentate ligand containing a mesoionic moiety.

The first attempt to prepare such complexes based on sydnones was described in [2]. 4-Phosphino derivatives of sydnones, **1**, were chosen as the subject of the investigation. It was suggested by the authors that the exocyclic oxygen atom, bearing a negative charge, of the sydnone ring can act as a second donor center. However, the reaction of 3-(4-methoxyphenyl)-4-(ditertbutylphosphino)-sydnone **1** (R = –OMe) with $PdCl_2$ in EtOH gave the cyclometallation product, **2**. The cyclometallation process does not occur in the absence of a donor substituent at the 3 position of the phenyl group (Scheme 1). In this case, only the formation of the bis(phosphine) complex **3** is observed.

Sydnone imines, **4** in Fig. 1, are nitrogen analogues of sydnones and their exocyclic nitrogen atom also bears a significant negative charge [3]. However, the electron donating properties of the exocyclic nitrogen atom in sydnone imines are substantially stronger than those of the oxygen atom in sydnones. Sydnone imines, in contrast to sydnones, form salts with strong acids. The pK_a values for sydnone imines **4** vary from 2.5 to 4.6, depending on the substituents [4,5]. In addition, sydnone imines **4** react with methyl iodide to give the quaternary ammonium salt of the exocyclic nitrogen [5,6].

4-Phosphino substituted derivatives of sydnone imines, **5** in Fig. 1, should be more prone to act as bidentate ligands than their sydnone analogues (**1** in Scheme 1). Thus, coordination of **5** to transition metals could give rise to chelated complexes, **6** in Fig. 1.

2. Results and discussion

2.1. Synthesis of 4-diphenylphosphinosydnone imines

To synthesize new 4-diphenylphosphino derivatives of the sydnone imines **5** we have used the reaction of 4-lithium derivatives of sydnone imines [7] with diphenylphosphine chloride (Scheme 2, Table 1). Both the lithiation of sydnone imines and the addition of Ph_2PCl were carried out at the temperatures below −90 °C. At higher temperatures the formation of large amounts of decomposition products was observed, especially at the lithiation stage. Furthermore, both *n*-BuLi and Ph_2PCl must be slowly added to the reaction mixture to avoid overheating of the solution.

The 3-substituted-4-diphenylphosphinosydnone imines obtained belong to the class of hemilabile ligands, which contain both soft and hard donor atoms. The π-acceptor character of the phosphorus atom can stabilize a metal center in a low oxidation state, while the π-donor ability of the nitrogen atom makes the metal atom more susceptible to oxidative addition reactions.

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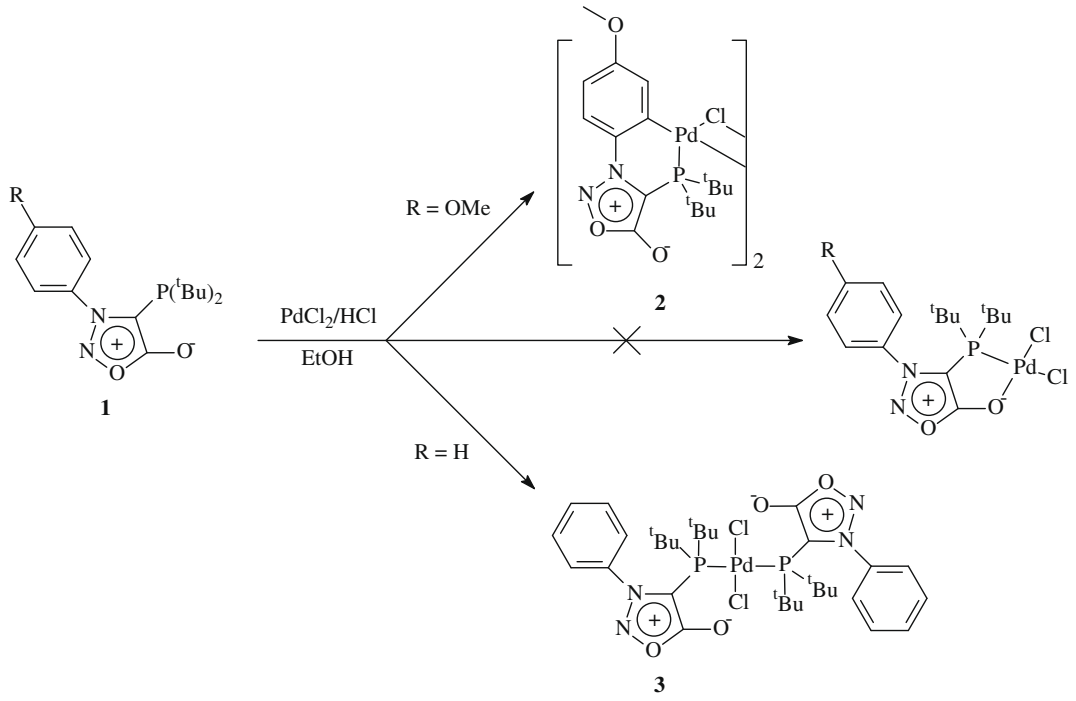


Scheme 1.

