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Preparation of complexes of palladium chloride with di-*tert*-butylsydnonylphosphine and diphenylsydnonylphosphine and structural analysis of the sydnone ring containing phosphine and palladium complex

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Abstract

Three sydnonylphosphinepalladium(II) chloride were prepared. X-ray analyses of complexes of diphenylsydnonylphosphine with palladium chloride reveals that the sydnone ring contributes electrons through phosphorus to metal resulting in decreasing substantial bond lengths. By comparing the bond length of P–C(sydnone) and P–C(phenyl) suggests that phenyl rings are able to contribute more electrons to phosphorus for chelation leading to short P–C(phenyl) bond lengths. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Sydnonylphosphines; Crystal structures; Sydnonylphosphinepalladium chloride; Mesoionic compounds; Disubstituted sydnones

1. Introduction

The chemical and physical properties of sydnone and its derivatives have attracted significant interest due to their unique electronic structure and their physical properties. In general, the sydnone ring demonstrates the electron-withdrawing character on N(3) and electron-donating properties on C(4) and are also confirmed by various calculations [1]. This dual character of the ring has been observed in the nitration of 3-(4-alkylphenyl)sydnones and 3-benzylsydnones, resulting in the formation of 3-(4-alkyl-3-nitrophenyl)sydnone and 3-(3-nitrobenzyl)sydnone, respectively [2]. Electrophilic substitution, i.e. formylation and acetylation, takes place at the C(4) position [3]. Position C(4) can be functionalized by various functional groups, such as phosphino, silyl, alkyl, halide, etc. [4]. The structure of the sydnone ring shall be influenced by the addition of the phosphino group at C(4), and even the formation of a complex with a metal halide. A number of crystal structures of sydnones have been reported [5], but none of them containing a phosphine moiety. In this work, we attempted to compare the variation of bond lengths of the sydnone ring in compounds **3**, **4**, and **8** by means of X-ray analyses. From the comparison of the bond length of phosphorus–carbon [P–C(sydnone) or P(s)–C(4), P–C(phenyl) or P(s)–C(p)] in compounds **4** and **8** to conclude the ability of electron-donating of the sydnone ring relating to the phenyl ring. Substantial shorter bonds in the sydnone ring were observed after the formation of the palladium complex is reported (Scheme 1).

2. Results and discussion

Sydnones containing the phosphino group at the 4-position were prepared in 1986 [6]. However, in our previously work, it was the first report dealing with the preparation of the palladium complex from sydnonylphosphine [7]. Reaction of di-*tert*-butyl-4-anisylsydnonylphosphine (**2**) with $PdCl_2$ in the presence of

