Electronic Supplementary Information for Dalton Transactions

Supporting Information

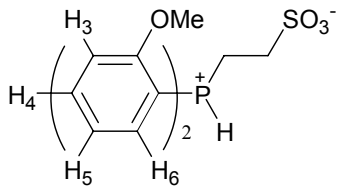
New alkyl derivates phosphine sulphonate (P-O) ligands. Catalytic activity in Pd-catalysed Suzuki-Miyaura reaction in water

Eduardo J. García Suárez,[a] Aurora Ruiz,[a] Sergio Castillón,*[,b] Werner Oberhauser,[c] Claudio Bianchini,[c] and Carmen Claver*[,a]

General Considerations

All reactions were carried out under dry nitrogen atmosphere using standard Schlenk techniques. Solvents were obtained from commercial sources and distilled over dehydrating reagents and were deareated before use. Deuterated solvents (dichloromethane-d_2 or chloroform-d_1) were used as purchased from Sigma-Aldrich. Commercial reagents were used as supplied, unless otherwise stated. Bis(*o*-mehoxy)phenylphosphine[1] and $[Pd_2(\mu\text{-}Cl)_2\{\eta\text{-}^1,\eta^2\text{-}C_8H_{12}OMe\}_2]$[2] were prepared according to the literature methods. ^{1}H-NMR spectra (chemical shifts relative to residual solvent), were recorded on a Varian Mercury VX 400 MHz or Varian Gemini 300 MHz spectrometer. Gas chromatographic analyses were run on a Hewlett-Packard HP 5890A instrument equipped with a Hewlett-Packard HP 366 series II integrator, using an HP-5(25 m x 0.25 mm d. i.). Elemental analyses were performed using a Carlo Erba Model 1108 elemental analyser Microwave experiments were performed in a CEM microwave Discover model.

Synthesis of 2-{bis(*o*-methoxyphenyl)phosphino}ethanesulphonic Acid (1)

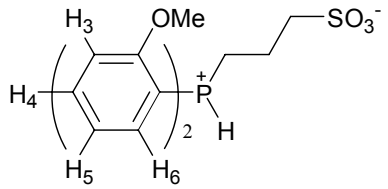


To a solution of bis(*o*-methoxy)phenylphosphine (1.00 g, 4.07 mmol) in deareated THF (50 ml) was added dropwise *n*-BuLi (3.1 mL, 4.9 mmol) at 0 ^{o}C. The reaction mixture was allowed to warm to room temperature and was further stirred for 1 h in order to form the corresponding lithium salt. Afterwards the THF solution of the lithium salt was added to a

flask containing the sodium salt of 2-bromoethane sulfonic acid (0.83 g, 3.9 mmol). The mixture was then allowed to stir for 1.5 h at room temperature. The reaction was quenched with water and the solvent evaporated to yield a slightly yellow solid, which was dissolved in water (20 ml) and then acidified with HCl (37% in water) to pH 2. The acqueous phase was extracted with dichloromethane (3 x 80 mL). Afterwards the combined organic phases were dried over $MgSO_4$ and the solvent was evaporated to yield a white powder.

Ligand 1: 746.3 mg (54%). $C_{16}H_{19}O_5PS.H_2O$ (372.35 g/mol): calc. C 51.61, H 5.68, S 8.61; found: C 52.11, H 5.42, S 8.49. $^{31}P\{^1H\}$ NMR (δ, 121.50 MHz, CD_2Cl_2, 21 ^oC) 0.5 (br s); ^{31}P NMR (δ, 121.5 MHz, CD_2Cl_2, -60 ^oC) 2.86 (d, $^1J_{PH}$ = 544,9 Hz); ^1H NMR (δ, 300.13 MHz, CD_2Cl_2, 21 ^oC) 2.96 (m, 1H, SCH_2), 3.04 (m, 1H, SCH_2), 3.17 (m, 2H, PCH_2), 3.90 (s, 6H, OCH_3), 7.08 (m, 2H, *H*-3), 7.19 (m, 2H, *H*-5), 7.60 (m, 2H, *H*-6), 7.72 (m, 2H, *H*-4); $^{13}C\{^1H\}$ NMR (δ, 75.00 MHz, $CDCl_3$, 21° C)16.7 (d, $^1J_{PC}$ = 56.1Hz, P*C*H_2), 44.2 (d, $^2J_{PC}$ = 3.9Hz, S*C*H_2), 56.7 (s, O*C*H_3), 104.4 (d, $^1J_{PC}$ = 90.25 Hz, *ipso*-*C*), 111.9 (d, $^3J_{PC}$ = 6.1Hz, *C*-3), 122.5 (d, $^3J_{PC}$ = 12.9Hz, *C*-5), 135.3 (d, $^2J_{PC}$ = 7.6Hz, *C*-6), 137.2 (s, *C*-4), 161.7 (s, *C*-2).

