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Tetrahedron: *Asymmetry* 18 (2007) 2011–2015

# Enantiomerically pure cyclopalladated diazaphospholidine

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Received 19 July 2007; accepted 5 September 2007

**Abstract**—Enantiomerically pure (*S*)-2-(anilinomethyl)pyrrolidine (*S*)-**2** was obtained from (*S*)-proline using a modified four-step procedure in a total yield of 56%. Diamine (*S*)-**2** was converted to diazaphospholidine (*S*)-**1** using $^{o}$TolP(NMe$_2$)$_2$. The enantiomeric purity of ligand (*S*)-**1** and diamine (*S*)-**2** was determined by $^{31}$P and $^{1}$H NMR spectroscopy, respectively, using a *CN*-palladacycle for their chiral derivatization. Direct cyclopalladation of (*S*)-**1**, using Pd(OAc)$_2$ in toluene under mild conditions regioselectively afforded the cyclopalladated complex with the (sp$^2$)C–Pd bond. The aromatic C–H bond activation was confirmed by NMR spectral data and X-ray diffraction study of the PPh$_3$ derivative of the new *P**,*C**,*N**-chiral phosphapalladacycle.
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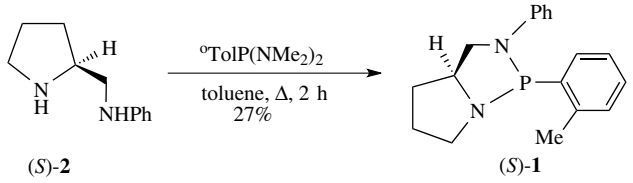
## 1. Introduction

The preparation and applications of enantiopure phosphapalladacycles represent a new and promising field in the chemistry of organometallic compounds. Only nine years ago the preparation of the first optically active complex of this kind was reported.[1] Over the last decade, the first representatives of *CP*- and *PCP*-complexes of several stereochemical types have been described, including *P**-chiral,[2] planar chiral,[3] and axially chiral structures.[4] These complexes were prepared mainly from mono- or bidentate phosphines. Examples of chiral cyclopalladated derivatives of other classes of *P*-donor ligands remain rather scarce. They include a couple of phosphite *CP*-palladacycles,[5] and several pincer *PCP*-[6a–c] or *PCN*-complexes[6d] derived from phosphites,[6a,b] phosphinites,[6d] or phosphoramidites,[6c] containing the {$O_3$P:}, {$C_2$OP:}, or {$NO_2$P:} donor groups, respectively. Herein we report our results on the preparation of the first chiral *CP*-palladacycle containing the {$N_2$CP:} donor group in the polycyclic framework.[7]

## 2. Results and discussion

Diazaphospholidine ligand (*S*)-**1** was obtained[8] from diamine (*S*)-**2** by the method described for its *P*-*ortho*-anisyl substituted analogue[9] (Scheme 1).[10,11]




**Scheme 1.** Synthesis of diazaphospholidine (*S*)-**1**.

For the preparation of diamine (*S*)-**2** from (*S*)-proline, a modified version was developed combining advantages of two known four-step protocols[12a,b] (Scheme 2). First, the hydrogenation at the deprotection step was replaced by the hydrolysis of anilide (*S*)-**4** with $CF_3COOH$[12b,c] by using the *tert*-butyl carbamate (BOC) protection of (*S*)-proline[13] instead of benzyloxycarbonyl. Secondly, in the amidation step *c* the yield of anilide (*S*)-**4** was increased from 77–79%[12a,d,e] to 85% by using $CH_2Cl_2$ instead of EtOAc as the solvent. Thirdly, in the reduction step *f*, the time was shortened to 6 h and the yield of diamine (*S*)-**2** was

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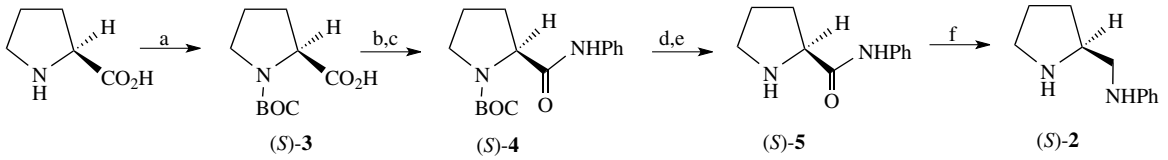
doi:10.1016/j.tetasy.2007.09.005