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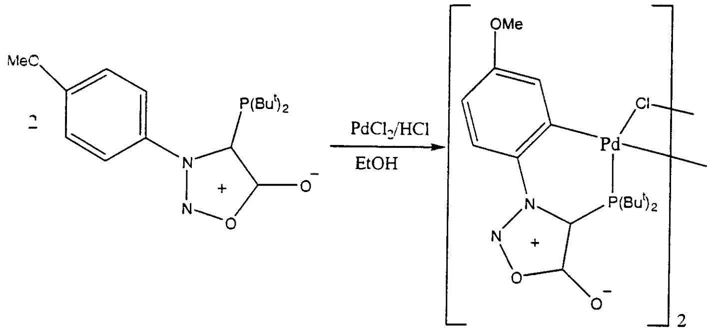
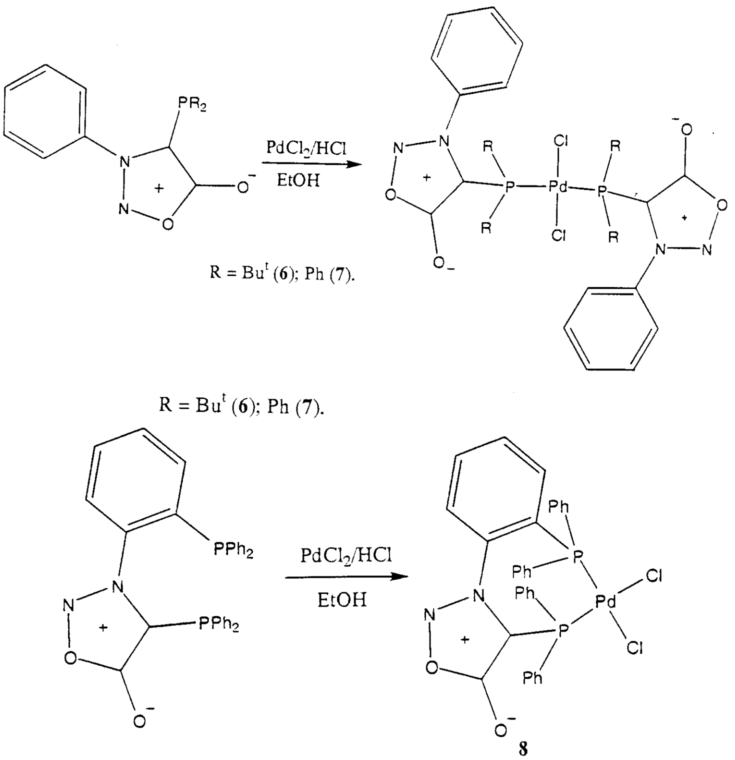
concentrated HCl resulting in a dimeric product **5** with *ortho*-metallation at the phenyl ring [7] (Scheme 2) Under the same condition, di-*tert*-butyl(phenylsydnonyl)phosphine (**1**), diphenyl(phenylsydnonyl)phosphine (**3**), and diphenyl(2-diphenylphosphinophenylsydnonyl)phosphine (**4**) were reacted with $PdCl_2$, instead of **2**, resulting in the complexes **6**, **7**, and **8**, respectively, without *ortho*-metallation (Scheme 3). Apparently, the combination of the methoxyl group on the phenyl ring and the *tert*-butyl group on the phosphorus is essential for palladium to insert into the C(phenyl)–H bond. The IR absorption by the carbonyl group of the sydnone ring in compounds **6**, **7**, and **8** have the same wavenumber as the free state of **1**, **3**, and **4**. The ^{31}P-NMR of complex **8** exhibits two doublets at δ 25.95 and 12.78 with a coupling constant of 15 Hz. The small coupling constant indicates two phosphorus atoms chelate with a palladium atom in the *cis*-form. Those air-stable complexes are quite stable under heating before the decomposition point, except complex **8**, which changes from yellow to orange, to red and then melted at 125, 135, and 232–235°C, respectively.

The C(4) of the sydnone ring has been recognized as an electron-donating character. In this study, we would like to investigate the structure of sydnone ring in compounds **3**, **4**, and **8** by means of X-ray diffraction analyses (Figs. 1–3). Their crystal data and experimental parameters are given in Table 1. The bond length of



5

Scheme 1.



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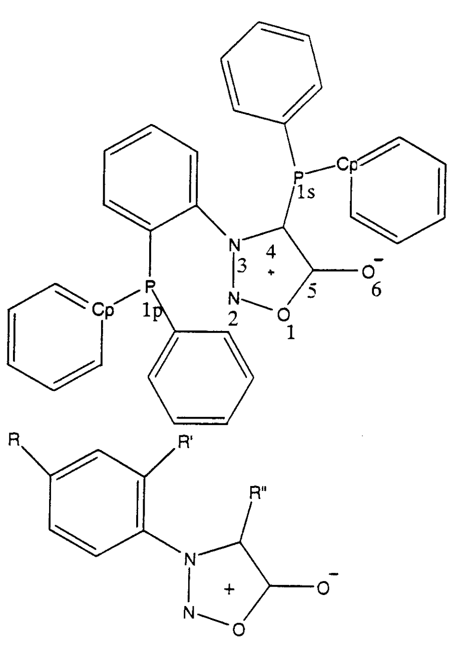
Scheme 2.



R, R′, R″ : H, H, $\mathrm{P(Bu^t)_2}$ (**1**); MeO, H, $\mathrm{P(Bu^t)_2}$ (**2**);
H, H, $\mathrm{PPh_2}$ (**3**); H, $\mathrm{PPh_2}$, $\mathrm{PPh_2}$ (**4**).

Scheme 3.

the sydnone ring, the selected bond lengths, and bond angles in compounds **3**, **4**, **5**, and **8** along with the average value obtained from five four-substituted 3-arylsydnones were summarized in Table 2. The bond length of 4-substituted sydnones was chosen for comparing the influence of the phosphino group at C(4).

