Lp effects. Program(s) used to solve structure: *MULTAN*11/84 (Main, Germain & Woolfson, 1984). Program(s) used to refine structure: *SHELX*76 (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* ($\mathring{A}^2$)

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

	x	y	z	B_{eq}
Ni	1	0.02797 (9)	$\frac{3}{4}$	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* ($\mathring{A}$, °)

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^i	86.1 (2)	N1—Ni—N2^i	95.8 (2)
N1—Ni—N3^i	169.9 (2)	N2—Ni—N3	92.9 (2)
N2—Ni—N2^i	170.6 (2)	N2—Ni—N3^i	93.5 (2)
N3—Ni—N1^i	169.9 (2)	N3—Ni—N3^i	93.9 (2)
Ni—N3—C11	172.8 (5)	N3—C11—O1	179.8 (7)

Symmetry code: (i) $2 - x, y, \frac{3}{2} - z$.

Table 3. *Distortion Δ of the* [NiN$_6$] *polyhedron in the* [Ni(bipy)$_2$(NCO)$_2$] *compound*

Δ has been calculated using the formula:

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

Dihedral angle	Octahedron (°)	NiN$_6$ (°)	Trigonal prism (°)
$\delta b_{1,1}$	70.5	62.3 [N3'—N2—N1'—N1]	0
$\delta b_{1,2}$	70.5	75.6 [N1'—N2—N3'—N3]	0
$\delta b_{1,3}$	70.5	70.0 [N2'—N1—N3—N2]	0
$\delta b_{2,1}$	70.5	67.2 [N3'—N2—N3—N1]	120
$\delta b_{2,2}$	70.5	69.1 [N2'—N3'—N1'—N2]	120
$\delta b_{2,3}$	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) $2 - x, y, \frac{3}{2} - z$.

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

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Abstract

The structures of di-μ-benzenethiolato-bis{[1,2-bis-(diphenylphosphino)ethane]nickel(II)}   perchlorate acetonitrile   solvate,   [Ni$_2$(SPh)$_2$(dppe)$_2$]-(ClO$_4$)$_2$.2MeCN (1), and di-μ-benzenethiolato-bis-

[(benzenethiolato)(triphenylphosphino)palladium(II)] acetonitrile solvate, $[Pd_2(SPh)_4(PPh_3)_2].MeCN$ (2), have been determined by X-ray diffraction. The dinuclear $[Ni_2(SPh)_2(dppe)_2]^{2+}$ cation is crystallographically centrosymmetric about the midpoint of Ni···Ni' and is formed by the edge sharing of two square-planar NiP_2S_2 coordinations. The dinuclear $[Pd_2(SPh)_4(PPh_3)_2]$ molecule is located on a crystallographic inversion centre at (0,0,0) and comprises two $PdPS_3$ coordination planes sharing two μ-SPh ligands.

Comment

Nickel thiolate clusters which have been structurally characterized include the cyclic neutral molecules $[Ni_n(SR)_{2n}]$ (n = 2, 4, 6, 8) and the anionic acyclic species $[Ni_n(SR)_{2n+2}]^{2-}$ (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 $[Ni(SPh)_4]^2$ (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, $[Ni_3(\mu_3-S)(\mu_2-SPh)_3(SPh)_3]^{2-}$ (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 $[Ni_2\{S(CH_2)_3NMe_2\}_2-(dppe)_2]^{2+}$ (Capdevila, Gonzalez-Duarte, Foces-Foces, Cano & Matinez-Ripoll, 1990). In the central Ni_2S_2 ring, the S—Ni—S' angle of 87.50 (6)° in (1) is larger, while the Ni—S—Ni' angle of 92.50 (6)° is smaller than those [84.6 (1) and 95.5 (1)°] found in $[Ni_2\{S(CH_2)_3NMe_2\}_2(dppe)_2]^{2+}$, indicating a shorter Ni···Ni' separation [3.254 (2) Å] in (1), although the Ni—S bond lengths are 0.016 Å (on average) longer in (1). The bridging benzenethiolate group produces a small compression (0.056 Å) in the Ni···Ni' direction in the Ni_2S_2 ring of (1). The geometric parameters of the Ni(dppe) moieties in both complexes are almost identical.