**Scheme 2.** Synthesis of diamine (*S*)-**2**. Reagents and conditions: (a) ($^t$BuOCO)$_2$O, $CH_2Cl_2$, 0 °C, 2.5 h, 95%; (b) $ClCO_2Et$, *N*-methylmorpholine, 0 °C, 10 min; (c) $PhNH_2$, $CH_2Cl_2$, 0 °C, 1 h; rt, 12 h, 85%; (d) TFA, $CH_2Cl_2$, 20 °C, 4 h; (e) $NaOH_{aq}$, 83%; (f) $LiAlH_4$, THF, −15 °C, 0.5 h; 0 °C, 0.5 h; 65 °C, 6 h, 83%.

increased from 63–66%[12b,e] to 83% by refluxing the reaction mixture.

It should be noted that our attempts to prepare diamine (*S*)-**2** from (*S*)-glutamic acid using a shorter two-step protocol[14] provided only a racemic or scalemic diamine (<85% ee) in low yields. The enantiomeric composition of the samples obtained was significantly dependent upon reaction conditions.

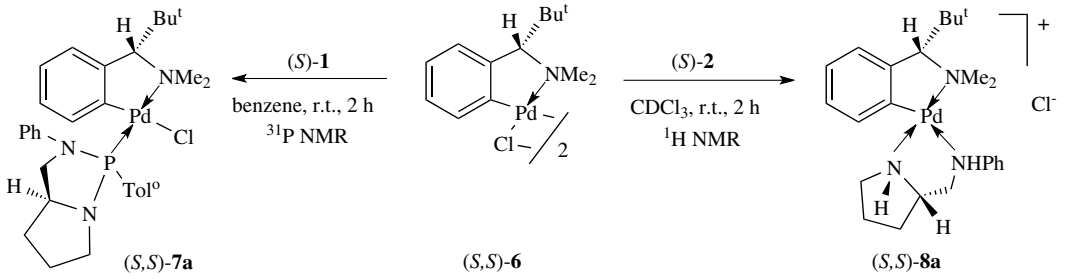
The structures of diazaphospholidine (*S*)-**1**, diamine (*S*)-**2**, and the synthetic intermediates (*S*)-**3**–**5** were confirmed by $^1$H NMR spectra. Enantiomeric purity of ligand (*S*)-**1**[15] and diamine (*S*)-**2** was determined by means of $^{31}$P and $^1$H NMR spectroscopy, respectively, using optically active *CN*-dimer (*S*,*S*)-**6**[16] for their in situ coordinative chiral derivatization (Scheme 3).

The $^{31}$P NMR spectrum of the racemic diazaphospholidine adduct with the cyclopalladated reagent revealed a significant difference in the chemical shift values of the signals belonging to the two diastereomers, (*S*,*S*)-**7a** and (*R*,*S*)-**7b** ($\Delta\delta$ 6.83 ppm). In the $^1$H NMR spectrum of the racemic diamine adduct with the same reagent, (*S*,*S*)-**8a**/(*R*,*S*)-**8b**, a good diastereomeric signal resolution ($\Delta\delta$ 0.11 ppm) for the anilide PhN*H* proton was observed; the signals of the α-CH proton and the $NMe^{ax}$ and $NMe^{eq}$ groups were also resolved, but at a lesser extent ($\Delta\delta \sim 0.01$ ppm). Therefore, the presence of only one signal in the $^{31}$P NMR spectrum of (*S*,*S*)-**7a** and one set of signals in the $^1$H NMR spectrum of (*S*,*S*)-**8a** may be considered as evidence of the complete enantiomeric purity (>98% ee) of the (*S*)-**1** sample with $[\alpha]_D^{24} = -375$ (*c* 1, $CHCl_3$) and the diamine (*S*)-**2** sample with $[\alpha]_D^{24} = +20.4$ (*c* 1, EtOH).