In general, compound containing diphenylphosphino group at C(4) as well as C′(2) leads to a slight change in the bond length. The lengths of the N(3)–C(4), C(4)–C(5) and C(5)–O(1) [1.363(5), 1.420(4), 1.412(6) Å (**3**); 1.359(6), 1.429(7), 1.422(6) Å (**4**)], are apparently longer than those of the five independent molecules with disubstituents at the 3-, 4-positions which are 1.350–1.358 Å, [average, 1.352 Å], 1.413–1.420 Å, [average 1.417], 1.399–1.419 Å, [average 1.408 Å], respectively. There are larger effects on the N(3)–C(1p) and N(2)–N(3) bonds [1.419(3), 1.302(5) Å (**3**), 1.420(5), 1.300(6) Å (**4**)], for which the range of lengths for the disubstituted compounds is 1.447–1.467 Å, [average 1.456 Å] and 1.295–1.325 Å, [average 1.313 Å]. The phosphino group is able to donate the electron to the sydnone ring to increase the bonds connected to C(4) and to decrease the bond length of bonds connected to N(3). In addition, the bond length of C(4)–P(1s) [1.807(4) Å], is much shorter than that of P(1s)–C(p) [1.832(2) and 1.838(2) Å]. It suggests that the phosphorus atom is bound well with C(4) of sydnone ring. Evidently, the presence of the phosphorus moiety decreases the bonding ability of C(4) and C(5), and enhances the ability of N(2) and N(3). It might indicate more electron localization for the compounds containing the phosphine group at C(4) position.

When a ligand binds with a metal, it will donate the electron pair to the metal for complexation. During this process, the electron density of the ligand will be lower

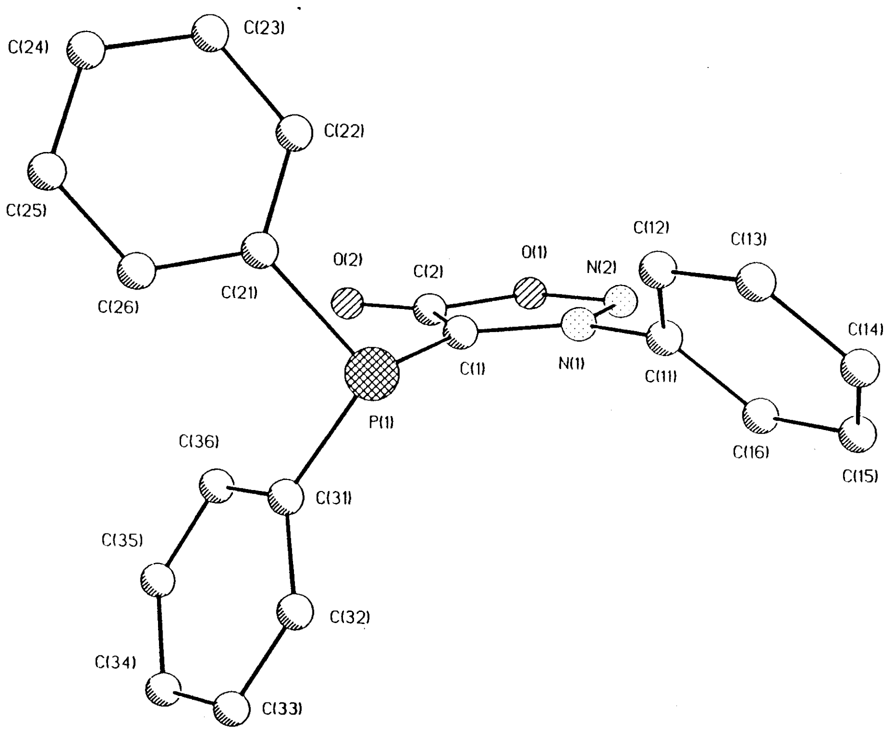


Fig. 1. ORTEP drawing of **3** with thermal ellipsoids shown at the 30% probability level.

