

Lp effects. Program(s) used to solve structure: *MULTAN11/84* (Main, Germain & Woolfson, 1984). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). H atoms from difference Fourier synthesis and refined isotropically. Molecular graphics: *SCHAKAL* (Keller, 1988). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B _{eq}
Ni	1	0.02797 (9)	$\frac{1}{2}$	3.67 (2)
N1	0.9315 (3)	-0.1288 (4)	0.6792 (3)	3.99 (12)
N2	0.8664 (3)	0.0104 (4)	0.8148 (3)	3.92 (10)
N3	0.9497 (3)	0.1683 (5)	0.6645 (4)	5.77 (16)
C11	0.9311 (4)	0.2517 (8)	0.6164 (4)	5.52 (19)
O1	0.9108 (4)	0.3413 (6)	0.5648 (4)	10.23 (22)
C1	0.9699 (4)	-0.2058 (7)	0.6146 (4)	4.63 (18)
C2	0.9249 (4)	-0.3158 (6)	0.5796 (4)	5.44 (18)
C3	0.8353 (5)	-0.3485 (7)	0.6091 (5)	5.75 (21)
C4	0.7940 (4)	-0.2722 (6)	0.6736 (5)	4.86 (17)
C5	0.8425 (3)	-0.1615 (5)	0.7072 (5)	3.75 (13)
C6	0.8038 (3)	-0.0754 (5)	0.7775 (4)	3.49 (13)
C7	0.7090 (4)	-0.0781 (6)	0.8054 (4)	4.88 (17)
C8	0.6801 (4)	0.0023 (7)	0.8727 (5)	6.15 (22)
C9	0.7441 (5)	0.0869 (7)	0.9116 (4)	5.65 (19)
C10	0.8370 (4)	0.0874 (6)	0.8820 (4)	5.03 (18)

Table 2. Geometric parameters (Å, °)

Ni—N1	2.112 (4)	Ni—N2	2.116 (4)
Ni—N3	2.024 (5)	C11—O1	1.215 (9)
N3—C11	1.131 (9)		
N1—Ni—N2	77.3 (2)	N1—Ni—N3	90.8 (2)
N1—Ni—N1 ¹	86.1 (2)	N1—Ni—N2 ¹	95.8 (2)
N1—Ni—N3 ¹	169.9 (2)	N2—Ni—N3	92.9 (2)
N2—Ni—N2 ¹	170.6 (2)	N2—Ni—N3 ¹	93.5 (2)
N3—Ni—N1 ¹	169.9 (2)	N3—Ni—N3 ¹	93.9 (2)
Ni—N3—C11	172.8 (5)	N3—C11—O1	179.8 (7)

Symmetry code: (i) 2 - x, y, $\frac{1}{2}$ - z.

Table 3. Distortion Δ of the [NiN₆] polyhedron in the [Ni(bipy)₂(NCO)₂] compound

Δ has been calculated using the formula:

$$\Delta = \sum \frac{[\delta b_1 - \delta b_{1oct}]}{846} + \sum \frac{[\delta b_2 - \delta b_{2oct}]}{594} + \sum \frac{[\delta_1 - \delta_{oct}]}{234}$$

Dihedral angle	Octahedron (°)	NiN ₆ (°)	Trigonal prism (°)
δb _{1,1}	70.5	62.3 [N3—N2—N1—N1]	0
δb _{1,2}	70.5	75.6 [N1—N2—N3—N3]	0
δb _{1,3}	70.5	70.0 [N2—N1—N3—N2]	0
δb _{2,1}	70.5	67.2 [N3—N2—N3—N1]	120
δb _{2,2}	70.5	69.1 [N2—N3—N1—N2]	120
δb _{2,3}	70.5	62.3 [N3—N2—N1—N1]	120
δ ₁	70.5	79.6 [N3—N1—N2—N1]	90
δ ₂	70.5	75.6 [N3—N2—N3—N1]	90
δ ₃	70.5	72.6 [N2—N3—N3—N2]	90
δ ₄	70.5	67.2 [N3—N3—N2—N1]	90
δ ₅	70.5	67.5 [N2—N1—N1—N2]	90
δ ₆	70.5	79.6 [N1—N2—N1—N3]	90
Δ	0	0.11	1

Symmetry code: (i) 2 - x, y, $\frac{1}{2}$ - z.