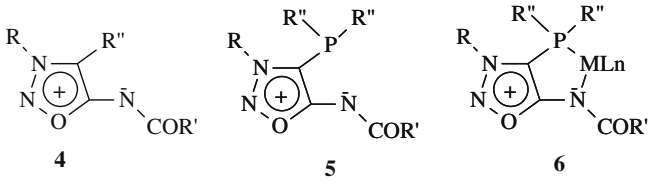
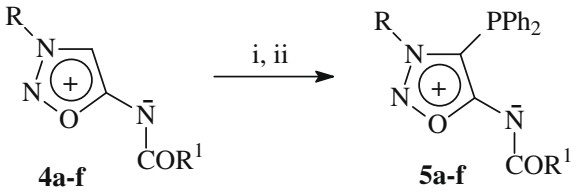


Fig. 1. Starting materials, ligands and target complexes.



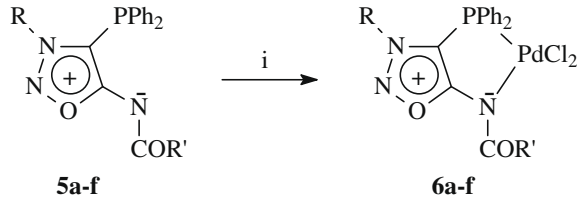
Scheme 2. (i) 1 equiv. *n*-BuLi, THF, −90 °C and (ii) 1 equiv. Ph_2PCl, −90 °C → r.t (slowly).

Table 1
Synthesis of 3-substituted-4-diphenylphosphinosydnone imines.

Compound	R	R_1	Yield, %
5a	*n*-Bu	Me	67
5b	*n*-Bu	Ph	80
5c	*n*-Bu	CF_3	56
5d	*n*-Bu	*t*-Bu	86
5e	Me_2N	Me	75
5f	Me_2N	Ph	70

2.2. Bidentate coordination chemistry of 3-substituted-4-diphenylphosphinosydnone imines

Treatment of the 4-diphenylphosphinosydnone imine **5a** with $[PdCl_2(MeCN)_2]$ in MeCN resulted in the formation of only one product, **6a** (Scheme 3). According to the X-ray structural data of complex **6a**, the ligand coordinates with palladium by P(1) and N(6) atoms forming the five-membered metallocycle (Fig. 2).



Scheme 3. (i) $[PdCl_2(MeCN)_2]$, MeCN.

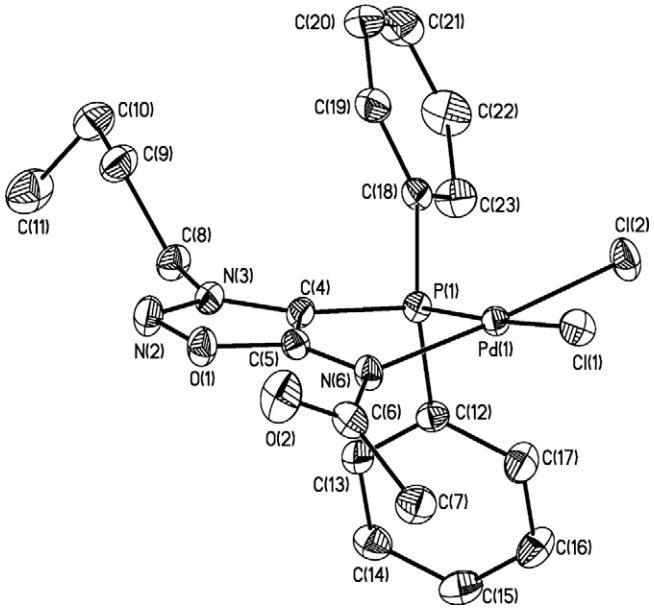


Fig. 2. General view of compound **6a**, atoms represented by 50% thermal ellipsoids.

Table 2
Synthesis of palladium complexes of 3-substituted-4-diphenylphosphinosydnone imines.

Compound	R	R_1	Yield,%
6a	*n*-Bu	Me	90
6b	*n*-Bu	Ph	85
6c	*n*-Bu	CF_3	53
6d	*n*-Bu	*t*-Bu	85
6e	Me_2N	Me	83
6f	Me_2N	Ph	95

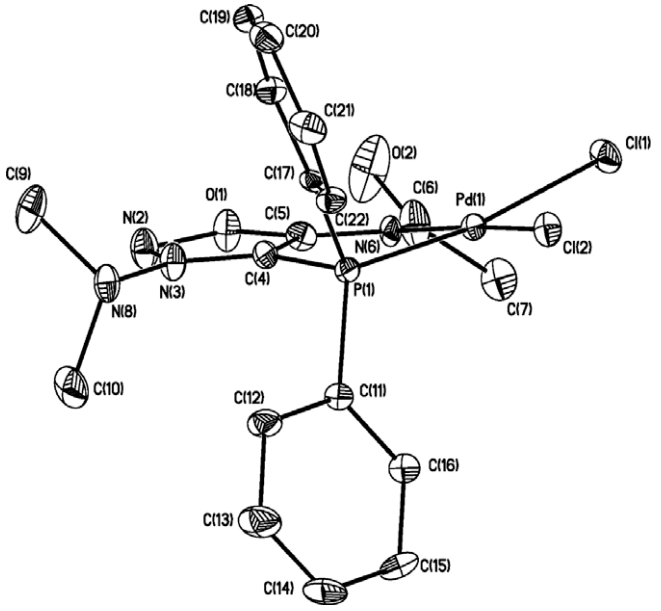


Fig. 3. General view of the complex **6e**, atoms represented by 50% thermal ellipsoids.