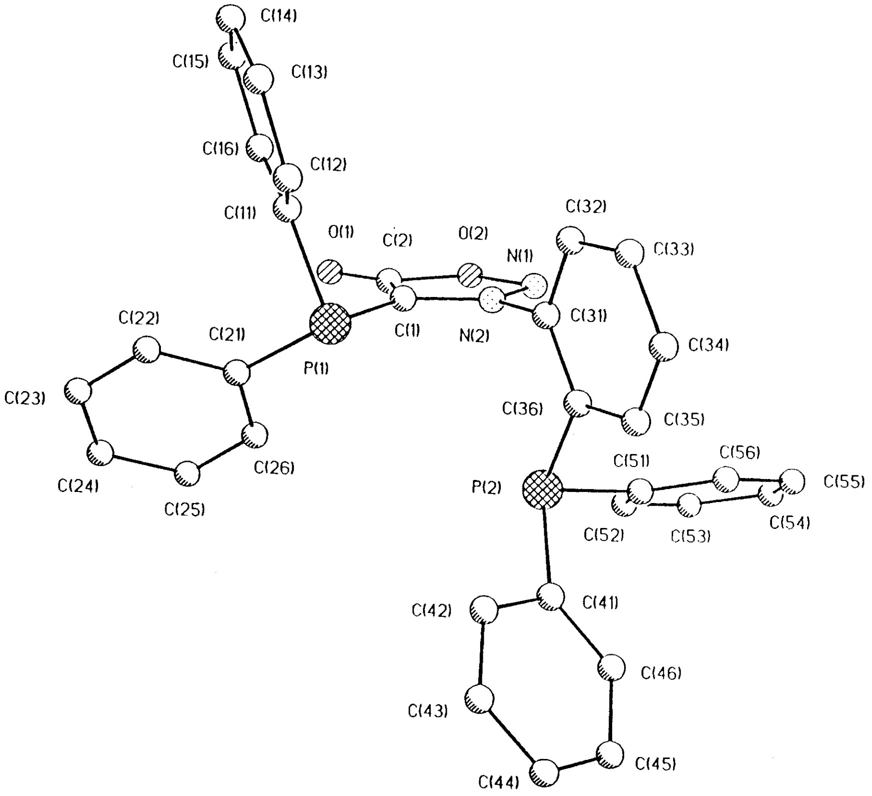


Fig. 2. ORTEP drawing of **4** with thermal ellipsoids shown at the 30% probability level.

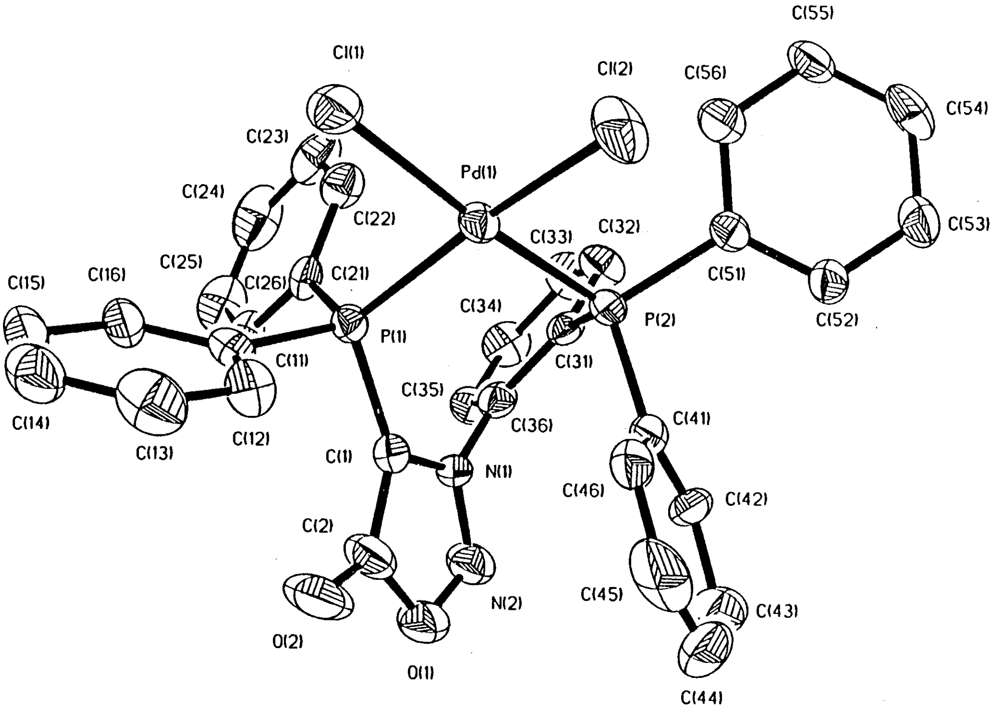


Fig. 3. ORTEP drawing of **8** with thermal ellipsoids shown at the 30% probability level.