Synthesis of 3-{bis(*o*-methoxyphenyl)phosphino}propanesulphonic Acid (2):



To a solution of bis(*o*-methoxy)phenylphosphine (1.00 g, 4.07 mmol) in THF (50 ml) was added dropwise *n*-BuLi (3.1 mL, 4.9 mmol) at 0 ^oC. The reaction mixture was allowed to warm to room temperature and was further stirred for 1h in order to form the corresponding lithium salt. The THF solution of the latter salt was added to a flask containing the sodium salt fo 3-bromopropane sulfonic acid (0.88 g, 3.9 mmol).The mixture was then allowed to stir for 1.5 h at room temperature. The reaction was quenched with water and the solvent evaporated to yield a slightly yellow solid, which was dissolved in water (20 ml). The obtained solution was then acidified with HCl (37% in water) to pH 2 and extracted with dichloromethane (3 x 80 ml). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated to yield a white powder, which was recrystallised from MeOH.

Ligand 2: 589.1 mg (41%). $C_{17}H_{21}O_5PS$ (368.39 g/mol): calc. C 55.43, H 5.75, S 8.70; found: C 55.67, H 5.22, S 8.56. $^{31}P\{^1H\}$ NMR (δ, 121.5 MHz, $CDCl_3$, 21 ^oC) -3.94 (br s); ^{31}P NMR (δ, 121.5 MHz, $CDCl_3$, -60 ^oC) -2.73 (d, $^1J_{PH}$ = 532.89 Hz); ^1H NMR (δ, 300.13 MHz, $CDCl_3$, 21 ^oC) 2.14 (m, 2H, PCH_2CH_2), 2.99 (t, $^3J_{HH}$ = 6.3 Hz, 2H, SCH_2), 3.10 (m, 2H, PCH_2), 3.87 (s, 6H, OCH_3), 7.00 (m, 2H, *H*-3), 7.10 (m, 2H, *H*-5), 7.59 (m, 2H, *H*-4), 7.79 (m, 2H, *H*-6); $^{13}C\{^1H\}$ NMR (δ, 75.00 MHz, $CDCl_3$, 21 ^oC) 17.94 (d, $^1J_{PC}$ = 49 Hz, PCH_2), 19.6 (s, PCH_2CH_2) 50.6 (d, $^3J_{PC}$ = 15.9, SCH_2), 56.9 (s, OCH_3), 105.2 (d, $^1J_{PC}$ = 83.4 Hz, *ipso-C*), 112.0 (d, $^3J_{PC}$ = 5.9 Hz, *C*-3), 122.3 (d, $^3J_{PC}$ = 12.9 Hz, *C*-5), 135.3 (d, $^2J_{PC}$ = 8.4 Hz, *C*-6), 135.8 (s, *C*-4), 161.9 (s, *C*-2)

Synthesis of Complex 1a.

NaH (3.6 mg, 0.15 mmol) was added to a Schlenk flask containing a solution of ligand **1** (49.6 mg, 0.14 mmol) in deareated dichloromethane (5 ml). After this solution had been stirred for 30 minutes $[Pd_2(\mu\text{-}Cl)_2\{\eta^1,\eta^2\text{-}C_8H_{12}OMe\}_2]$ (39.2 mg, 0.07 mmol) was added under stirring at -20 ^oC. The reaction mixture was allowed to stir for 1 h at RT, followed by concentration of the solution to a small volume (2 ml) and on addition of diethyl-ether (10 mL) compound **1a** precipitated as yellow solid, which was filtered off and dried under a flow of nitrogen.

Complex 1a: 51.2 mg (57%). $C_{25}H_{33}O_6PdPS$ (598.9 g/mol): calc. C 50.09, H 5.51, S 5.34; found: C 50.27, H 5.22, S 5.23. $^{31}P\{^1H\}$ NMR (δ, 121.5 MHz, $CDCl_3$, 21 ^oC) 20.3 (s); ^1H NMR (δ, 300.13 MHz, CD_2Cl_2, 21 ^oC) 1.79-2.82 (m, 10H, (COD)), 2.37 (s, 3H, OCH_3, (COD)), 3.01-3.12 (m, 4H, PCH_2CH_2S), 3.76 (s, 3H, OCH_3), 4.02 (s, 3H, OCH_3), 6.20 (m, 1H, PdC*H*), 6.45 (m, 1H, C*H,* (COD*)*), 6.92 (m, 2H, Ar-H), 7.15 (m, 2H, Ar-H), 7.42 (m, 2H, Ar-H), 7.62 (m, 2H, Ar-H); $^{13}C\{^1H\}$ NMR (δ, 75.00 MHz, $CDCl_3$, 21 ^oC) 23.50 (d, $^1J_{PC}$ = 29.6Hz, PCH_2), 25.25 (s, CH_2(COD)), 29.07 (s, CH_2(COD)), 31.58 (s, CH_2(COD)), 35.41 (s, CH_2(COD)), 41.4 (s, *C*H(COD)), 46.92 (s, SCH_2), 55.61 (s, OCH_3), 55.72 (s, OCH_3), 55.81 (s, OCH_3), 82.06 (s, Pd*C*H), 111.5 (d, $^1J_{PC}$ = 19.5Hz, *C*-ipso, Ar), 120.30 (*C*, Ar), 121.24 (d, $^2J_{PC}$ = 7.95Hz, *C*, Ar), 121.63 (d, $^2J_{PC}$ = 10.8Hz, *C*, Ar), 122.20 (d, $^2J_{PC}$ = 7.35Hz, *C*, Ar), 133.25 (s, *C*, Ar), 134.57 (s, *C*, Ar), 161.9 (s, *C*, Ar).