This work has been supported financially by a grant from the Universidad del País Vasco - Euskal Herriko Unibertsitatea (UPV 130.310. E116/91), which we gratefully acknowledge.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71431 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1051]

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Acta Cryst. (1994). **C50**, 58–61

Structures of Mixed Benzenethiolato-Phosphino Dinuclear Complexes of Nickel(II) and Palladium(II)

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(Received 18 November 1992; accepted 16 June 1993)

Abstract

The structures of di-μ-benzenethiolato-bis{[1,2-bis-(diphenylphosphino)ethane]nickel(II)} perchlorate acetonitrile solvate, [Ni₂(SPh)₂(dppe)₂](ClO₄)₂·2MeCN (1), and di-μ-benzenethiolato-bis-

[(benzenethiolato)(triphenylphosphino)palladium(II)] acetonitrile solvate, $[\text{Pd}_2(\text{SPh})_4(\text{PPh}_3)_2] \cdot \text{MeCN}$ (2), have been determined by X-ray diffraction. The dinuclear $[\text{Ni}_2(\text{SPh})_2(\text{dppe})_2]^{2+}$ cation is crystallographically centrosymmetric about the midpoint of $\text{Ni} \cdots \text{Ni}'$ and is formed by the edge sharing of two square-planar NiP_2S_2 coordinations. The dinuclear $[\text{Pd}_2(\text{SPh})_4(\text{PPh}_3)_2]$ molecule is located on a crystallographic inversion centre at (0,0,0) and comprises two PdS_3 coordination planes sharing two μ -SPh ligands.

Comment

Nickel thiolate clusters which have been structurally characterized include the cyclic neutral molecules $[\text{Ni}_n(\text{SR})_{2n}]$ ($n = 2, 4, 6, 8$) and the anionic acyclic species $[\text{Ni}_n(\text{SR})_{2n+2}]^{2-}$ ($n = 2, 3, 6$) (Tremel, Kriege, Krebs & Henkel, 1988, and references therein). The coordination around each Ni^{II} atom in these clusters is square planar. The reaction between Ni^{2+} and benzenethiolate (SPh) produces the mononuclear tetrahedral complex $[\text{Ni}(\text{SPh})_4]^{2-}$ (Yamamura, Miyamae, Katayama & Sasaki, 1985; Rosenfield, Armstrong & Mascharak, 1986, and references therein). Cyclic or acyclic nickel benzenethiolate clusters have not, however, been reported. We are interested in benzenethiolate as a bridging ligand and have previously synthesized a mixed benzenethiolato-sulfido nickel cluster, $[\text{Ni}_3(\mu_3\text{-S})(\mu_2\text{-SPh})_3(\text{SPh})_3]^{2-}$ (Matsumoto, Nakano & Ooi, 1988), in which each Ni^{II} has square-planar coordination with a terminal SPh^- ligand, two bridging SPh^- ligands and a triply bridging S^{2-} ligand. In this paper we describe the crystal structures of the mixed benzenethiolato-phosphino nickel binuclear complex (1) and the palladium analogue (2).

The structures of the binuclear complexes (1) and (2) are shown in Figs. 1 and 2, respectively. Complex (1) is similar in structure to $[\text{Ni}_2\{\text{S}(\text{CH}_2)_3\text{NMe}_2\}_2(\text{dppe})_2]^{2+}$ (Capdevila, Gonzalez-Duarte, Foces-Foces, Cano & Matinez-Ripoll, 1990). In the central Ni_2S_2 ring, the $\text{S}-\text{Ni}-\text{S}'$ angle of $87.50(6)^\circ$ in (1) is larger, while the $\text{Ni}-\text{S}-\text{Ni}'$ angle of $92.50(6)^\circ$ is smaller than those [$84.6(1)$ and $95.5(1)^\circ$] found in $[\text{Ni}_2\{\text{S}(\text{CH}_2)_3\text{NMe}_2\}_2(\text{dppe})_2]^{2+}$, indicating a shorter $\text{Ni} \cdots \text{Ni}'$ separation [$3.254(2) \text{ \AA}$] in (1), although the $\text{Ni}-\text{S}$ bond lengths are 0.016 \AA (on average) longer in (1). The bridging benzenethiolate group produces a small compression (0.056 \AA) in the $\text{Ni} \cdots \text{Ni}'$ direction in the Ni_2S_2 ring of (1). The geometric parameters of the $\text{Ni}(\text{dppe})$ moieties in both complexes are almost identical.