Very similar results were obtained in the case of phosphines **5b–f** (Scheme 3, Table 2).

The electron donating ability of N(6) in **5** is high. Even the presence of such electron-withdrawing groups as trifluoroacetyl (**5c**) does not prevent the formation of the chelate complex with palladium, although the yield of the product is low.

It should be noted that for compounds **5e** and **5f**, the dimethylamino group could provide an alternative coordination site. Nevertheless, the X-ray study of **6e** shows that the reactions of these compounds with $[PdCl_2(MeCN)_2]$ in MeCN give rise only to complexes in which the ligand acts as a bidentant ligand bound to palladium by the P(1) and N(6) atoms. (Fig. 3).

Despite the certain differences in the geometry of the ligands, the geometrical parameters of the two complexes **6a** and **6e** are similar (see Table 3). In both complexes the coordination of palladium is close to planar, with a slight tetrahedral distortion. The angles between the planes Pd(1)P(1)N(6) and Pd(1)Cl(1)Cl(2) are equal to 3.0(1)° and 8.5(1)° in **6a** and **6e**, respectively. The bite angles N(6)Pd(1)P(1) in both complexes are almost equal (87.13(9)° and 88.5(1)°). The five-membered metallocycles in **6a** and **6e** are characterized by an envelope conformation, with a deviation of the Pd(1) atom from the plane C(4)C(5)P(1)N(6) of 0.54 Å in **6a** and 0.32 Å in **6e**. In turn, the angles of bend along the P(1)···N(6) line in the complexes **6a** and **6e** are 20.5° and 12.2°. Despite the different substituents at N(3), the bond lengths of the metallocycles in **6a** and **6e** are almost the same. Comparing the geometrical parameters of the sydnone imine ring, one can conclude that the introduction of the Me_2N group leads to a slight shortening of the N(3)–C(4) bond, considerable shortening of the C(5)–N(6) and an increase of the N(6)–C(6) bond length.

Table 3
Selected bond lengths (Å) and angles (°) for the compounds **6a**, **6e** and **5e**.

Parameter	**6a**	**6e**	**5e**
Bond lengths			
Pd(1)–Cl(1)	2.361(1)	2.351(1)	
Pd(1)–Cl(2)	2.286(1)	2.282(1)	
Pd(1)–P(1)	2.232(1)	2.224(1)	
Pd(1)–N(6)	2.096(3)	2.104(4)	
P(1)–C(4)	1.796(4)	1.785(5)	1.811(2)
O(1)–N(2)	1.395(4)	1.390(5)	1.382(2)
O(1)–C(5)	1.364(4)	1.366(6)	1.391(2)
N(2)–N(3)	1.295(5)	1.301(6)	1.300(2)
N(3)–C(4)	1.356(5)	1.337(6)	1.349(2)
C(4)–C(5)	1.391(5)	1.394(6)	1.409(2)
C(5)–N(6)	1.323(5)	1.310(6)	1.296(2)
N(6)–C(6)	1.414(5)	1.435(6)	1.380(2)
N(3)–N(8)		1.428(5)	1.410(2)
Bond angles			
P(1)–Pd(1)–N(6)	87.1(1)	88.5(1)	
Cl(1)–Pd(1)–Cl(2)	92.16(5)	91.84(5)	
N(2)–O(1)–C(5)	109.2(3)	109.3(3)	110.2(1)
O(1)–N(2)–N(3)	104.9(3)	103.7(3)	103.4(1)
N(2)–N(3)–C(4)	114.2(3)	116.1(4)	116.8(1)
N(3)–C(4)–C(5)	104.9(3)	103.6(4)	103.5(1)
C(4)–C(5)–O(1)	106.8(3)	107.2(4)	105.9(1)

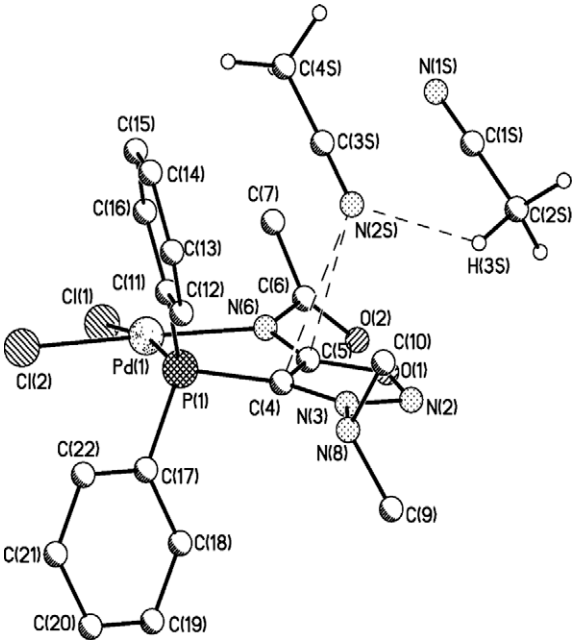


Fig. 4. The fragment of crystal packing illustrating the interaction of complex **6e** with acetonitrile molecules.