Catalysis

In a 25 mL round botton flask was added ligand **1** or **2** (0.05 mol%) to a solution of K_2CO_3 (3 mmol) in 3 mL of non-deareated water. This mixure was allowed to stirr for 5 minutes. Afterwards were added successively aryl bromide (1.5 mmol), arylboronic acid (1.72 mmol) and $Pd(OAc)_2$ (0.05 mol%). After stitting the solution at 80 ^oC for 2 h, the reaction was quenched by cooling it by means of an ice-bath. In those reactions were microwave heating was employed, the water solution was heated to 150 ^oC for 5 or 10 minutes, followed by quenching the reaction with an ice-bath. The organic product was extracted with CH_2Cl_2 (3 x 15 mL) and the organic extracts were dried over magnesium sulfate, followed by concentration of the solution to dryness. The catalytic conversion, which is reported as average value of two analyses, was estimated by GC or ^{1}H-NMR spectroscopy.

X-ray structure analysis

Suitable crystals of compound **1a** were obtained by diffusion of diethyl-ether into a saturated solution of the latter compound in CH_2Cl_2.

Diffraction data were collected on a Bruker Smart diffractometer with Mo Kα-radiation and graphite monochromator. The absorption correction was carried out using Bruker-SAINT program. The structure was solved by direct methods and refined by full-matrix F^2 refinement. Anisotropic thermal parameters were assigned to all non-hydrogen atoms, while hydrogen atoms were introduced in their calculated positions. All calculations were performed on a PC using SIR97[3], SHELX-97[4] and ORTEP-3[5] programs. CCDC reference number 640968 for **1a**.

---

[1] C. Bianchini, G. Lenoble, W. Oberhauser, S. Parisel and F. Zanobini, *Eur. J. Inorg. Chem.*, **2005**, 4794

[2] C. T. Bailey, G. C. Lisensky, *J. Chem. Educ*., **1985**, *62*, 896.

[3] A. Altomare, M. C. Burla, M. Cavalli, G. L. Cascarano, C. Giacovazzo, A. Gagliardi, G. G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 1999, 32, 115.

[4] G. M. Sheldrick, SHELXL-97, University of Göttingen; Göttingen, Germany, 1997.