Complex (2) is analogous to $[\text{Pd}_2(\text{SC}_6\text{F}_5)_4(\text{PPh}_3)_2]$ (Fenn & Segrott, 1970, 1972). The geometry of the central Pd_2S_2 ring of (2) is, however, similar to that in $[\text{Pd}_2\text{Cl}_2(\text{SPh})_2(\text{PET}_3)_2]$ (Padilla, Golen, Richmann

& Jensen, 1991), although the $\text{Pd}-\text{S}$ bond lengths are longer by 0.027 \AA (on average) and consequently, the $\text{Pd} \cdots \text{Pd}$ separation is 0.043 \AA longer in (2).

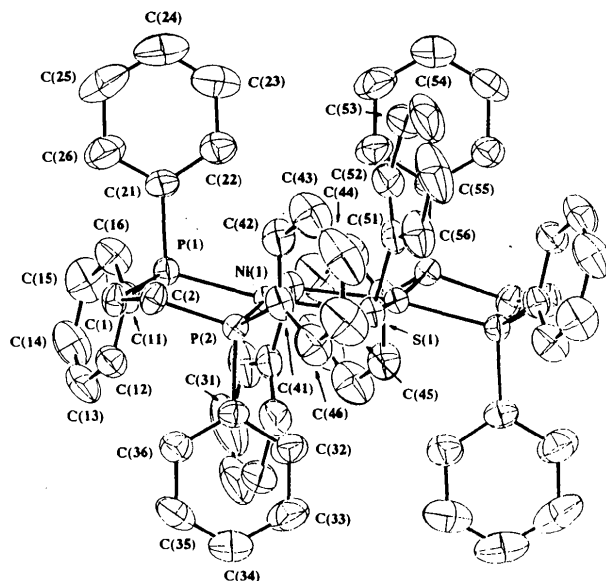


Fig. 1. ORTEP drawing (Johnson, 1976) of the $[\text{Ni}_2(\text{SPh})_2(\text{dppe})_2]^{2+}$ cation showing the labelling of the non-H atoms. Thermal ellipsoids are drawn at the 50% probability level.

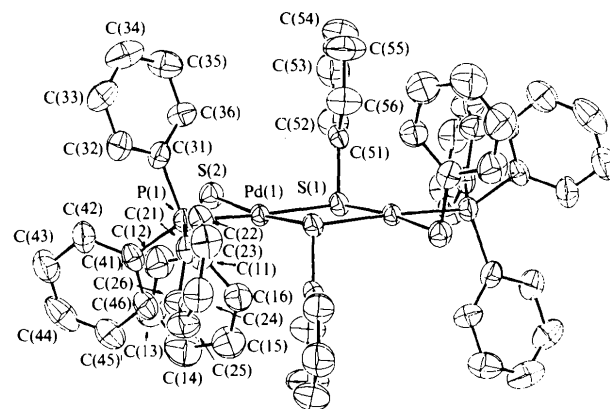


Fig. 2. ORTEP drawing (Johnson, 1976) of the $[\text{Pd}_2(\text{SPh})_4(\text{PPh}_3)_2]$ molecule showing the labelling of the non-H atoms. Thermal ellipsoids are drawn at the 50% probability level.

Experimental

Compound (1)

Crystal data

$[\text{Ni}_2(\text{C}_{26}\text{H}_{24}\text{P}_2)_2(\text{C}_6\text{H}_5\text{S})_2] \cdot (\text{ClO}_4)_2 \cdot 2\text{C}_2\text{H}_3\text{N}$
 $M_r = 1413.6$
 Triclinic

$Z = 1$
 $D_x = 1.42 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$

$P\bar{1}$
 $a = 13.160$ (6) Å
 $b = 13.565$ (6) Å
 $c = 11.077$ (5) Å
 $\alpha = 109.75$ (3)°
 $\beta = 79.52$ (3)°
 $\gamma = 116.88$ (3)°
 $V = 1659.1$ (10) Å³