It should be mentioned that two solvate acetonitrile molecules in the crystal of **6e** are assembled into a dimer *via* the shortened C(1S)···C(3S) (3.344(3) Å) and N(2S)···H(3S) (2.51 Å) contacts (Fig. 4). In addition to the above contacts, one of the acetonitrile molecules participates in rather rare N···π binding with the mesoionic cycle, with a shortening of the N(2S)···C(4) and N(2S)···C(5) distances to 3.114(4) and 3.128(4) Å, respectively.

In order to analyze the influence of the complex formation on the distribution of bond lengths in the mesoionic moiety, we also performed an X-ray diffraction study of **5e** (Fig. 5). A comparison of the geometries of the free ligand **5e** and its complex **6e** shows that the coordination of N(6) to palladium causes the conjugation

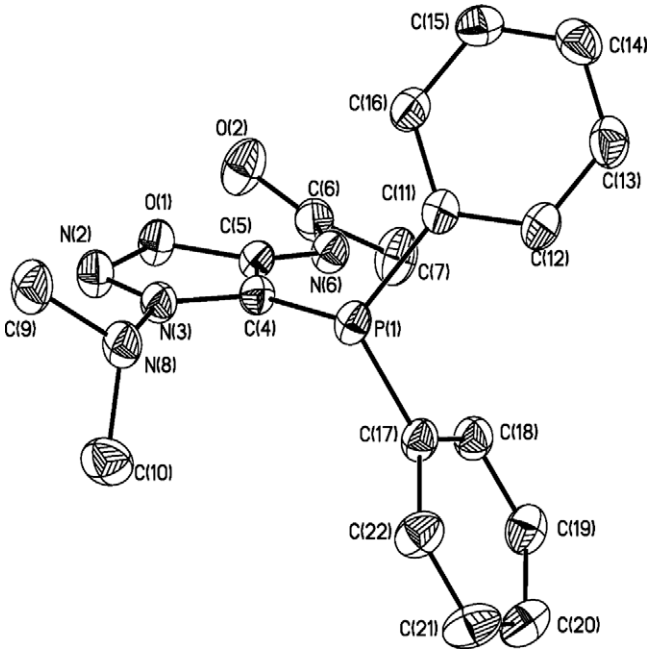


Fig. 5. General view of compound **5e**, atoms represented by 50% thermal ellipsoids.

of the N(6) atom with the π-system of the mesoionic ring and C=O group to decrease. As a result, the O(1)–C(5) bond in **5e** is considerably longer and the C(5) atom of the cycle deviates from the O(1)N(2)N(3)C(4) plane by 0.06 Å.

An analysis of IR spectra of the free ligands and the corresponding palladium complexes shows that the coordination of the mesoionic fragment by palladium atom gives no significant variation of the vibration spectrum character. The characteristic C=O and C=N bond vibrations of the mesoionic fragment are slightly blue shifted by 10–20 cm^{-1}.

The character of the chemical bonding in the mesoionic cycle, as well as the conjugation with the amide group, has been analyzed on the basis of a DFT calculation (m052x/6-311G(d,p)) of the molecule **5a** [8]. The obtained geometry is rather close to those observed in the complexes **6a** and **5e**. In particular, the C(5)–N(6) and C(6)–N(6) bond lengths are equal to 1.288 and 1.396 Å. An examination of the chemical bonding in **5a** has been performed within the "Atoms in Molecules" theory [9]. First of all, it should be noted that the charges obtained by integration over the atomic basins indicate that the most negative value is observed for the N(6) atom (−1.17 e). For comparison, the charge of the N(3) atom is significantly lower than those of the N(6) and N(8) atoms, which are −0.4 and −0.62 e. The total charge of the mesoionic cycle is close to zero (−0.02 e). According to the ellipticity values (ε) (the ratio of the Hessian eigenvalues in the critical points of the corresponding bonds), the mesoionic cycle is characterized by a significant contribution of π-character. Indeed, the maximum value of ε is observed for the N(2)–N(3) bond (0.41), while the minimum one – for the C(5)–O(1) bond (0.29). Both bonds formed by the N(6) atom are also characterized by substantial contributions of the π-component, with the ellipticity values being 0.20 and 0.30 for the N(6)–C(5) and N(6)–C(6) bonds, respectively.

The $^{31}P\{^1H\}$ NMR spectra of the obtained complexes show the variation of the chemical shift of the phosphorus atom (Table 4) upon complex formation.

2.2.1. Conclusion

In this work, the first representatives of 4-phosphorus substituted sydnone imines have been synthesized. It was shown that that these molecules can serve as hemilabile bidentante ligands and coordinate to a palladium atom by the phosphorus and exocyclic nitrogen N(6) atoms. The charge distribution in the mesoinic fragment was analyzed by DFT calculations, while the peculiarities of the geometries for the complexes were investigated by means of X-ray diffraction analysis. The presence of such a zwitterionic group as sydnone imine, which is unusual for palladium complexes, can provide them with rather unusual catalytic properties.

Table 4
$^{31}P\{^1H\}$ NMR parameters for the compounds **5a–f** and **6a–f**.