[5] M. N. Burnet, C. K. Johnson, ORTEP-3, Report ORNL-6895, Oak Ridge National Laboratory: Oak Ridge, TN, 1996.

```
#------------------------------------------------------------------------#
                    CHEMICAL INFORMATION
#------------------------------------------------------------------------#

_chemical_formula_sum                'C25 H33 O6 P Pd S'
_chemical_formula_weight              598.94

#------------------------------------------------------------------------#
                    UNIT CELL INFORMATION
#------------------------------------------------------------------------#
_symmetry_cell_setting                          monoclinic
_symmetry_space_group_name_H-M          'P 2(1)/n'
loop_
   _symmetry_equiv_pos_as_xyz
'x, y, z'
'-x+1/2, y+1/2, -z+1/2'
'-x, -y, -z'
'x-1/2, -y-1/2, z-1/2'

_cell_length_a                                   9.4428(3)
_cell_length_b                                  14.8530(5)
_cell_length_c                                  17.7593(6)
_cell_angle_alpha                               90
_cell_angle_beta                                100.5950(10)
_cell_angle_gamma                               90
_cell_volume                                    2448.35(14)
_cell_formula_units_Z                           4
_cell_measurement_temperature                   100(2)

#------------------------------------------------------------------------#
                    CRYSTAL INFORMATION
#------------------------------------------------------------------------#

_exptl_crystal_size_max                         0.2
_exptl_crystal_size_mid                         0.1
_exptl_crystal_size_min                         0.1
_exptl_crystal_density_diffrn                   1.625
_exptl_crystal_density_method                    'not measured'
_exptl_crystal_F_000                            1232

#------------------------------------------------------------------------#
                    ABSORPTION CORRECTION
#------------------------------------------------------------------------#

_exptl_absorpt_coefficient_mu                   0.948
_exptl_absorpt_correction_type                  empirical
_exptl_absorpt_correction_T_min                 0.892
_exptl_absorpt_correction_T_max                 0.910
```

```
_exptl_absorpt_process_details          'SADABS (Sheldrick, 1986)'

#------------------------------------------------------------------------------#
                    DATA COLLECTION
#------------------------------------------------------------------------------#

_diffrn_ambient_temperature             293(2)
_diffrn_radiation_wavelength            0.71073
_diffrn_radiation_type                  MoK\a
_diffrn_radiation_monochromator         graphite
_diffrn_reflns_av_R_equivalents         0
_diffrn_reflns_av_unetI/netI            0.013
_diffrn_reflns_number                   4275
_diffrn_reflns_limit_h_min              -11
_diffrn_reflns_limit_h_max              11
_diffrn_reflns_limit_k_min              0
_diffrn_reflns_limit_k_max              17
_diffrn_reflns_limit_l_min              0
_diffrn_reflns_limit_l_max              21
_diffrn_reflns_theta_min                3.75
_diffrn_reflns_theta_max                25
_diffrn_reflns_theta_full               25
_diffrn_measured_fraction_theta_full    0.993
_diffrn_measured_fraction_theta_max     0.993
_reflns_number_total                    4275
_reflns_number_gt                       4153
_reflns_threshold_expression            >2sigma(I)

#------------------------------------------------------------------------------#
                    COMPUTER PROGRAMS USED
#------------------------------------------------------------------------------#
_computing_structure_solution           'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement         'SHELXL-97 (Sheldrick, 1997)'
_computing_molecular_graphics           'ORTEP-3 (Farrugia, 1997)'

#------------------------------------------------------------------------------#
                    REFINEMENT INFORMATION
#------------------------------------------------------------------------------#

Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
```

```
_refine_ls_structure_factor_coef              Fsqd
_refine_ls_matrix_type                        full
_refine_ls_weighting_scheme                   calc
_refine_ls_weighting_details
      'calc w=1/[\s^2^(Fo^2^)+(0.0250P)^2^+7.0731P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary                  direct
_atom_sites_solution_secondary                difmap
_atom_sites_solution_hydrogens                geom
_refine_ls_hydrogen_treatment                 constr
_refine_ls_extinction_method                  none
_refine_ls_number_reflns                      4275
_refine_ls_number_parameters                  310
_refine_ls_number_restraints                  0
_refine_ls_R_factor_all                       0.0297
_refine_ls_R_factor_gt                        0.029
_refine_ls_wR_factor_ref                      0.0701
_refine_ls_wR_factor_gt                       0.0696
_refine_ls_goodness_of_fit_ref                1.057
_refine_ls_restrained_S_all                   1.057
_refine_ls_shift/su_max                       0.001
_refine_ls_shift/su_mean                      0
_refine_diff_density_max                      1.755
_refine_diff_density_min                      -1.447
_refine_diff_density_rms                      0.077

#---------------------------------------------------------------------------#
            ATOMIC TYPES, COORDINATES AND THERMAL PARAMETERS
#---------------------------------------------------------------------------#

   _atom_type_symbol
   _atom_type_description
   _atom_type_scat_dispersion_real
   _atom_type_scat_dispersion_imag
   _atom_type_scat_source
C C 0.0033 0.0016 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
H H 0 0 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
O O 0.0106 0.006 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
P P 0.1023 0.0942 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
S S 0.1246 0.1234 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
Pd Pd -0.9988 1.0072 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

loop_
   _atom_site_label
   _atom_site_type_symbol
   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
```

```
   _atom_site_U_iso_or_equiv
   _atom_site_adp_type
   _atom_site_occupancy
   _atom_site_symmetry_multiplicity
   _atom_site_calc_flag
   _atom_site_refinement_flags
   _atom_site_disorder_assembly
   _atom_site_disorder_group
Pd1 Pd -0.02627(2) 0.325933(13) 0.220672(11) 0.01418(8) Uani 1 1 d . . .
S1 S -0.11341(7) 0.19614(4) 0.35761(4) 0.01482(14) Uani 1 1 d . . .
P1 P 0.12476(7) 0.37652(4) 0.32771(4) 0.01160(14) Uani 1 1 d . . .
O1 O 0.3448(2) 0.24389(13) 0.32163(13) 0.0263(5) Uani 1 1 d . . .
O2 O 0.2585(2) 0.47532(13) 0.46809(11) 0.0196(4) Uani 1 1 d . . .
O3 O 0.2372(2) 0.45537(14) 0.08918(13) 0.0264(5) Uani 1 1 d . . .
O4 O -0.1385(2) 0.22758(15) 0.27755(12) 0.0266(5) Uani 1 1 d . . .
O5 O -0.1806(2) 0.25238(16) 0.40685(13) 0.0307(5) Uani 1 1 d . . .
O6 O -0.1494(2) 0.10190(14) 0.35947(14) 0.0288(5) Uani 1 1 d . . .
C1 C 0.3065(3) 0.39852(18) 0.31212(15) 0.0152(5) Uani 1 1 d . . .
C2 C 0.3506(3) 0.48496(19) 0.29583(15) 0.0170(5) Uani 1 1 d . . .
H2A H 0.2906 0.5339 0.2993 0.02 Uiso 1 1 calc R . .
C3 C 0.4835(3) 0.4985(2) 0.27439(16) 0.0233(6) Uani 1 1 d . . .
H3A H 0.5121 0.5561 0.2632 0.028 Uiso 1 1 calc R . .
C4 C 0.5725(3) 0.4256(2) 0.26985(18) 0.0273(7) Uani 1 1 d . . .
H4A H 0.6609 0.4348 0.2551 0.033 Uiso 1 1 calc R . .
C5 C 0.5327(3) 0.3393(2) 0.28682(17) 0.0246(7) Uani 1 1 d . . .
H5A H 0.5946 0.291 0.2848 0.029 Uiso 1 1 calc R . .
C6 C 0.3986(3) 0.32604(19) 0.30702(17) 0.0195(6) Uani 1 1 d . . .
C7 C 0.4408(4) 0.1689(2) 0.3320(2) 0.0331(8) Uani 1 1 d . . .
H7A H 0.3951 0.1189 0.3521 0.05 Uiso 1 1 calc R . .
H7B H 0.5269 0.1849 0.3671 0.05 Uiso 1 1 calc R . .
H7C H 0.4648 0.1524 0.2836 0.05 Uiso 1 1 calc R . .
C8 C 0.0698(3) 0.48380(18) 0.36169(15) 0.0140(5) Uani 1 1 d . . .
C9 C -0.0469(3) 0.52978(19) 0.31943(16) 0.0170(6) Uani 1 1 d . . .
H9A H -0.0985 0.5037 0.2752 0.02 Uiso 1 1 calc R . .
C10 C -0.0877(3) 0.6138(2) 0.34222(17) 0.0230(6) Uani 1 1 d . . .
H10A H -0.1657 0.644 0.3136 0.028 Uiso 1 1 calc R . .
C11 C -0.0103(4) 0.6520(2) 0.40827(18) 0.0261(7) Uani 1 1 d . . .
H11A H -0.0362 0.7086 0.4235 0.031 Uiso 1 1 calc R . .
C12 C 0.1049(3) 0.6076(2) 0.45220(17) 0.0217(6) Uani 1 1 d . . .
H12A H 0.1549 0.6339 0.4968 0.026 Uiso 1 1 calc R . .
C13 C 0.1454(3) 0.52332(18) 0.42926(15) 0.0159(5) Uani 1 1 d . . .
C14 C 0.3290(3) 0.5096(2) 0.54031(16) 0.0235(6) Uani 1 1 d . . .
H14A H 0.4043 0.469 0.5625 0.035 Uiso 1 1 calc R . .
H14B H 0.2605 0.5154 0.5738 0.035 Uiso 1 1 calc R . .
H14C H 0.3696 0.5675 0.5332 0.035 Uiso 1 1 calc R . .
C15 C 0.0525(3) 0.42175(19) 0.15677(16) 0.0195(6) Uani 1 1 d . . .
H15A H 0.1015 0.4675 0.1919 0.023 Uiso 1 1 calc R . .
```