than in the free state. When compound **4** chelates with $PdCl_2$, we expect the electron of the sydnone ring to flow to the metal via a phosphorus atom and result in a change of the bond length of the ring. Indeed, the bond lengths of the sydnone ring decrease substantial, especially for O(1)–N(2) [1.382(5) (**4**) vs. 1.332(16) Å

(**8**)] and C(5)–O(6) [1.202(6)(**4**) vs. 1.159(19) Å (**8**)]. The decrease of bond lengths of the C(4)–P(1s) [1.796(5) (**4**) vs. 1.802(12) Å (**8**)] is much less than that of P(1s)–C(p) [1.822(5), 1.835(3) (**4**) vs. 1.784(9), 1.789(10) Å (**8**)]. It suggests that the phenyl ring is a better electron donator than the sydnone ring to phosphorus. Although the bond lengths of the sydnone ring are varied substantially, the bond angles do not exhibit a significant change.

By comparison with the bond lengths of P(s)–Pd in compounds **5** [2.257(1) Å] and **8** [2.237(3) Å], the former is longer due to the better electron-donating nature of the *tert*-butyl group on the phosphorus atom for binding with Pd^{II}. The Pd–Cl distance [2.344(4), 2.336(4) Å] are closed to *cis*-$PdCl_2$ in Calix[6]arene [2.309(3), 2.317(2) Å] [11]. For comparison, the bond lengths of Pd–Cl in some recent reports are [2.3917(8), 2.4018(8) Å], 2.408(1) Å for Cl *trans* respective to aryl [12], and the CH_2SCH_3 group [13], respectively, and 2.437(1) Å in a bridging type in our previous report [7]. The *trans*-effect resulted in different Pd–Cl distances, further suggesting the *cis*-relationship of two chlorine atoms.

In this study, we find that the phosphino group at C(4) possesses an electron-donating nature leading to more electron localization in the sydnone ring. The bond lengths of the sydnone ring are reduced by bonding with metals, suggesting an electron flow during the complexation. In comparison, the bond lengths of P–C(sydnone) and P–C(phenyl) suggest that phenyl rings are able to contribute more electrons to phosphorus for chelation, leading to smaller P–C(phenyl) bond lengths.

3. Experimental

All melting points were measured with a Yanaco MP-J3 apparatus and are uncorrected. ^1H- and ^{31}P-NMR spectra were recorded on a Bruker AC-250 spectrometer at 250 and 101.20 MHz, respectively. IR data were obtained using a Perkin–Elmer 883 spectrophotometer. FAB mass spectra were measured on a JEOL JM5-SX/SX 102A spectrometer, using 3-nitrobenzyl alcohol as a solvent. Microanalyses were performed on a Heraeus CHN–O rapid analyzer. Di-*tert*-butyl(3-phenylsydnonyl)phosphine (**1**), diphenyl(3-phenylsydnonyl)phosphine (**3**), and diphenyl[3-(2-diphenylphosphinophenylsydonyl)phosphine (**4**), were prepared as described in the literature [4].