Cell parameters from 22 reflections
 $\theta = 6 - 13.5^\circ$
 $\mu = 0.86 \text{ mm}^{-1}$
 $T = 295 \text{ K}$
 Rectangular prism
 $0.50 \times 0.30 \times 0.18 \text{ mm}$
 Brown

C(53)	0.3505 (8)	0.7492 (7)	0.1669 (11)	7.7 (4)
C(54)	0.3209 (8)	0.7790 (8)	0.2912 (13)	8.9 (4)
C(55)	0.3472 (8)	0.7410 (8)	0.3770 (10)	8.4 (4)
C(56)	0.4070 (7)	0.6699 (7)	0.3345 (8)	5.3 (2)
Cl(1)	0.8384 (2)	0.2054 (2)	0.1474 (3)	5.965 (8)
O(1)	0.7786 (6)	0.2174 (7)	0.0629 (8)	8.7 (3)
O(2)	0.8753 (7)	0.1185 (6)	0.0857 (12)	12.9 (4)
O(3)	0.9332 (6)	0.3097 (6)	0.1908 (9)	10.2 (3)
O(4)	0.7615 (8)	0.1737 (12)	0.2489 (12)	14.7 (7)
N(61)	0.054 (1)	0.048 (1)	0.341 (1)	10.0 (3)†
C(61)	0.005 (1)	0.099 (1)	0.391 (1)	7.6 (3)†
C(62)	-0.054 (2)	0.166 (2)	0.449 (2)	11.7 (4)†

Data collection

Philips PW1100 diffractometer
 ω scans
 Absorption correction: none
 5838 measured reflections
 5838 independent reflections
 3890 observed reflections
 $[F_o^2 \geq 2\sigma(F_o^2)]$

$\theta_{\max} = 25^\circ$
 $h = -15 \rightarrow 15$
 $k = -16 \rightarrow 14$
 $l = 0 \rightarrow 13$
 3 standard reflections
 frequency: 240 min
 intensity variation: <1.7%

† Isotropic B.

Refinement

Refinement on F
 $R = 0.054$
 $wR = 0.086$
 $S = 0.26$
 3890 reflections
 383 parameters
 H-atom parameters not refined

$w = [\sigma^2(F_o) + 0.008F_o^2]^{-1}$
 $(\Delta/\sigma)_{\max} = 0.5$
 $\Delta\rho_{\max} = 0.47 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = 0.52 \text{ e \AA}^{-3}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters (Å²) for (1)

	$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$			
	x	y	z	B/B _{eq}
Ni(1)	0.38105 (6)	0.38959 (6)	0.01168 (6)	2.131 (2)
S(1)	0.50581 (12)	0.54572 (12)	0.14902 (13)	2.649 (4)
P(1)	0.24733 (13)	0.25402 (12)	-0.11865 (14)	2.553 (4)
P(2)	0.28348 (12)	0.30317 (13)	0.15633 (14)	2.415 (4)
C(1)	0.1519 (5)	0.1389 (5)	-0.0470 (6)	3.0 (2)
C(2)	0.1432 (5)	0.1933 (6)	0.0971 (6)	3.1 (2)
C(11)	0.2885 (5)	0.1802 (5)	-0.2752 (6)	3.1 (2)
C(12)	0.3330 (6)	0.1030 (6)	-0.2807 (7)	3.8 (2)
C(13)	0.3702 (7)	0.0483 (6)	-0.3986 (8)	5.2 (3)
C(14)	0.3644 (8)	0.0698 (7)	-0.5083 (8)	5.5 (3)
C(15)	0.3181 (8)	0.1441 (8)	-0.5013 (7)	5.8 (3)
C(16)	0.2792 (7)	0.1994 (6)	-0.3865 (7)	4.4 (2)
C(21)	0.1605 (6)	0.3185 (6)	-0.1417 (6)	3.4 (2)
C(22)	0.1997 (7)	0.4378 (7)	-0.1051 (7)	4.4 (2)
C(23)	0.1320 (9)	0.4866 (9)	-0.1165 (9)	6.4 (4)
C(24)	0.0287 (8)	0.4245 (10)	-0.1599 (9)	6.5 (4)
C(25)	-0.0158 (8)	0.3046 (11)	-0.1944 (11)	7.8 (5)
C(26)	0.0535 (7)	0.2514 (8)	-0.1880 (9)	5.8 (3)
C(31)	0.3636 (5)	0.2284 (6)	0.1723 (6)	3.0 (2)
C(32)	0.4737 (6)	0.2918 (7)	0.2162 (8)	4.5 (2)
C(33)	0.5400 (7)	0.2376 (8)	0.2178 (9)	5.7 (3)
C(34)	0.4955 (7)	0.1189 (8)	0.1766 (8)	5.5 (3)
C(35)	0.3876 (8)	0.0559 (7)	0.1348 (7)	5.1 (3)
C(36)	0.3198 (6)	0.1100 (6)	0.1335 (7)	3.9 (2)
C(41)	0.2523 (6)	0.3839 (5)	0.3138 (6)	3.2 (2)
C(42)	0.1783 (6)	0.4338 (6)	0.3205 (7)	4.4 (2)
C(43)	0.1480 (8)	0.4951 (8)	0.4371 (9)	6.1 (3)
C(44)	0.1894 (9)	0.5057 (8)	0.5460 (9)	7.6 (4)
C(45)	0.2628 (10)	0.4583 (9)	0.5440 (8)	7.3 (4)
C(46)	0.2953 (8)	0.3974 (7)	0.4269 (7)	5.1 (3)
C(51)	0.4348 (5)	0.6381 (5)	0.2042 (7)	3.6 (2)
C(52)	0.4080 (7)	0.6788 (7)	0.1225 (8)	5.0 (2)