C16 C -0.0762(3) 0.46643(19) 0.10588(17) 0.0213(6) Uani 1 1 d . . .
H16A H -0.0416 0.5009 0.0665 0.026 Uiso 1 1 calc R . .
H16B H -0.1197 0.5084 0.1367 0.026 Uiso 1 1 calc R . .
C17 C -0.1929(3) 0.4008(2) 0.06698(18) 0.0243(6) Uani 1 1 d . . .
H17B H -0.2866 0.4291 0.0628 0.029 Uiso 1 1 calc R . .
H17A H -0.1774 0.3879 0.0156 0.029 Uiso 1 1 calc R . .
C18 C -0.1921(3) 0.31362(19) 0.11081(16) 0.0200(6) Uani 1 1 d . . .
H18A H -0.2877 0.2949 0.119 0.024 Uiso 1 1 calc R . .
C19 C -0.0970(3) 0.24398(19) 0.11194(16) 0.0193(6) Uani 1 1 d . . .
H19A H -0.139 0.1859 0.122 0.023 Uiso 1 1 calc R . .
C20 C 0.0265(3) 0.2342(2) 0.06933(17) 0.0238(6) Uani 1 1 d . . .
H20A H -0.0089 0.2011 0.0226 0.029 Uiso 1 1 calc R . .
H20B H 0.0991 0.1969 0.1003 0.029 Uiso 1 1 calc R . .
C21 C 0.1018(3) 0.3195(2) 0.04735(18) 0.0255(7) Uani 1 1 d . . .
H21B H 0.1797 0.3017 0.0217 0.031 Uiso 1 1 calc R . .
H21A H 0.0334 0.3539 0.0111 0.031 Uiso 1 1 calc R . .
C22 C 0.1630(3) 0.3802(2) 0.11512(17) 0.0221(6) Uani 1 1 d . . .
H22A H 0.2318 0.3453 0.1519 0.027 Uiso 1 1 calc R . .
C23 C 0.3714(3) 0.4322(2) 0.06880(19) 0.0280(7) Uani 1 1 d . . .
H23A H 0.4282 0.4856 0.0676 0.042 Uiso 1 1 calc R . .
H23B H 0.3546 0.4045 0.0191 0.042 Uiso 1 1 calc R . .
H23C H 0.4219 0.3909 0.1059 0.042 Uiso 1 1 calc R . .
C24 C 0.1318(3) 0.29954(18) 0.41002(15) 0.0163(5) Uani 1 1 d . . .
H24A H 0.231 0.2956 0.4366 0.02 Uiso 1 1 calc R . .
H24B H 0.0763 0.3261 0.4452 0.02 Uiso 1 1 calc R . .
C25 C 0.0762(3) 0.20415(18) 0.39120(16) 0.0175(6) Uani 1 1 d . . .
H25A H 0.1014 0.1673 0.4368 0.021 Uiso 1 1 calc R . .
H25B H 0.1253 0.1793 0.3525 0.021 Uiso 1 1 calc R . .