Table 1
Crystal data for compounds **3**, **4**, and **8**

	Compound **3**	Compound **4**	Compound **8**
Formula	$C_{20}H_{15}O_2N_2P$	$C_{32}H_{24}N_2O_2P_2$	$C_{32}H_{24}Cl_2N_2O_2P_2Pd$
Crystal size (mm)	0.2 × 0.4 × 0.5	0.3 × 0.4 × 0.5	0.3 × 0.4 × 0.5
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P2_12_12_1$
Formula weight	346.3	530.5	723.8
a (Å)	9.814(2)	13.336(2)	10.145(2)
b (Å)	10.214(2)	13.524(1)	12.758(2)
c (Å)	10.273(2)	15.538(1)	28.174(2)
α (°)	72.15(1)		
β (°)	78.80(1)	100.28(1)	
γ (°)	62.98(1)		
V (Å^3)	871.3(3)	2757.4(4)	3646.6(5)
Z	2	4	4
D_{calc} (g cm^{-3})	1.320	1.278	1.318
Crystal color	Yellow	Colorless	Yellow
μ (mm^{-1})	0.173	0.190	0.774
Reflections measured	2411	3787	3655
Unique reflections	2252	3606	3626
Observed reflections	1835	2322	2634
Criterion for observation	$F>3\sigma(F)$	$F>4\sigma(F)$	$F>4\sigma(F)$
R_{int}	0.0211	0.0295	0.0000
Variables	190	283	320
R; R_w [a]	0.0471; 0.0540	0.0574; 0.0643	0.0553; 0.0653
g	0.0002	0.0006	0.0005
Goodness-of-fit	1.66	1.34	1.44
Max. shift/σ	0.000	0.001	0.001
Residual electron density (e Å^{-3})	0.26	0.34	0.47

[a] $R=\Sigma(|F_o|-|F_c|)/\Sigma(|F|)$; $R_w=[\Sigma\, w(|F_o|-|F_c|)^2/\Sigma\, w|F_o|]^2]^{1/2}$. $w=[\sigma^2(F_o)+gF_o^2]^{-1}$.

Table 2
Selected interatomic distances (Å) and angles (°) in compounds **3**, **4**, **5**, and **8**

	Compound **3**	Compound **4**	Compound **8**	Compound **5** [7]	Average [a]
Interatomic distances					
O(1)–N(2)	1.378(4)	1.382(5)	1.332(16)	1.363 (4)	1.378 (1.368–1.382)
N(2)–N(3)	1.302(5)	1.300(6)	1.286(15)	1.306(4)	1.313 (1.295–1.325)
N(3)–C(4)	1.363(5)	1.359(6)	1.356(16)	1.379(4)	1.352 (1.350–1.358)
C(4)–C(5)	1.420(4)	1.429(7)	1.411(19)	1.430(4)	1.417 (1.413–1.420)
C(5)–O(1)	1.412(6)	1.422(6)	1.403(19)	1.409(5)	1.408 (1.399–1.419)
C(5)–O(6)	1.209(5)	1.202(6)	1.159(19)	1.207(5)	1.205 (1.196–1.217)
N(3)–C(1p)	1.419(3)	1.420(5)	1.414(12)	1.427(5)	1.456 (1.447–1.467)
C(4)–P(1s)	1.807(4)	1.796(5)	1.802(12)	1.794(3)	
P(1s)–C(p)	1.832(2), 1.838(2)	1.822(5), 1.835(3)	1.784(9), 1.789(10)		
P(1p)–C(p)		1.837(4), 1.842(4), 1.866(3)	1.784(10), 1.816(8), 1.857(7)		
P(1s)–Pd			2.237(3)	2.257(1)	
P(1p)–Pd			2.262(3)		
Pd–Cl(1)			2.344(4)	2.437(1)	
Pd–Cl(2)			2.336(4)		
Interatomic angles					
O(1)–N(2)–C(4)	104.3(4)	103.1(3)	105.8(10)	104.8(3)	
N(2)–N(3)–C(4)	115.8(3)	117.7(4)	115.1(10)	115.5(3)	
N(3)–C(4)–C(5)	104.6(4)	103.8(4)	103.8(11)	103.8(3)	
C(4)–C(5)–O(1)	104.4(3)	104.1(4)	104.6(12)	104.5(3)	
C(5)–O(1)–N(2)	110.8(3)	111.3(3)	110.6(10)	111.2(3)	
C(4)–C(5)–O(6)	136.3(5)	136.2(5)	136.1(15)	136.8(4)	
N(2)–N(3)–C(1p)	115.5(3)	116.3(4)	117.0(9)	116.5(3)	
N(3)–C(4)–P(1s)	123.0(2)	121.8(3)	122.7(9)	122.6(2)	
P(1s)–Pd–P(2p)			93.4(1)		
P(1s)–Pd–Cl(1)			88.5(1)	102.8(1)	
P(2p)–Pd–Cl(2)			90.4(1)		
Cl(1)–Pd–Cl(2)			90.1(1)		

[a] Average values from five 3,4-disubstituted sydnones [4-acetyl-3-(4-toyl)sydnone [8], 4-acetyl-3-phenylsydnone oxime [8]. 4-(3-Methyl-1-buten-2-yl)-3-phenylsydnone [9]. 4-Cyclohexenyl-3-phenylsydnone [9]. 3-Phenyl-4-(*N*-carbamyl-1,4,2-oxathiazolimin-3-yl)sydnone] [10].