Complex (2) is analogous to $[Pd_2(SC_6F_5)_4(PPh_3)_2]$ (Fenn & Segrott, 1970, 1972). The geometry of the central Pd_2S_2 ring of (2) is, however, similar to that in $[Pd_2Cl_2(SPh)_2(PEt_3)_2]$ (Padilla, Golen, Richmann

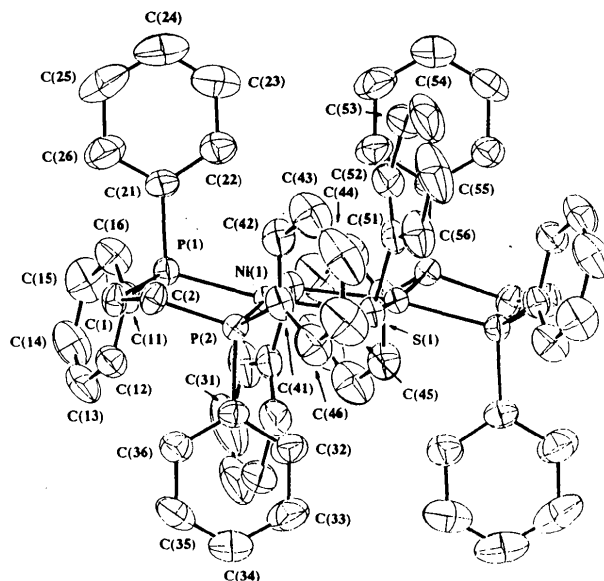& Jensen, 1991), although the Pd—S bond lengths are longer by 0.027 Å (on average) and consequently, the Pd···Pd separation is 0.043 Å longer in (2).

Fig. 1. ORTEP drawing (Johnson, 1976) of the $[Ni_2(SPh)_2-(dppe)_2]^{2+}$ cation showing the labelling of the non-H atoms. Thermal ellipsoids are drawn at the 50% probability level.

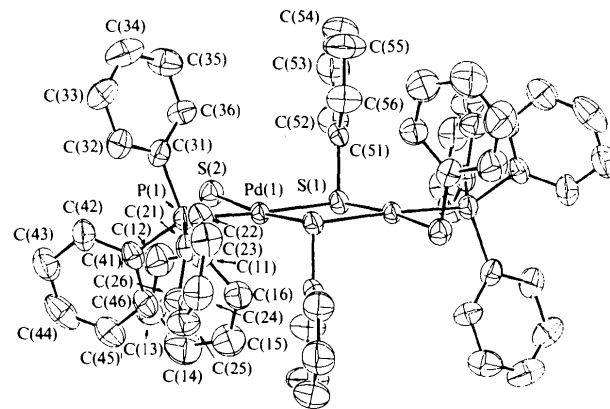Fig. 2. ORTEP drawing (Johnson, 1976) of the $[Pd_2(SPh)_4(PPh_3)_2]$ molecule showing the labelling of the non-H atoms. Thermal ellipsoids are drawn at the 50% probability level.

Experimental

Compound (1)

Crystal data

$[Ni_2(C_{26}H_{24}P_2)_2(C_6H_5S)_2]-(ClO_4)_2.2C_2H_3N$	Z = 1
	D_x = 1.42 Mg m^{-3}
M_r = 1413.6	Mo $K\alpha$ radiation
Triclinic	λ = 0.71069 Å

$P\bar{1}$
a = 13.160 (6) Å
b = 13.565 (6) Å
c = 11.077 (5) Å
α = 109.75 (3)°
β = 79.52 (3)°
γ = 116.88 (3)°
V = 1659.1 (10) Å^3

Cell parameters from 22 reflections
θ = 6 - 13.5°
μ = 0.86 mm^{-1}
T = 295 K
Rectangular prism
0.50 × 0.30 × 0.18 mm
Brown

Data collection

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

θ_{max} = 25°
h = -15 → 15
k = -16 → 14
l = 0 → 13
3 standard reflections
frequency: 240 min
intensity variation: <1.7%

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 e Å^{-3}
$\Delta\rho_{min}$ = 0.52 e Å^{-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* (Å^2) *for* (1)

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

	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 (6)	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 (6)	0.1225 (8)	5.0 (2)
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)†

† Isotropic B.