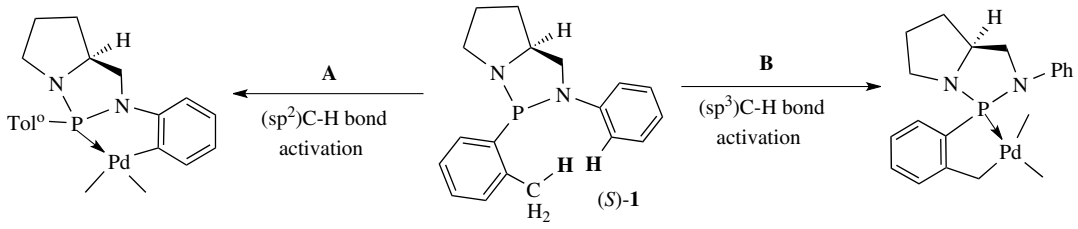
To note, despite a wide application of diamine (*S*)-**2** as a chiral auxiliary, its enantiomeric composition was estimated mainly by using polarimetry,[12a,d–f] although the reported $[\alpha]_D$ values vary from +15.3[12f] to +19.7[12d] (*c* 1.0–1.1, EtOH). It is known that this method cannot be considered as being very reliable.[17a] Thus far, only one example of the spectral ($^{31}$P NMR) determination of diamine (*S*)-**2** enantiopurity using covalent derivatization procedures has been reported.[14c] However, the absence of any information regarding diastereomeric signal dispersion, the use of the reagent applicable only to $C_2$ symmetric substrates,[17b] along with general disadvantages of covalent derivatization methodology, do not allow to consider this method as a correct one.

Diazaphospholidine ligand (*S*)-**1** has two alternative sites suitable for cyclopalladation: the ($sp^2$)C–H bond of the NPh-group (path **A**) and ($sp^3$)C–H bond of the *ortho*-Me group of the PTol$^o$-substituent (path **B**); the latter route was proposed in a retracted article.[10,11] Although both directions can result in the formation of optimal five-membered palladacycles, the first one has to be considered as the preferred one by taking into account a higher reactivity of aromatic C–H bond over aliphatic in cyclopalladation (Scheme 4).[18]

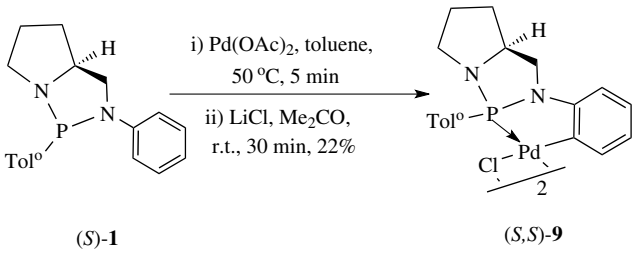
Diazaphospholidine (*S*)-**1** has showed a low reactivity toward cyclopalladation. As a consequence, the conditions of the C–H bond activation were optimized using racemic ligand **1**. Diverse metallation agents and conditions (varying the base and solvent nature, reaction temperature and time) were tested. The best result was obtained in the reaction of $[PdCl_2(NCPh)_2]$ with ligand **1** in the presence of AcONa in 1:1:1 ratio in a benzene–MeOH mixture under mild conditions (rt, 2 h); the cyclopalladated dimer *rac*-**9** was isolated in a yield of 27%.[19] Both racemic dimer **9** and enantiopure (*S*,*S*)-**9** were prepared in yields of 22–25% using the more electrophilic reagent $Pd(OAc)_2$ without any base followed by anion metathesis (Scheme 5).[20] Under any conditions used, the reaction occurred regioselectively to furnish dimer **9** as the only cyclopalladated complex;




**Scheme 3.** Determination of the enantiomeric purity of diazaphospholidine (*S*)-**1** and diamine (*S*)-**2**.



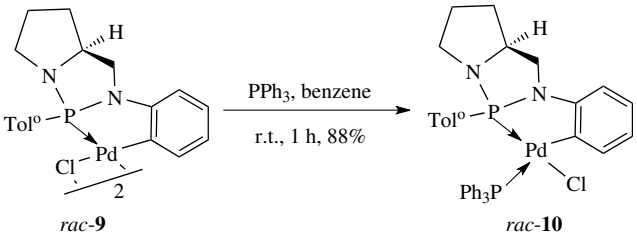

**Scheme 4.** Alternative routes for the C–H bond activation of diazaphospholidine (*S*)-**1**.




**Scheme 5.** Cyclopalladation of diazaphospholidine (*S*)-**1**.

intermediate coordination compounds and palladium(0) were detected as side products.