Table 2. Selected geometric parameters (Å, °) for (1)

Ni(1)—S(1)	2.254 (2)	P(1)—C(1)	1.830 (7)
Ni(1)—P(1)	2.183 (2)	P(1)—C(11)	1.810 (7)
Ni(1)—P(2)	2.179 (2)	P(1)—C(21)	1.815 (8)
Ni(1)—S(1 ¹)	2.251 (2)	P(2)—C(2)	1.831 (8)
Ni(1)···Ni(1 ¹)	3.254 (2)	P(2)—C(31)	1.824 (8)
S(1)···S(1 ¹)	3.115 (4)	P(2)—C(41)	1.807 (7)
S(1)—C(51)	1.775 (8)		
S(1)—Ni(1)—P(1)	171.65 (7)	Ni(1)—S(1)—C(51)	102.4 (3)
S(1)—Ni(1)—P(2)	95.54 (7)	Ni(1)—P(1)—C(1)	111.4 (3)
P(1)—Ni(1)—P(2)	85.78 (7)	Ni(1)—P(1)—C(11)	118.6 (3)
P(1)—Ni(1)—S(1 ¹)	92.65 (6)	Ni(1)—P(1)—C(21)	107.1 (3)
S(1)—Ni(1)—S(1 ¹)	87.50 (6)	Ni(1)—P(2)—C(2)	110.3 (3)
P(2)—Ni(1)—S(1 ¹)	169.59 (7)	Ni(1)—P(2)—C(31)	104.2 (3)
Ni(1)—S(1)—Ni(1 ¹)	92.50 (6)	Ni(1)—P(2)—C(41)	121.0 (3)

Symmetry code: (i) 1 - x, 1 - y, -z.

Compound (2)

Crystal data

[Pd₂(C₁₈H₁₅P)₂(C₆H₅S)₄].C₂H₃N

 $M_r = 1215.4$

Triclinic

 $P\bar{1}$ $a = 14.395$ (9) Å $b = 12.483$ (10) Å $c = 9.625$ (5) Å $\alpha = 66.85$ (5)° $\beta = 105.09$ (5)° $\gamma = 115.97$ (6)° $V = 1421.6$ (13) Å³ $Z = 1$ $D_x = 1.42 \text{ Mg m}^{-3}$ Mo K α radiation $\lambda = 0.71069$ Å

Cell parameters from 14 reflections

 $\theta = 6 - 13.5^\circ$ $\mu = 0.86 \text{ mm}^{-1}$ $T = 295 \text{ K}$

Rectangular prism

 $0.55 \times 0.50 \times 0.45 \text{ mm}$

Red

Data collection

Philips PW1100 diffractometer

 ω scans

Absorption correction: none

4994 measured reflections

4994 independent reflections

3700 observed reflections

 $[F_o^2 \geq 2\sigma(F_o^2)]$

Refinement

Refinement on F $R = 0.055$ $wR = 0.088$ $S = 0.30$ $\theta_{\max} = 25^\circ$ $h = -17 \rightarrow 16$ $k = -13 \rightarrow 14$ $l = 0 \rightarrow 11$