Compound	Chemical shifts (ppm) for compounds **5a–f**	Chemical shifts (ppm) for compounds **6a–f**
a	−35.91	−7.44
b	−35.89	−15.50
c	−35.84	13.48
d	−36.26	10.07
e	−35.83	−5.85
f	−35.81	−5.77

3. Experimental

3.1. General

Unless otherwise indicated, all the reactions were performed in a dry argon atmosphere. The starting sydnone imines **4a–b** [10], **4c** [11], **4d** [12], **4e** [13] and **4f** [6] were prepared according to the described procedures. All commercially available reagents were used without further purification. IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet Magna-IR 750 FT-IR spectrophotometer. ^1H NMR spectra were recorded on a Bruker Avance-400 spectrometer operating at a frequency of 400.13 MHz. ^{31}P NMR spectra were recorded on a Bruker Avance-400 spectrometer operating at a frequency of 161.98 MHz. Elemental analyses for C, H and N were performed on a Carlo Erba Elemental Analyzer – 1106 automatic analyzer. Melting points were determined with an electrically heated Gallenkamp apparatus.

3.2. Preparations

*3.2.1. N6-acetyl-3-butyl-4-diphenylphosphinosidnonimine (**5a**)*

To a solution of N6-acetyl-3-butylsidnonimine (0.5 g, 2.73 mmol) in THF (50 ml) at −90 °C, a 1.6 M solution of *n*-BuLi in hexane (1.9 ml, 3.00 mmol) was added. The solution was stirred for 10 min at the same temperature. Then chlorodiphenylphosphine (0.55 g, 3.13 mmol) was added. Reaction mixture was stirred for 10 min at the same temperature and then it was heated to room temperature. The solvent was removed under reduced pressure and the residue was dissolved in ethyl acetate, filtered through a layer of Al_2O_3 (2 × 3 cm) and washed away with ethyl acetate. The solvent was removed under reduced pressure and the residue was crystallized from a mixture of ether and hexane. Yield: 0.67 g (67%). M.p. 94–95 °C. *Anal.* Calc. for $C_{20}H_{22}N_3O_2P$ (367.39): C, 65.39; H, 6.04; N, 11.44. Found: C, 65.20; H, 6.50; N, 11.83%. IR data (KBr-pellet, cm^{-1}): 2960w, 2780w, 1660s, 1570vs, 1430m, 1250w, 1090m, 999m, 815w, 747w, 528m. ^1H NMR (DMSO-d_6): δ 0.76–0.80 (m, 3H, $CH_3CH_2CH_2CH_2$), 1.12–1.28 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.81–1.87 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.95 (s, 3H, $COCH_3$), 4.75–4.79 (m, 2H, $CH_3CH_2CH_2CH_2$), 7.28–7.45 (m, 6H, *p*-C_6H_5 + *m*-C_6H_5), 7.50–7.54 (m, 4H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −35.91 (s).

*3.2.2. N6-benzoyl-3-butyl-4-diphenylphosphinosidnonimine (**5b**)*

The title compound was prepared in the same way as compound **5a**, starting from **4b** (2 g, 8.16 mmol), 5.6 ml of a 1.6 M solution of *n*-BuLi in hexane (8.98 mmol) and 1.7 ml of chlorodiphenylphosphine (9.38 mmol). Yield 2.8 g (80%). M.p. 107–108 °C. *Anal.* Calc.

for $C_{25}H_{24}N_3O_2P$ (429.46): C, 69.92; H, 5.63; N, 9.78. Found: C, 69.32; H, 5.89; N, 9.50%. IR data (KBr-pellet, cm^{-1}): 3052vw, 2959vw, 2874vw, 1635s, 1571vs, 1432m, 1312m, 1240m, 1207m, 1090m, 989s, 814w, 735w, 695m, 533w. ^1H NMR (DMSO-d_6): δ 0.74–0.81 (m, 3H, $CH_3CH_2CH_2CH_2$), 1.11–1.29 (m, 2H, CH_3CH_2-CH_2CH_2), 1.86–1.89 (m, 2H, $CH_3CH_2CH_2CH_2$), 4.84–4.87 (m, 2H, $CH_3CH_2CH_2CH_2$), 7.19–7.26 (m, 2H, *o*-($NCOC_6H_5$)), 7.29–7.43 (m, 6H, *p*-$(C_6H_5)_2P$ + *m*-$(C_6H_5)_2P$), 7.45–7.48 (m, 3H, *p*-($NCOC_6H_5$) + *m*-($NCOC_6H_5$)), 7.54–7.62 (m, 4H, *o*-$(C_6H_5)_2P$). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −35.89 (s).

3.2.3. N6-trifluoroacetyl-3-butyl-4-diphenylphosphinosidnonimine (**5c**)

The title compound was prepared in the same way as compound **5a** starting from **4c** (0.7 g, 2.95 mmol), 2.1 ml of a 1.6 M solution of *n*-BuLi in hexane (3.39 mmol) and 0.63 ml of chlorodiphenylphosphine (3.54 mmol). Yield 0.7 g (56%). M.p. 125–126 °C. *Anal.* Calc. for $C_{20}H_{19}F_3N_3O_2P$ (421.36): C, 57.01; H, 4.55; N, 9.97. Found: C, 57.25; H, 5.01; N, 9.21%. IR data (KBr-pellet, cm^{-1}): 3052vw, 2963vw, 2874vw, 1653s, 1568vs, 1435w, 1202m, 1165s, 1132m, 1017m, 866w, 747w, 696w. ^1H NMR (DMSO-d_6): δ 0.77–0.81 (m, 3H, $CH_3CH_2CH_2CH_2$), 1.24–1.30 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.84–1.91 (m, 2H, $CH_3CH_2CH_2CH_2$), 4.88–4.91 (m, 2H, CH_3CH_2-CH_2CH_2), 7.33–7.41 (m, 6H, *p*-C_6H_5 + *m*-C_6H_5), 7.52–7.56 (m, 4H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −35.84 (s).