To confirm the proposed regiochemistry of cyclopalladation, dimer *rac*-**9** was converted into its mononuclear phosphane derivative *rac*-**10** (Scheme 6).[21]




**Scheme 6.** Synthesis of mononuclear derivative *rac*-**10**.

The $^{31}$P NMR spectrum of the latter contains only two doublets, which is the indicative of regioselective coordination of the auxiliary ligand with the *CP*-palladacycle. The *cis*(*P*,*P*)-geometry of this complex is evident from a low value of the $^{2}J_{PP}$ constant (33.4 Hz).[22] The $^{1}$H NMR spectrum of adduct **10** supports the aromatic C–H bond activation: (i) it contains the [3H] singlet of the intact Me group of the PTol$^{o}$-substituent ($\delta$ 2.70 ppm) and (ii) four [1H] signals of the $C_6H_4N$ group.

The most conclusive evidence of the proposed structure and stereochemistry of the new phosphapalladacycle was obtained from the X-ray diffraction study of complex *rac*-**10** (Fig. 1).[23] It unambiguously confirms the formation of the (sp$^2$)C–Pd bond, relative $(S_C S_{N^1} S_{N^3} S_P)^*$-configuration of the *CP*-palladacycle, and *cis*(*P*,*P*)-geometry of the phosphane adduct. The *CP*-palladacycle has a slightly distorted envelope conformation with an interplanar angle {PdCCN$^1$}/{PdP$^2$N$^1$} of 5.6°. A short contact of the metal with the Me group of the *ortho*-tolyl substituent is to be noted, with a Pd···H(27) distance of 2.74(4) Å compared

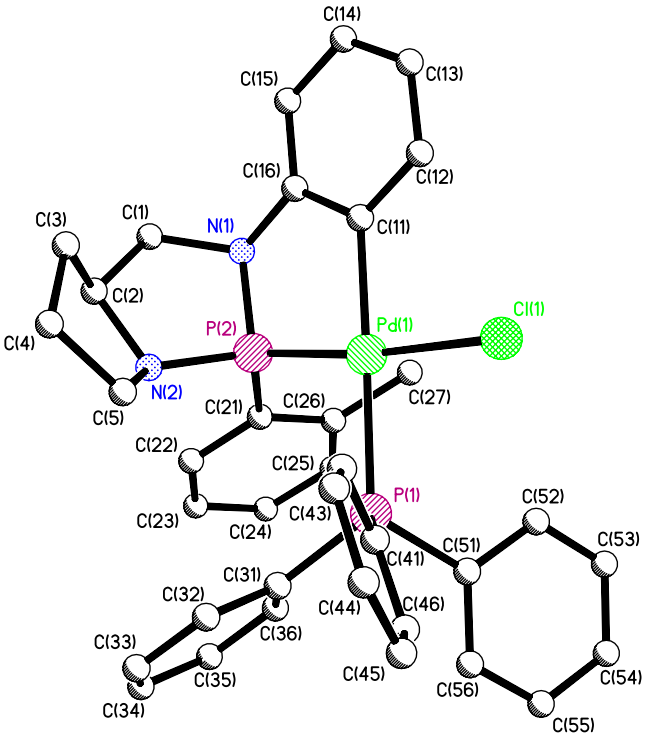



**Figure 1.** Molecular structure and numbering scheme for complex *rac*-**10** (benzene hemisolvate).

to the sum of van-der-Vaals radii of these atoms of 3.1 Å.[24] Despite this proximity, the activation of the aliphatic C–H bond was not observed in our experiments. This may be considered as evidence of the greater reactivity of the (sp$^2$)C–H bonds compared to the (sp$^3$)C–H ones.

## 3. Conclusions

The first representative of chiral *CP*-palladacycles containing the {$N_2$CP} donor group was prepared. Complete regioselectivity of cyclopalladation has been established in favor of the aromatic C–H bond activation. It has been shown that the new phosphapalladacycle is capable of selective *cis*(*P*,*P*)-coordination of the auxiliary *P*-donor ligand. The structure and stereochemistry of the *CP*-palladacycle was unambiguously established by using NMR spectroscopy and X-ray crystallography.

A modified protocol for the synthesis of the key synthetic intermediate, (*S*)-2-(anilinomethyl)pyrrolidine, has been

developed. The enantiomeric purity of this diamine and diazaphospholidine ligand was determined by $^{1}H$ or $^{31}P$ NMR spectroscopy, respectively, using the *CN*-palladacycle for chiral derivatization.