loop_
_atom_site_aniso_label
_atom_site_aniso_U_11
_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12
Pd1 0.01463(12) 0.01431(12) 0.01358(12) -0.00056(7) 0.00253(8) -0.00582(8)
S1 0.0127(3) 0.0145(3) 0.0181(3) 0.0005(3) 0.0049(3) -0.0017(2)
P1 0.0104(3) 0.0109(3) 0.0136(3) -0.0005(2) 0.0023(2) -0.0010(2)
O1 0.0206(11) 0.0142(10) 0.0469(13) 0.0034(9) 0.0134(10) 0.0063(8)
O2 0.0202(10) 0.0186(10) 0.0178(10) -0.0039(8) -0.0025(8) 0.0045(8)
O3 0.0264(11) 0.0218(11) 0.0341(12) 0.0042(9) 0.0138(9) -0.0029(9)
O4 0.0194(10) 0.0347(12) 0.0241(11) 0.0073(9) 0.0001(8) -0.0122(9)
O5 0.0191(11) 0.0391(13) 0.0349(12) -0.0164(10) 0.0072(9) 0.0009(9)
O6 0.0218(11) 0.0193(11) 0.0461(14) 0.0024(10) 0.0082(10) -0.0065(9)
C1 0.0122(12) 0.0181(13) 0.0153(13) -0.0009(10) 0.0027(10) -0.0019(10)

C2 0.0159(13) 0.0179(14) 0.0164(13) -0.0017(11) 0.0008(10) -0.0040(11)
C3 0.0219(15) 0.0267(16) 0.0209(14) 0.0000(12) 0.0030(12) -0.0121(13)
C4 0.0144(14) 0.0428(19) 0.0252(15) -0.0035(14) 0.0047(12) -0.0093(13)
C5 0.0140(14) 0.0329(17) 0.0271(16) -0.0030(13) 0.0046(12) 0.0034(12)
C6 0.0158(14) 0.0197(14) 0.0228(15) -0.0014(11) 0.0036(11) 0.0010(11)
C7 0.0343(18) 0.0222(16) 0.044(2) 0.0017(14) 0.0111(16) 0.0144(14)
C8 0.0136(12) 0.0134(13) 0.0165(13) 0.0010(10) 0.0067(10) 0.0003(10)
C9 0.0127(13) 0.0231(14) 0.0164(13) 0.0028(11) 0.0056(10) 0.0006(11)
C10 0.0202(14) 0.0261(16) 0.0251(15) 0.0069(12) 0.0104(12) 0.0120(12)
C11 0.0344(17) 0.0192(15) 0.0278(16) -0.0004(12) 0.0142(14) 0.0109(13)
C12 0.0271(15) 0.0196(14) 0.0198(14) -0.0044(11) 0.0082(12) 0.0020(12)
C13 0.0148(13) 0.0157(13) 0.0179(13) 0.0004(11) 0.0050(11) 0.0012(11)
C14 0.0255(15) 0.0249(15) 0.0178(14) -0.0023(12) -0.0018(12) -0.0030(12)
C15 0.0205(14) 0.0161(14) 0.0213(14) -0.0008(11) 0.0025(11) -0.0026(11)
C16 0.0246(15) 0.0159(14) 0.0221(14) 0.0020(11) 0.0006(12) -0.0014(12)
C17 0.0213(15) 0.0232(15) 0.0258(15) 0.0010(12) -0.0024(12) -0.0015(12)
C18 0.0184(14) 0.0222(15) 0.0176(14) -0.0022(11) -0.0013(11) -0.0077(11)
C19 0.0236(15) 0.0163(13) 0.0171(13) -0.0051(11) 0.0014(11) -0.0089(11)
C20 0.0302(16) 0.0184(15) 0.0244(15) -0.0050(12) 0.0091(13) -0.0024(12)
C21 0.0270(16) 0.0266(16) 0.0246(16) -0.0018(12) 0.0090(13) -0.0015(13)
C22 0.0215(15) 0.0223(15) 0.0229(15) 0.0017(12) 0.0049(12) -0.0043(12)
C23 0.0249(16) 0.0313(17) 0.0300(17) 0.0010(14) 0.0109(13) -0.0047(13)
C24 0.0146(13) 0.0168(13) 0.0166(13) 0.0025(11) 0.0008(10) -0.0007(11)
C25 0.0132(13) 0.0152(13) 0.0232(14) 0.0050(11) 0.0015(11) 0.0000(11)

#---#
MOLECULAR GEOMETRY
#---#

_geom_special_details;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.

loop_
_geom_bond_atom_site_label_1
_geom_bond_atom_site_label_2
_geom_bond_distance
_geom_bond_site_symmetry_2
_geom_bond_publ_flag
Pd1 C15 2.044(3) . ?
Pd1 O4 2.161(2) . ?
Pd1 C18 2.274(3) . ?
Pd1 C19 2.276(3) . ?