3.2.4. N6-trimethylacetyl-3-butyl-4-diphenylphosphinosidnonimine (**5d**)

The title compound was prepared in the same way as compound **5a** starting from **4d** (1.0 g, 4.44 mmol), 3.0 ml of a 1.6 M solution of *n*-BuLi in hexane (4.89 mmol) and 0.92 ml of chlorodiphenylphosphine (5.10 mmol). Yield 1.56 g (86%). M.p. 104–105 °C. *Anal.* Calc. for $C_{23}H_{28}N_3O_2P$ (409.47): C, 67.47; H, 6.89; N, 10.26. Found: C, 67.30; H, 7.01; N, 10.63%. IR data (KBr-pellet, cm^{-1}): 3059w, 2956w, 2867w, 1634s, 1601vs, 1579s, 1475w, 1435m, 1383w, 1313w, 1172m, 1109w, 999m, 744w, 692w, 515vw. ^1H NMR (DMSO-d_6): δ 0.77–0.92 (m, 12H, $CH_3CH_2CH_2CH_2$ + $C(CH_3)_3$), 1.20–1.27 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.83–1.91 (m, 2H, CH_3CH_2-CH_2CH_2), 4.80–4.83 (m, 2H, $CH_3CH_2CH_2CH_2$), 7.34–7.36 (m, 6H, *p*-C_6H_5 + *m*-C_6H_5), 7.51–7.54 (m, 4H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −36.26 (s).

3.2.5. N6-acetyl-3-dimethylamino-4-diphenylphosphinosidnonimine (**5e**)

The title compound was prepared in the same way as compound **5a** starting from **4e** (2.5 g, 14.70 mmol), 10.0 ml of a 1.6 M solution of *n*-BuLi in hexane (16.20 mmol) and 3.0 ml of chlorodiphenylphosphine (16.90 mmol). Yield 3.9 g (75%). M.p. 126–127 °C *Anal.* Calc. for $C_{18}H_{19}N_4O_2P$ (354.35): C, 61.01; H, 5.40; N, 15.81. Found: C, 60.59; H, 6.00; N, 15.20%. IR data (KBr-pellet, cm^{-1}): 2785w, 2459w, 1671s, 1580vs, 1435s, 1390w, 1265w, 1150m, 1121m, 1032w, 725m, 699m, 555w. ^1H NMR (DMSO-d_6): δ 1.86 (s, 3H, $COCH_3$), 3.07 (s, 6H, $(CH_3)_2N$), 7.35–7.37 (m, 6H, *m*-C_6H_5 + *p*-C_6H_5), 7.52–7.56 (m, 4H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −35.83 (s.).

3.2.6. N6-benzoyl-3-dimethylamino-4-diphenylphosphinosidnonimine (**5f**)

The title compound was prepared in the same way as compound **5a** starting from **4f** (2.0 g, 8.60 mmol), 5.9 ml of a 1.6 M solution of *n*-BuLi in hexane (9.50 mmol) and 1.8 ml of chlorodiphenylphosphine (9.90 mmol). Yield 2.5 g (70%). M.p. 123–124 °C. *Anal.* Calc. for $C_{23}H_{21}N_4O_2P$ (416.42): C, 66.34; H, 5.08; N, 13.45. Found: C, 65.99; H, 5.22; N, 13.25%. IR data (KBr-pellet, cm^{-1}): 3040w, 2878vw, 1620s, 1550vs, 1430m, 1340m, 1255m, 1140w, 1000m, 750w, 532w. ^1H NMR (DMSO-d_6): δ 3.15 (s, 6H, $(CH_3)_2N$), 7.22–7.27 (m, 2H, *o*-($NCOC_6H_5$)), 7.33–7.42 (m, 6H, *p*-$(C_6H_5)_2P$ + *m*-$(C_6H_5)_2P$), 7.57–7.65 (m, 7H, *p*-($NCOC_6H_5$) + *m*-($NCOC_6H_5$) + *o*-$(C_6H_5)_2P$). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −35.81 (s).