*3.1. Reaction of diphenyl(3-phenylsydnonyl)phosphine (**3**) and PdCl$_2$*

A mixture of PdCl$_2$ (35.4 mg, 0.2 mmol) in HCl (conc. 8.0 ml) solution and compound **3** (141.0 mg, 0.4 mmol) was heated at 80°C for 4 h. The yellow crystals were filtered out and then crystallized from CH$_2$Cl$_2$ with the aid of diffusion of diethyl ether to give 149.0 mg (86% yield) of compound **7** as orange crystals. M.p. (dec.) 226–228°C; IR (KBr) 1762 cm^{-1}($\nu_{C=O}$); ^{1}H-NMR (CDCl$_3$) δ 7.35–7.58 (m, 20H), 7.70–7.83 (m, 10H); ^{31}P-NMR (CDCl$_3$) δ 39.80 (s); FAB-MS m/z (relative intensity) 833 (M + 1 − HCl, 15), 460 (M + 1 − 346 − HCl–CO, 100), 429 (M + 1 − 346 − HCl–CO–NO, 31); Anal. Calc. for C$_{40}$H$_{30}$Cl$_2$N$_4$O$_4$P$_2$Pd: C, 55.22; H, 3.48; N, 6.44. Found: C, 55.07; H, 3.29; N, 6.45%.

*3.2. Reaction of di-tert-butyl(3-phenylsydnonyl)phosphine (**1**) and PdCl$_2$*

Same procedure was adapted for this preparation to give 131.0 mg (83% yield) of compound **6** as red needle crystals. M.p. (dec.) 188–200°C; IR (KBr) 1743 cm^{-1}($\nu_{C=O}$); ^{1}H-NMR (CDCl$_3$) δ 1.40 (s, 18H), 1.49 (s, 18H), 7.53–7.65 (m, 10H); ^{31}P-NMR (CDCl$_3$) δ 50.53 (s); FAB-MS m/z (relative intensity) 753 (M + 1 − HCl, 7), 585 (M + 1 − 306 − HCl, 100), 412 (M + 1 − 306 − HCl–Cl, 41), 354 (M + 1 − 306 − HCl–Cl–CO–NO, 51); Anal. Calc. for C$_{32}$H$_{46}$Cl$_2$N$_4$O$_4$P$_2$Pd: C, 48.65; H, 5.87; N, 7.09. Found: C, 48.39; H, 5.94; N, 7.09%.

*3.3. Reaction of diphenyl[3-(2-diphenylphosphino-phenylsydonyl)]phosphine (**4**) and PdCl$_2$*

A mixture of PdCl$_2$ (35.2 mg, 0.2 mmol) in HCl (conc. 8.0 ml) solution and compound **4** (120 mg, 0.2 mmol) was heated at 80°C for 4 h. The yellow crystals were filtrated out and then crystallized from CH$_2$Cl$_2$ with the aid of diffusion of diethyl ether to give 106.0 mg (68% yield) of compound **8** as yellow cubic crystals; M.p. (dec.) 232–235°C; IR (KBr) 1760 cm^{-1}($\nu_{C=O}$); ^{1}H-NMR (CDCl$_3$) δ 7.45–7.68 (m, 24H); ^{31}P-NMR (CDCl$_3$) δ 25.95 (d, J = 15 Hz), 12.78 (d, J = 15 Hz); FAB-MS (relative intensity) m/z 671(M + 1 − HCl, 80), 613 (M + 1 − Cl–CO–NO, 25), 578 (M + 1 − 2Cl–CO–NO, 100); Anal. Calc. for $C_{32}H_{24}Cl_2N_2O_2P_2Pd$: C, 54.30; H, 3.42; N, 3.96. Found: C, 54.06; H, 3.55; N, 4.02%.