Pd1 P1 2.2836(7) . ?
S1 O5 1.439(2) . ?
S1 O6 1.442(2) . ?
S1 O4 1.474(2) . ?
S1 C25 1.784(3) . ?
P1 C8 1.813(3) . ?
P1 C1 1.818(3) . ?
P1 C24 1.847(3) . ?
O1 C6 1.365(3) . ?
O1 C7 1.426(4) . ?
O2 C13 1.361(3) . ?
O2 C14 1.426(3) . ?
O3 C23 1.422(4) . ?
O3 C22 1.438(3) . ?
C1 C2 1.396(4) . ?
C1 C6 1.397(4) . ?
C2 C3 1.391(4) . ?
C2 H2A 0.93 . ?
C3 C4 1.381(5) . ?
C3 H3A 0.93 . ?
C4 C5 1.384(5) . ?
C4 H4A 0.93 . ?
C5 C6 1.392(4) . ?
C5 H5A 0.93 . ?
C7 H7A 0.96 . ?
C7 H7B 0.96 . ?
C7 H7C 0.96 . ?
C8 C9 1.393(4) . ?
C8 C13 1.407(4) . ?
C9 C10 1.389(4) . ?
C9 H9A 0.93 . ?
C10 C11 1.384(5) . ?
C10 H10A 0.93 . ?
C11 C12 1.383(4) . ?
C11 H11A 0.93 . ?
C12 C13 1.392(4) . ?
C12 H12A 0.93 . ?
C14 H14A 0.96 . ?
C14 H14B 0.96 . ?
C14 H14C 0.96 . ?
C15 C22 1.517(4) . ?
C15 C16 1.527(4) . ?
C15 H15A 0.98 . ?
C16 C17 1.536(4) . ?
C16 H16A 0.97 . ?
C16 H16B 0.97 . ?
C17 C18 1.511(4) . ?

C17 H17B 0.97 . ?
C17 H17A 0.97 . ?
C18 C19 1.368(4) . ?
C18 H18A 0.98 . ?
C19 C20 1.509(4) . ?
C19 H19A 0.98 . ?
C20 C21 1.538(4) . ?
C20 H20A 0.97 . ?
C20 H20B 0.97 . ?
C21 C22 1.530(4) . ?
C21 H21B 0.97 . ?
C21 H21A 0.97 . ?
C22 H22A 0.98 . ?
C23 H23A 0.96 . ?
C23 H23B 0.96 . ?
C23 H23C 0.96 . ?
C24 C25 1.526(4) . ?
C24 H24A 0.97 . ?
C24 H24B 0.97 . ?
C25 H25A 0.97 . ?
C25 H25B 0.97 . ?

loop_
_geom_angle_atom_site_label_1
_geom_angle_atom_site_label_2
_geom_angle_atom_site_label_3
_geom_angle
_geom_angle_site_symmetry_1
_geom_angle_site_symmetry_3
_geom_angle_publ_flag
C15 Pd1 O4 171.89(10) . . ?
C15 Pd1 C18 80.98(11) . . ?
O4 Pd1 C18 91.56(9) . . ?
C15 Pd1 C19 88.93(11) . . ?
O4 Pd1 C19 86.70(9) . . ?
C18 Pd1 C19 34.99(11) . . ?
C15 Pd1 P1 89.87(8) . . ?
O4 Pd1 P1 96.78(6) . . ?
C18 Pd1 P1 165.24(8) . . ?
C19 Pd1 P1 157.36(8) . . ?
O5 S1 O6 114.67(14) . . ?
O5 S1 O4 113.07(14) . . ?
O6 S1 O4 109.44(13) . . ?
O5 S1 C25 106.62(13) . . ?
O6 S1 C25 106.45(13) . . ?
O4 S1 C25 105.95(12) . . ?
C8 P1 C1 103.22(12) . . ?