3.2.7. N6-acetyl-3-butyl-4-diphenylphosphinosidnonimine palladium dichloride (**6a**)

To a solution of N6-acetyl-3-butyl-4-diphenylphosphinosidnonimine **5a** (0.5 g, 1.36 mmol) in CH_3CN (10 ml), $[PdCl_2(MeCN)_2]$ (0.35 g, 1.36 mmol) was added. The solution was stirred for 30 min at room temperature. The solvent was removed under reduced pressure and the residue was crystallized from a mixture of CH_3CN and ether. Yield: 0.67 g (90%). M.p. 214 °C (dec.). *Anal.* Calc. for $C_{20}H_{22}Cl_2N_3O_2PPd$ (544.71): C, 44.10; H, 4.07; N, 7.71. Found: C, 44.29; H, 4.52; N, 7.13%. IR data (KBr-pellet, cm^{-1}): 3052w, 2964w, 2900w, 1671s, 1585vs, 1422m, 1377w, 1265w, 1080m, 1002m, 837w, 768w, 540w. ^1H NMR (DMSO-d_6): δ 0.57–0.60 (m, 3H, $CH_3CH_2CH_2CH_2$), 1.00–1.07 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.26–1.29 (m, 2H, $CH_3CH_2CH_2CH_2$), 2.47 (s, 3H, $COCH_3$), 4.16–4.20 (m, 2H, $CH_3CH_2CH_2CH_2$), 7.63–7.64 (m, 4H, *m*-C_6H_5), 7.73–7.76 (m, 2H, *p*-C_6H_5) 7.98–8.03 (m, 4H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −7.44 (s).

3.2.8. N6-benzoyl-3-butyl-4-diphenylphosphinosidnonimine palladium dichloride (**6b**)

The title compound was prepared in the same way as compound **6a** starting from **5b** (0.2 g, 0.475 mmol) and $[PdCl_2(MeCN)_2]$ (0.12 g, 0.475 mmol). Yield 0.25 g (85%). M.p. 194 °C (dec.). *Anal.* Calc. for $C_{25}H_{24}Cl_2N_3O_2PPd$ (606.78): C, 49.49; H, 3.99; N, 6.93. Found: C, 49.10; H, 4.20; N, 6.55%. IR data (KBr-pellet, cm^{-1}): 3059vw, 2963vw, 2874vw, 1656s, 1568vs, 1431m, 1257m, 1169vw, 1098w, 1013m, 747w, 688m. ^1H NMR (DMSO-d_6): δ 0.63–0.75 (m, 3H, $CH_3CH_2CH_2CH_2$), 1.05–1.16 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.50–1.63 (m, 2H, $CH_3CH_2CH_2CH_2$), 4.05–4.18 (m, 2H, $CH_3CH_2CH_2CH_2$), 7.18–7.25 (m, 2H, *o*-($NCOC_6H_5$)), 7.29–7.43 (m, 3H, *p*-($NCOC_6H_5$) + *m*-($NCOC_6H_5$)), 7.52–7.65 (m, 6H, *p*-$(C_6H_5)_2P$ + *m*-$(C_6H_5)_2P$), 8.04–8.21 (m, 4H, *o*-$(C_6H_5)_2P$). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ −15.50 (s).

3.2.9. N6-trifluoroacetyl-3-butyl-4-diphenylphosphinosidnonimine palladium dichloride (**6c**)

The title compound was prepared in the same way as compound **6a** starting from **5c** (0.2 g, 0.475 mmol) and $[PdCl_2(MeCN)_2]$ (0.12 g, 0.475 mmol). Yield 0.15 g (53%). M.p. 190 °C (dec.). *Anal.* Calc. for $C_{20}H_{19}Cl_2F_3N_3O_2PPd$ (598.68): C, 40.12; H, 3.20; N, 7.02. Found: C, 40.32; H, 3.05; N, 6.89%. IR data (KBr-pellet, cm^{-1}): 3050vw, 2963vw, 2877vw, 1665s, 1571vs, 1440w, 1220m, 1140m, 1120w, 1030m, 869vw, 758w, 675w. ^1H NMR (DMSO-d_6): δ 0.70–0.74 (m, 3H, $CH_3CH_2CH_2CH_2$), 1.11–1.18 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.52–1.67 (m, 2H, $CH_3CH_2CH_2CH_2$), 4.48–4.57 (m, 2H, $CH_3CH_2CH_2CH_2$), 7.53–7.59 (m, 4H, *m*-C_6H_5), 7.63–7.67 (m, 2H, *p*-C_6H_5), 8.09–8.17 (m, 4H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 13.48 (s).

3.2.10. N6-trimethylacetyl-3-butyl-4-diphenylphosphinosidnonimine palladium dichloride (**6d**)

The title compound was prepared in the same way as compound **6a** starting from **5d** (0.5 g, 1.22 mmol) and $[PdCl_2(MeCN)_2]$ (0.32 g, 1.22 mmol). Yield 0.61 g (85%). M.p. 204 °C (dec.). *Anal.* Calc. for $C_{23}H_{28}Cl_2N_3O_2PPd$ (586.79): C, 47.08; H, 4.81; N, 7.16. Found: C, 46.95; H, 5.11; N, 7.64%. IR data (KBr-pellet, cm^{-1}): 2963w, 2874vw, 1723m, 1619vs, 1568m, 1479w, 1435m, 1095m, 1006m, 751w, 688w, 529m. ^1H NMR (DMSO-d_6): δ 0.69–0.77 (m, 12H, $CH_3CH_2CH_2CH_2$ + $C(CH_3)_3$), 1.11–1.16 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.61–1.68 (m, 2H, $CH_3CH_2CH_2CH_2$), 4.59–4.69 (m, 2H, CH_3CH_2-CH_2CH_2), 7.48–7.65 (m, 6H, *p*-C_6H_5 + *m*-C_6H_5), 7.95–8.05 (m, 4H, *o*-C_6H_5). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 10.07 (s.).

Table 5
Crystal data and structure refinement parameters for **5e**, **6a** and **6e**.