All crystals were mounted on a glass fiber for X-ray structural analysis. Cell constants were derived from least-square refinements of 25 high-angle reflections having of $15 < 2\theta < 25$. Intensity data were collected using a ω scan mode on a Siemens P4 diffractometer equipped with graphite monochromatized Mo–K_α radiation ($\lambda = 0.71073$ Å). An empirical absorption correction based on a series of Ψ-scans was applied to the data. Three standard reflections were measured every 300 reflections and only small ($< 6\%$) random variations were observed. Lorentz and polarization corrections were applied.

The structure was determined by the heavy-atom method using SHELXTL-PLUS software package [14]. The palladium atom was revealed on a Patterson map. All other atoms were located from subsequent Fourier difference syntheses. The structure was refined by the full-matrix least-square methods. Heavy atoms were refined anisotropically. $\Sigma\, w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma^2(F_o) + gF_o^2]$. Details of the crystal data are listed in Table 1.

4. Supplementary material

Tables of atomic coordinates and displacement parameters and complete lists of bond lengths and angles have been deposited at the Cambridge Crystallographic Database Centre. The deposition numbers CCDC 142603, 142604, and 142605 have been allocated to the compounds **3**, **8**, and **4**, respectively. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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References

[1] (a) C.G. Newton, C.A. Ramsden, Tetrahedron 35 (1982) 1965. (b) W.D. Ollis, C.A. Ramsden, Adv. Heterocycl. Chem. 19 (1976) 1. (c) D.D. Shillady, S. Cutler, L.F. Jones, L.B. Kier, Int. J. Quant. Chem. 24 (1990) 153. (d) J.O. Morley, J. Chem. Soc. Perkin Trans. 2 (1995) 253.

[2] P.M. Weintraub, R.E. Bambury, Tetrahedron Lett. (1969) 579.

[3] H.J. Tien, M. Ohta, Bull. Chem. Soc. Jpn. 45 (1972) 2944.

[4] (a) S.T. Lin, H.S. Cheo, B.I. Chen, Z.Y. Own, Heteroat. Chem. 9 (1998) 549. (b) V.N. Kalinin, S.F. Min, J. Organomet. Chem. 352 (1988) C34. (c) V.N. Kalinin, S.F. Min, P.V. Petrovskii, J. Organomet. Chem. 379 (1989) 195. (d) L.N. Morozova, L.S. Isaeva, P.V. Petrovaskii, D.N. Kravtsov, S.F. Min, V.N. Kalinin, J. Organomet. Chem. 381 (1990) 281.

[5] U. Rychleswa, D.J. Hodgson, A. Yeh, H.J. Tien, J. Chin. Chem. Soc. 38 (1991) 467, and references cited therein.

[6] T. Fuchigami, C.S. Chen, T. Nonaka, Bull. Chem. Soc. Jpn. 59 (1986) 483, 487.

[7] S.T. Lin, H.S. Cheo, L.S. Liu, J.C. Wang, Organometallics 16 (1997) 1803.

[8] C.H. Ueng, Y. Wang, M.Y. Yeh, Acta Crystallogr. Sect. C 43 (1987) 1122.

[9] J. Hasek, J. Obrda, K. Huml, S. Nespurek, H. Chojnacki, M. Sorm, Acta Crystallogr. Sect. B 34 (1978) 2756.

[10] J. Hasek, J. Obrda, K. Huml, S. Nespurek, M. Sorm, Acta Crystallogr. Sect. B 34 (1978) 2449.

[11] F.J. Parlevliet, M.A. Zuidevell, C. Kiener, H. Kooijman, A.L. Spek, P.C.J. Kamer, P.W.N.M. van Leeuwen, Organometallics 18 (1999) 3394.

[12] J. Vicente, J.-A. Abad, B. Rink, F.-S. Hernández, M.C.R. de Arellano, Organometallics 16 (1997) 5269.

[13] T. Chenal, R. Naigre, I. Ciprés, P. Kalck, J.-C. Daran, J. Vaissermann, J. Chem. Soc. Chem. Commun. (1993) 747.

[14] SHELXTL-PLUS, Release 4.2, Siemens Analytical X-ray Instruments, Karlsruhe, German, 1991.