C8 P1 C24 104.57(12) . . ?
C1 P1 C24 109.52(12) . . ?
C8 P1 Pd1 113.14(9) . . ?
C1 P1 Pd1 113.27(9) . . ?
C24 P1 Pd1 112.41(9) . . ?
C6 O1 C7 118.2(2) . . ?
C13 O2 C14 117.5(2) . . ?
C23 O3 C22 113.8(2) . . ?
S1 O4 Pd1 131.26(12) . . ?
C2 C1 C6 118.9(2) . . ?
C2 C1 P1 121.5(2) . . ?
C6 C1 P1 119.2(2) . . ?
C3 C2 C1 120.5(3) . . ?
C3 C2 H2A 119.8 . . ?
C1 C2 H2A 119.8 . . ?
C4 C3 C2 119.5(3) . . ?
C4 C3 H3A 120.3 . . ?
C2 C3 H3A 120.3 . . ?
C3 C4 C5 121.4(3) . . ?
C3 C4 H4A 119.3 . . ?
C5 C4 H4A 119.3 . . ?
C4 C5 C6 118.9(3) . . ?
C4 C5 H5A 120.6 . . ?
C6 C5 H5A 120.6 . . ?
O1 C6 C5 124.3(3) . . ?
O1 C6 C1 114.7(2) . . ?
C5 C6 C1 120.9(3) . . ?
O1 C7 H7A 109.5 . . ?
O1 C7 H7B 109.5 . . ?
H7A C7 H7B 109.5 . . ?
O1 C7 H7C 109.5 . . ?
H7A C7 H7C 109.5 . . ?
H7B C7 H7C 109.5 . . ?
C9 C8 C13 118.8(2) . . ?
C9 C8 P1 119.9(2) . . ?
C13 C8 P1 121.3(2) . . ?
C10 C9 C8 121.2(3) . . ?
C10 C9 H9A 119.4 . . ?
C8 C9 H9A 119.4 . . ?
C11 C10 C9 118.9(3) . . ?
C11 C10 H10A 120.5 . . ?
C9 C10 H10A 120.5 . . ?
C12 C11 C10 121.4(3) . . ?
C12 C11 H11A 119.3 . . ?
C10 C11 H11A 119.3 . . ?
C11 C12 C13 119.6(3) . . ?
C11 C12 H12A 120.2 . . ?

C13 C12 H12A 120.2 . . ?
O2 C13 C12 123.7(3) . . ?
O2 C13 C8 116.2(2) . . ?
C12 C13 C8 120.1(3) . . ?
O2 C14 H14A 109.5 . . ?
O2 C14 H14B 109.5 . . ?
H14A C14 H14B 109.5 . . ?
O2 C14 H14C 109.5 . . ?
H14A C14 H14C 109.5 . . ?
H14B C14 H14C 109.5 . . ?
C22 C15 C16 115.6(2) . . ?
C22 C15 Pd1 109.92(19) . . ?
C16 C15 Pd1 107.45(18) . . ?
C22 C15 H15A 107.9 . . ?
C16 C15 H15A 107.9 . . ?
Pd1 C15 H15A 107.9 . . ?
C15 C16 C17 114.7(2) . . ?
C15 C16 H16A 108.6 . . ?
C17 C16 H16A 108.6 . . ?
C15 C16 H16B 108.6 . . ?
C17 C16 H16B 108.6 . . ?
H16A C16 H16B 107.6 . . ?
C18 C17 C16 112.2(2) . . ?
C18 C17 H17B 109.2 . . ?
C16 C17 H17B 109.2 . . ?
C18 C17 H17A 109.2 . . ?
C16 C17 H17A 109.2 . . ?
H17B C17 H17A 107.9 . . ?
C19 C18 C17 126.6(3) . . ?
C19 C18 Pd1 72.61(16) . . ?
C17 C18 Pd1 108.08(18) . . ?
C19 C18 H18A 113.8 . . ?
C17 C18 H18A 113.8 . . ?
Pd1 C18 H18A 113.8 . . ?
C18 C19 C20 129.1(3) . . ?
C18 C19 Pd1 72.40(16) . . ?
C20 C19 Pd1 110.10(18) . . ?
C18 C19 H19A 112.5 . . ?
C20 C19 H19A 112.5 . . ?
Pd1 C19 H19A 112.5 . . ?
C19 C20 C21 119.0(2) . . ?
C19 C20 H20A 107.6 . . ?
C21 C20 H20A 107.6 . . ?
C19 C20 H20B 107.6 . . ?
C21 C20 H20B 107.6 . . ?
H20A C20 H20B 107 . . ?
C22 C21 C20 114.3(2) . . ?

C22 C21 H21B 108.7 . . ?
C20 C21 H21B 108.7 . . ?
C22 C21 H21A 108.7 . . ?
C20 C21 H21A 108.7 . . ?
H21B C21 H21A 107.6 . . ?
O3 C22 C15 105.1(2) . . ?
O3 C22 C21 110.0(2) . . ?
C15 C22 C21 115.4(2) . . ?
O3 C22 H22A 108.7 . . ?
C15 C22 H22A 108.7 . . ?
C21 C22 H22A 108.7 . . ?
O3 C23 H23A 109.5 . . ?
O3 C23 H23B 109.5 . .
H23A C23 H23B 109.5 . .
O3 C23 H23C 109.5 . .
H23A C23 H23C 109.5 . .
H23B C23 H23C 109.5 . .
C25 C24 P1 116.12(19) . .
C25 C24 H24A 108.3 . .
P1 C24 H24A 108.3 . .
C25 C24 H24B 108.3 . .
P1 C24 H24B 108.3 . .
H24A C24 H24B 107.4 . .
C24 C25 S1 114.74(19) . .
C24 C25 H25A 108.6 . .
S1 C25 H25A 108.6 . .
C24 C25 H25B 108.6 . .
S1 C25 H25B 108.6 . .
H25A C25 H25B 107.6 . .