3 standard reflections

frequency: 240 min

intensity variation: <1.5%

 $w = [\sigma^2(F_o) + 0.006F_o^2]^{-1}$ $(\Delta/\sigma)_{\max} = 0.2$ $\Delta\rho_{\max} = 1.5 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = 1.8 \text{ e \AA}^{-3}$

3700 reflections
308 parameters
H-atom parameters not refined

Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Table 3. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters (\AA^2) for (2)

$$B_{\text{eq}} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B/B _{eq}
Pd(1)	0.11707 (4)	-0.01225 (5)	0.00164 (6)	2.468 (1)
S(1)	0.04921 (14)	0.06255 (17)	0.13044 (21)	2.880 (6)
S(2)	0.28348 (15)	0.06185 (19)	0.12543 (24)	3.566 (7)
P(1)	0.18464 (14)	-0.07262 (18)	-0.13123 (23)	2.924 (6)
C(11)	0.2889 (6)	-0.0612 (8)	0.2954 (9)	3.6 (3)
C(12)	0.3843 (7)	-0.0717 (10)	0.3623 (12)	5.2 (4)
C(13)	0.3899 (8)	-0.1672 (12)	0.4931 (13)	6.9 (5)
C(14)	0.3057 (10)	-0.2561 (12)	0.5594 (12)	7.2 (5)
C(15)	0.2074 (9)	-0.2459 (11)	0.4982 (11)	5.8 (4)
C(16)	0.1991 (7)	-0.1512 (9)	0.3682 (10)	4.3 (3)
C(21)	0.0912 (6)	-0.1767 (7)	-0.2386 (8)	2.9 (2)
C(22)	0.0466 (7)	-0.1260 (8)	-0.3807 (10)	4.1 (3)
C(23)	-0.0299 (8)	-0.2051 (10)	-0.4591 (11)	4.9 (3)
C(24)	-0.0621 (7)	-0.3339 (9)	-0.3944 (12)	5.1 (4)
C(25)	-0.0179 (8)	-0.3848 (8)	-0.2525 (11)	5.0 (3)
C(26)	0.0587 (7)	-0.3067 (8)	-0.1738 (10)	4.0 (3)
C(31)	0.2564 (6)	0.0665 (8)	-0.2760 (9)	3.4 (2)
C(32)	0.2897 (7)	0.0584 (9)	-0.3922 (11)	4.4 (3)
C(33)	0.3418 (8)	0.1653 (10)	-0.5030 (11)	5.3 (4)
C(34)	0.3628 (8)	0.2809 (10)	-0.4972 (11)	5.8 (4)
C(35)	0.3286 (9)	0.2908 (9)	-0.3831 (11)	5.3 (4)
C(36)	0.2765 (7)	0.1845 (8)	-0.2721 (10)	4.0 (3)
C(41)	0.2711 (6)	-0.1542 (7)	-0.0172 (9)	3.3 (2)
C(42)	0.3688 (6)	-0.1183 (8)	-0.0558 (11)	4.4 (3)
C(43)	0.4341 (8)	-0.1813 (10)	0.0372 (14)	6.0 (4)
C(44)	0.3987 (8)	-0.2761 (10)	0.1717 (13)	5.9 (4)
C(45)	0.3020 (8)	-0.3129 (9)	0.2097 (11)	4.9 (3)
C(46)	0.2395 (7)	-0.2504 (8)	0.1168 (9)	3.9 (3)
C(51)	0.1125 (6)	0.2279 (7)	0.0522 (9)	3.3 (2)
C(52)	0.1842 (8)	0.2909 (9)	0.1458 (12)	5.0 (3)
C(53)	0.2340 (9)	0.4192 (10)	0.0909 (14)	6.2 (4)
C(54)	0.2102 (9)	0.4853 (9)	-0.0558 (15)	6.8 (5)
C(55)	0.1401 (11)	0.4224 (10)	-0.1474 (15)	7.7 (5)
C(56)	0.0895 (9)	0.2920 (9)	-0.0953 (12)	5.5 (4)
C(60) †	0.500	0.500	0.0	8.0
C(61) ‡	0.435	0.362	0.026	8.0
N(61) ‡	0.546	0.605	-0.018	8.0
C(62) §	0.501	0.390	0.144	8.0
N(62) §	0.498	0.574	-0.114	8.0
C(63) §	0.431	0.422	-0.103	8.0
N(63) §	0.543	0.550	0.088	8.0
C(71) ‡	0.545	0.434	0.298	8.0
C(72) ‡	0.521	0.473	0.127	8.0
N(71) ‡	0.500	0.500	0.0	8.0