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^i)	2.251 (2)	P(2)—C(2)	1.831 (8)
Ni(1)···Ni(1^i)	3.254 (2)	P(2)—C(31)	1.824 (8)
S(1)···S(1^i)	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^i)	92.65 (6)	Ni(1)—P(1)—C(21)	107.1 (3)
S(1)—Ni(1)—S(1^i)	87.50 (6)	Ni(1)—P(2)—C(2)	110.3 (3)
P(2)—Ni(1)—S(1^i)	169.59 (7)	Ni(1)—P(2)—C(31)	104.2 (3)
Ni(1)—S(1)—Ni(1^i)	92.50 (7)	Ni(1)—P(2)—C(41)	121.0 (3)

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

Compound (2)

Crystal data

[Pd$_2$(C$_{18}$H$_{15}$P)$_2$(C$_6$H$_5$S)$_4$]-.C$_2$H$_3$N
M_r = 1215.4
Triclinic
$P\bar{1}$
a = 14.395 (9) Å
b = 12.483 (10) Å
c = 9.625 (5) Å
α = 66.85 (5)°
β = 105.09 (5)°
γ = 115.97 (6)°
V = 1421.6 (13) Å^3

Z = 1
D_x = 1.42 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 14 reflections
θ = 6 - 13.5°
μ = 0.86 mm^{-1}
T = 295 K
Rectangular prism
0.55 × 0.50 × 0.45 mm
Red

Data collection

Philips PW1100 diffractometer
ω scans
Absorption correction: none
4994 measured reflections
4994 independent reflections
3700 observed reflections
[$F_o^2 \geq 2\sigma(F_o^2)$]

θ_{max} = 25°
h = -17 → 16
k = -13 → 14
l = 0 → 11
3 standard reflections
frequency: 240 min
intensity variation: <1.5%

Refinement

Refinement on F
R = 0.055
wR = 0.088
S = 0.30

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

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

	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* ($\mathring{A}$, °) *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^i)	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^i)	3.506 (2)	P(1)—C(41)	1.820 (9)
S(1)···S(1^i)	3.169 (4)		
S(1)—Pd(1)—S(2)	91.69 (8)	Pd(1)—S(1)—Pd(1^i)	95.78 (7)
S(1)—Pd(1)—S(1^i)	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^i)	173.25 (8)	Pd(1)—P(1)—C(31)	108.5 (3)
P(1)—Pd(1)—S(1^i)	95.75 (8)	Pd(1)—P(1)—C(41)	114.9 (3)

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

For (1), a suspension of $NiCl_2$ (130 mg) and dppe (400 mg) in acetonitrile (15 cm^3) was stirred for 3 h and NaSPh (140 mg) was then added. After 20 h, $NaClO_4.H_2O$ (170 mg) in methanol (5 cm^3) 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 $[Ni_2(SC_6H_5)_2(C_{26}H_{24}P_2)_2](ClO_4)_2.2CH_3CN$: C 57.8, H 4.6, N 2.0%.

For (2), NaSPh (260 mg) was added to a stirred solution of $Pd(CH_3COO)_2$ (220 mg) in acetonitrile (10 cm^3) and N,N-dimethylformamide (10 cm^3). After 1 h, PPh_3 (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 $[Pd_2(SC_6H_5)_4\{P(C_6H_5)_3\}_2].CH_3CN$: C 61.3, H 4.4, N 1.2%.

For (1) and (2), phase problems were solved using *SHELXS*86 (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 ($B = 7.0 \mathring{A}^2$) for each H atom. The acetonitrile molecule in (2) is disordered. A local version of *UNICS* (*RCLS*-3, *RSSFR*-5, *HBLS-IV*, *DAPH*) (Sakurai, 1969) was used for computations on a HITAC M 660K.

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