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8. (2*R*,5*S*)-2-(2-Methylphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane, (*S*)-**1**. A solution of diamine (*S*)-**2** (0.01 mol, >98% ee) in toluene (25 mL) was treated with $^{o}$TolP(NMe$_2$)$_2$ (0.01 mol) under argon and refluxed while stirring for 2 h. After twofold distillation and threefold recrystallization from ethyl acetate ligand (*S*)-**1** was obtained as stable colorless crystals in the yield of 27%: $[\alpha]_D^{24} = -345$ (*c* 1.00, $CHCl_3$), bp 112 °C/1 mmHg. $^{31}P$ NMR ($\delta$, ppm): 98.23 (s). $^{1}H$ NMR ($\delta$, ppm; *J*, Hz): 7.24–7.14 (m, 4H, $^{o}$Tol), 7.07 (m, 2H, *m*-H of NPh), 6.82 (d, 2H, $^{3}J_{HH}$ 7.9, *o*-H of NPh), 6.78 (t, 1H, $^{3}J_{HH}$ 7.4, *p*-H of NPh), 3.91 (m, 1H, $^{3}J_{H^5H^{4A}}$ 8.5, $^{3}J_{H^5H^{4B}}$ 2.5, C$^5$*H*), 3.62 (ddd, 1H, $^{2}J_{HH}$ 8.8, $^{3}J_{H^{4A}H^5}$ 7.2, $^{3}J_{HP}$ 1.2, C$^4$*H*$^{A}$), 3.39 (m, 1H, C$^8$*H*$^{A}$), 3.23 (m, 1H, C$^8$*H*$^{B}$), 3.12 (ddd, 1H, $^{2}J_{HH}$ 8.8, $^{3}J_{H^{4B}H^5}$ 8.8, $^{3}J_{HP}$ 2.5, C$^4$*H*$^{B}$), 2.05 (m, 1H, C$^6$*H*$^{A}$), 1.92 (m, 2H, C$^7$*H*$_2$), 1.83 (m, 1H, C$^6$*H*$^{B}$).
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15. Determination of the enantiomeric purity of ligand (*S*)-**1**: A solution of *CN*-dimer (*S*,*S*)-**6** (0.018 mmol) and ligand (*S*)-**1** (0.0362 mmol) in $C_6H_6$ (1 mL) was stirred at rt for 2 h, then the solvent was evaporated. The crude diastereomer (*S*,*S*)-**7a** was dissolved in $CDCl_3$ and $^{31}P$ NMR spectrum was measured that contained one signal at $\delta$ 108.85 ppm (s). After using the same procedure for the racemic ligand **1**, two signals at $\delta$ 108.84 and 102.01 ppm were detected.
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19. Cyclopalladation of ligand *rac*-**1**: A solution of $[PdCl_2(PhCN)_2]$ (0.35 mmol) and ligand *rac*-**1** (0.35 mmol) in benzene (5 mL) was stirred at rt for 40 min; then a solution of AcONa (0.35 mmol) in MeOH (0.5 mL) was added and the reaction mixture stirred at rt for 2 h. After chromatographic purification on silica using a dry column (eluent $C_6H_6$) dimer (*R*,*S*)-**9** was isolated in a yield of 27%: mp (dec) 152–154 °C, $R_f$ 0.79 (10:1 $C_6H_6$–$Me_2CO$). $^{31}P$ NMR: $\delta$ 151.04 (s). Anal. Calcd for $C_{36}H_{40}N_4P_2Cl_2Pd_2$: C, 49.44; H, 4.62; N, 6.41. Found: C, 50.00; H, 4.49; N, 6.21.
20. Cyclopalladation of ligand (*S*)-**1**: A solution of $Pd(OAc)_2$ (0.1857 mmol) and ligand (*S*)-**1** (0.1856 mmol) in toluene (3 mL) was stirred at 50 °C for 5 min and then evaporated to dryness. The residue was treated with LiCl (0.370 mmol) in acetone (2 mL), the mixture was stirred at rt for 30 min and then evaporated to dryness. After chromatographic purification using dry column (eluents $C_6H_6$ and 20:1 $C_6H_6$–acetone), dimer (*S*,*S*)-**9** was isolated in a yield of 22% as a light-yellow amorphous powder. $[\alpha]_D^{25} = -106.4$ (*c* 0.235, $CH_2Cl_2$), $^{31}P$ NMR: $\delta$ 151.04 (s).
21. Phosphine adduct **10** preparation: A solution of dimer *rac*-**9** (0.0172 mmol) and $PPh_3$ (0.0378 mmol) in benzene (2 mL) was stirred at rt for 1 h. It was evaporated in vacuo to dryness, and the crude product was purified using dry column chromatography (eluents hexane, $C_6H_6$, 20:1 and 10:1 and $C_6H_6$–$Me_2CO$) to afford adduct *rac*-**10** in 88% yield as a colorless powder. After recrystallization from a dichloromethane/hexane mixture: mp (dec) 192–195 °C, $R_f$ 0.56 (15:1 $C_6H_6$–$Me_2CO$). Anal. Calcd for $C_{36}H_{35}N_2P_2ClPd$: C, 61.81; H, 5.05; N, 4.01. Found: C, 62.43; H, 5.05; N, 4.14. $^{1}H$ NMR: 7.46 (dd, 6H, $^{3}J_{HH}$ 7.6, $^{3}J_{HP}$ 10.2, *o*-H of $PPh_3$), 7.36 (t, 3H, $^{3}J_{HH}$ 7.7, *p*-H of $PPh_3$), 7.26 (m, 6H, *m*-H of $PPh_3$); 7.19 (dd, 1H, $^{3}J_{av}$ 7.5, H$^{4''}$ of Tol$^{o}$), 6.80 (m, 1H, H$^{3''}$ of Tol$^{o}$), 6.77 (dd, 1H, $^{3}J_{av}$ 7.4, H$^{5''}$ of Tol$^{o}$);[†] 8.60 (dddd, 1H, $^{4}J_{HP(PPh_3)}$ 7.2, $^{4}J_{HP^2}$ 24.0, $^{3}J_{HH}$ 7.6, $^{4}J_{HH}$ 1.3, H$^{6'}$ of $C_6H_4N$), 7.05 (dd, 1H,