	5e	6a	6e
Formula	$C_{18}H_{19}N_4O_2P$	$C_{20}H_{22}Cl_2N_3O_2PPd$	$C_{22}H_{25}Cl_2N_6O_2PPd$
Formula weight	354.34	544.68	613.75
T (K)	120	153	153
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
Z (Z′)	2 (1)	4 (1)	4 (1)
a (Å)	8.0945(12)	8.6676(17)	10.487(3)
b (Å)	9.6967(15)	14.121(3)	14.694(3)
c (Å)	11.3273(17)	18.115(4)	17.440(5)
α (°)	87.477(3)	90.00	90.00
β (°)	83.704(3)	97.97(3)	97.02(2)
γ (°)	89.965(3)	90.00	90.00
V (Å^3)	882.9(2)	2195.8(8)	2667.3(12)
d_{calc} (g cm^{-3})	1.333	1.648	1.528
μ (cm^{-1})	1.75	11.83	9.86
F(0 0 0)	372	1096	1240
$2\theta_{max}$ (°)	56	56	50
Reflections collected	7805	6509	4988
Independent reflections	4184	5281	4717
Observed reflections [$I > 2\sigma(I)$]	3183	4865	3184
Number of parameters	229	265	316
R_1	0.0489	0.0549	0.0411
wR_2	0.1210	0.1381	0.1016
Goodness-of-fit (GOF)	1.004	1.092	0.922
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.388/−0.261	1.265/−1.446	1.395/−0.976

*3.2.11. N6-acetyl-3-dimethylamino-4-diphenylphosphinosidnonimine palladium dichloride (**6e**)*

The title compound was prepared in the same way as compound **6a** starting from **5e** (0.5 g, 1.40 mmol) and [$PdCl_2(MeCN)_2$] (0.37 g, 1.40 mmol). Yield 0.62 g (83%). M.p. 195 °C (dec.). *Anal.* Calc. for $C_{18}H_{19}Cl_2N_4O_2PPd$ (531.67): C, 40.66; H, 3.60; N, 13.34. Found: C, 40.99; H, 3.82; N, 13.11%. IR data (KBr-pellet, cm^{-1}): 3052vw, 2926vw, 1693s, 1579s, 1557vs, 1435s, 1361w, 1213s, 1106m, 999w, 747w, 688m, 526m. ^{1}H NMR (DMSO-d_6): δ 2.36 (s, 3H, $COCH_3$), 2.80 (s, 6H, $(CH_3)_2N$), 7.55–7.62 (m, 4H, *m*-C_6H_5), 7.68–7.79 (m, 2H, *p*-C_6H_5), 7.98–8.02 (m, 4H, *o*-C_6H_5). ^{31}P{^{1}H} NMR (DMSO-d_6): δ −5.85 (s).

*3.2.12. N6-benzoyl-3-dimethylamino-4-diphenylphosphinosidnonimine palladium dichloride (**6f**)*

The title compound was prepared in the same way as compound **6a** starting from **5f** (0.5 g, 1.20 mmol) and [$PdCl_2(MeCN)_2$] (0.31 g, 1.20 mmol). Yield 0.68 g (95%). M.p. 189–190 °C (dec.). *Anal.* Calc. for $C_{23}H_{21}Cl_2N_4O_2PPd$ (593.75): C, 46.53; H, 3.56; N, 9.44. Found: C, 46.08; H, 3.28; N, 9.23%. IR data (KBr-pellet, cm^{-1}): 3052vw, 1639s, 1597vs, 1571s, 1446m, 1350w, 1279w, 1246m, 1158w, 1098m, 991m, 751w, 725w, 537w. ^{1}H NMR (DMSO-d_6): δ 3.20 (s, 6H, $(CH_3)_2N$), 7.19–7.26 (m, 2H, *o*-($NCOC_6H_5$)), 7.28–7.43 (m, 6H, *p*-($NCOC_6H_5$) + *m*-($NCOC_6H_5$)), 7.51–7.66 (m, 6H, *p*-$(C_6H_5)_2P$ + *m*-$(C_6H_5)_2P$)), 8.05–8.23 (m, 4H, *o*-$(C_6H_5)_2P$). ^{31}P{^{1}H} NMR (DMSO-d_6): δ −5.77 (s).

4. X-ray diffraction analysis

Crystals suitable for the X-ray diffraction analysis were obtained by slow evaporation from MeCN solutions. X-ray diffraction experiments of **5e** were carried out with a Bruker SMART 1000 CCD diffractometer (Mo Kα) = 0.71073 Å, ω-scans) at 110 K, while for **6a** and **6e** they were carried out with a Syntex P21 diffractometer (Mo Kα) = 0.71073 Å, ω-scans) at 153 K. The structures were solved by the direct method and refined by full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. The analysis of the Fourier density synthesis has revealed a disorder of the oxygen atom O(2) in **6e** over two positions with occupancies of 0.78 and 0.22. The positions of the hydrogen atoms were calculated. Crystal data and structure refinement parameters for **5e, 6a** and **6e** are given in Table 5. All calculations were performed using the SHELXTL software [14].

Supplementary data

CCDC 723513, 723514, and 723515 contain the supplementary crystallographic data for **5e**, **6a**, and **6e**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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