† Disordered, 0.35 site occupancy, isotropic B.

‡ Disordered, 0.15 site occupancy, isotropic B.

§ Disordered, 0.10 site occupancy, isotropic B.

Table 4. Selected geometric parameters (\AA , $^\circ$) for (2)

Pd(1)—S(1)	2.388 (2)	S(1)—C(51)	1.774 (9)
Pd(1)—S(2)	2.335 (3)	S(2)—C(11)	1.762 (10)
Pd(1)—S(1')	2.338 (2)	P(1)—C(21)	1.835 (9)
Pd(1)—P(1)	2.280 (3)	P(1)—C(31)	1.817 (10)
Pd(1)···Pd(1')	3.506 (2)	P(1)—C(41)	1.820 (9)
S(1)···S(1')	3.169 (4)		
S(1)—Pd(1)—S(2)	91.69 (8)	Pd(1)—S(1)—Pd(1')	95.78 (7)
S(1)—Pd(1)—S(1')	84.22 (7)	Pd(1)—S(1)—C(51)	101.7 (3)
S(1)—Pd(1)—P(1)	176.77 (8)	Pd(1)—S(2)—C(11)	105.9 (4)
S(2)—Pd(1)—P(1)	88.03 (9)	Pd(1)—P(1)—C(21)	116.6 (3)
S(2)—Pd(1)—S(1')	173.25 (8)	Pd(1)—P(1)—C(31)	108.5 (3)
P(1)—Pd(1)—S(1')	95.75 (8)	Pd(1)—P(1)—C(41)	114.9 (3)

Symmetry code: (i) $-x, -y, -z$.

For (1), a suspension of NiCl₂ (130 mg) and dppe (400 mg) in acetonitrile (15 cm³) was stirred for 3 h and NaSPh (140 mg) was then added. After 20 h, NaClO₄·H₂O (170 mg) in methanol (5 cm³) was added and the solution was stirred and filtered. The filtrate was stored in a refrigerator for 5 d. Brown crystals of (1) were obtained; yield 85 mg (12%). Analysis found: C 57.0, H 4.5, N 1.8%. Analysis calculated for [Ni₂(SC₆H₅)₂(C₂₆H₂₄P₂)₂](ClO₄)₂·2CH₃CN: C 57.8, H 4.6, N 2.0%.

For (2), NaSPh (260 mg) was added to a stirred solution of Pd(CH₃COO)₂ (220 mg) in acetonitrile (10 cm³) and *N,N*-dimethylformamide (10 cm³). After 1 h, PPh₃ (260 mg) was added and the mixture was stirred for 20 h. Red crystals of (2) were obtained from the filtrate after storage in a refrigerator for 3 d; yield 105 mg (17%). Analysis found: C 60.6, H 4.6, N 1.3%. Analysis calculated for [Pd₂(SC₆H₅)₄{P(C₆H₅)₃}₂].CH₃CN: C 61.3, H 4.4, N 1.2%.

For (1) and (2), phase problems were solved using *SHELXS86* (Sheldrick, 1986); all non-H atoms were obtained from Fourier maps and H atoms placed at calculated positions (C—H = 0.96 Å); block-diagonal least-squares techniques based on *F* were used, with anisotropic thermal parameters for non-H atoms and isotropic temperature factors ($B = 7.0 \text{ \AA}^2$) for each H atom. The acetonitrile molecule in (2) is disordered. A local version of *UNICS* (*RCLS-3*, *RSSFR-5*, *HBL5-IV*, *DAPH*) (Sakurai, 1969) was used for computations on a HITAC M 660K.

The authors thank Dr Jyun-ichi Gohda for elemental analysis.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71413 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1024]

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