[†] Signal of H$^{6''}$ proton of Tol$^{o}$ substituent is hidden under a solvent signal.

$^3J_{H^{4'}H^{5'}}$ 7.2, $^3J_{H^{4'}H^{3'}}$ 7.5, $H^{4'}$ of $C_6H_4N$), 6.82 (m, 1H, $H^{5'}$ of $C_6H_4N$), 6.48 (dd, 1H, $^5J_{HP(PPh_3)}$ 3.9, $^3J_{HH}$ 7.5, $H^{3'}$ of $C_6H_4N$); 3.82 (m, 1H, $C^8H^A$), 3.75 (m, 1H, $C^5H$), 3.23–3.31 (m, 2H, $C^4H_2$), 3.16 (m, 1H, $C^8H$), 2.70 (s, 3H, $CH_3$ of Tol$^o$), 2.00 (m, 1H, $C^6H$), 1.76 (m, 2H, $C^7H_2$), 1.53 (m, 1H, $C^6H$).

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23. $C_{36}H_{35}Cl_1N_2P_2Pd{\cdot}0.5C_6H_6$, $M = 738.50$, monoclinic, $a = 9.630(2)$, $b = 18.321(2)$, $c = 19.566(2)$ Å, $\beta = 100.06(1)°$, $V = 3399.0(9)$ Å$^3$, space group $P2_1/c$, $Z = 4$, $D_c = 1.443$ g/cm$^3$, $F(000) = 1516$, $\mu$(Mo K$\alpha$) = 0.750 mm$^{-1}$. The crystal of approximate dimensions $0.4 \times 0.3 \times 0.2$ was used for data collection. A total of 7865 reflections (5979 unique, $R_{int} = 0.0209$) were measured on an Enraf-Nonius CAD4 diffractometer (graphite monochromatized Mo K$\alpha$ radiation, $\lambda = 0.71073$ Å) at room temperature. Data were collected in the range $2.11 < \theta < 24.98$ ($-11 \leqslant h \leqslant 11$, $-2 \leqslant k \leqslant 21$, $-2 \leqslant l \leqslant 23$) using $\omega$ scan mode. The structure was solved by direct methods [SHELXS-97] and refined by full-matrix least-squares on $F^2$ [SHELXL-97] with anisotropic thermal parameters for all non-hydrogen atoms. All H atoms (except solvent benzene molecule) were found from difference Fourier synthesis and refined isotropically. Hydrogen atoms of solvent molecule were placed in calculated positions and refined using a riding model. The final residuals were $R_1 = 0.0253$, $wR_2 = 0.0616$ for 4083 reflections with $I > 2\sigma(I)$ and 0.0648, 0.0682 for all data and 546 parameters. Goof = 1.020, maximum $\Delta\rho = 0.326$ e Å$^{-3}$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-649695. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].
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