C1	0.3427 (5)	0.6974 (3)	0.5951 (4)	0.038 (1)
C2	0.3809 (6)	0.7011 (4)	0.7051 (4)	0.043 (1)
C3	0.4874 (5)	0.6316 (4)	0.7353 (3)	0.039 (1)
C4	0.2441 (5)	0.7863 (3)	0.5709 (3)	0.040 (1)
C5	0.1012 (5)	0.7275 (3)	0.4461 (3)	0.044 (1)
C6	−0.0192 (5)	0.8208 (4)	0.4629 (3)	0.049 (1)
C7	−0.0451 (7)	0.8595 (5)	0.5870 (4)	0.078 (2)
C8	0.1152 (7)	0.8328 (5)	0.6549 (4)	0.073 (2)
C13	0.5498 (5)	0.6567 (3)	0.8646 (3)	0.039 (1)
C14	0.7248 (5)	0.7765 (3)	0.9368 (3)	0.045 (1)
C15	0.8144 (6)	0.7581 (4)	1.0417 (3)	0.054 (1)
C16	0.7977 (7)	0.6206 (4)	0.9889 (4)	0.078 (2)
C17	0.6327 (7)	0.5557 (4)	0.8772 (4)	0.064 (1)
C12	0.4111 (6)	0.8963 (4)	0.5922 (5)	0.079 (2)
C10	0.1978 (8)	0.7147 (5)	0.3452 (4)	0.084 (2)
C9	−0.0245 (6)	0.6006 (4)	0.4171 (4)	0.077 (2)
C11	−0.2090 (6)	0.7755 (5)	0.3683 (4)	0.076 (1)
C18	0.3771 (6)	0.6646 (5)	0.9194 (4)	0.068 (1)
C20	0.6677 (7)	0.8982 (4)	0.9813 (4)	0.080 (2)
C19	0.8642 (6)	0.7803 (4)	0.8607 (4)	0.068 (1)
C21	1.0186 (6)	0.8405 (5)	1.1136 (4)	0.081 (2)

Table 2. *Selected geometric parameters (Å, °)*

Ni—O2	1.826 (2)	O2—C3	1.279 (4)
Ni—O1	1.842 (2)	C1—C2	1.375 (5)
O1—C1	1.279 (4)	C2—C3	1.395 (6)
Other C—C bond lengths in the range 1.518 (6)–1.572 (5) Å			
O2—Ni—O1	94.8 (1)	C2—C1—C4	122.1 (4)
C1—O1—Ni	125.9 (2)	C1—C2—C3	124.4 (4)
C3—O2—Ni	127.2 (2)	O2—C3—C2	122.7 (4)
O1—C1—C2	123.8 (4)	O2—C3—C13	116.6 (3)
O1—C1—C4	114.1 (3)	C2—C3—C13	120.6 (4)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CADHKL4* in *CADSHEL* (Kopf & Ruebcke, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1065). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[Re(NNPh)(NNHPh){2-S-C_5H_3N-3-$Si(CH_3)_3$}$(PPh_3)_2$]BPh_4

Martin B. Gernert,[a] Huub Kooijman,[a] Wolfgang P. Hiller,[a]* Jonathan R. Dilworth[b] and Suzanne J. Parrott[b]

[a]*Technische Universität München, Anorganisch-chemisches Institut, Lichtenbergstrasse 4, D-85747 Garching, Germany, and* [b]*Department of Chemistry, University of Essex, Wivenhoe Park, Colchester, Essex CO4 3SQ, England. E-mail: hiller@hild25.anorg.chemie.tu-muenchen.de*

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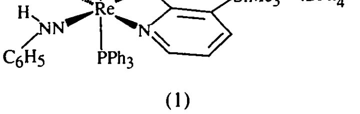
Abstract

We report the crystal structure of (phenyldiazenido-*N*)[phenylhydrazido(2−)-*N*][3-(trimethylsilyl)-2-pyridinethiolato-*S*,*N*]bis(triphenylphosphine-*P*)rhenium tetraphenylborate, $[Re(C_6H_5N_2)(C_6H_6N_2)(C_8H_{12}NSSi)(C_{18}H_{15}P)_2](C_{24}H_{20}B)$, prepared by the reaction of $[ReCl(C_6H_6N_2)_2(C_{18}H_{15}P)_2]$ with 3-(trimethylsilyl)-2-pyridinethiol in ethanol. The mixed diazenide/hydrazido(2−) complex represents a relatively rare class of complex.

Comment

The chemistry of hydrazido(2−) complexes has been of great interest since they were identified as intermediates in the protonation of coordinated dinitrogen to ammonia (Chatt, Pearman & Richards, 1975, 1977). As part of a continuing program aimed at defining structural parameters and the chemical reactivity of hydrazido(2−) ligands, we have previously synthesized a number of Mo and W (Chatt, Crichton, Dilworth, Dahlstrom, Gutkoska & Zubieta, 1982; Bishop, Chatt, Dilworth, Hursthouse & Motevalli, 1979; Bishop, Butler, Chatt, Dilworth & Leigh, 1979; Dilworth, Harrison, Walton & Schweda, 1985), Re (Dilworth, Jobanputra, Parrott, Thompson, Povey & Zubieta, 1992) and Tc (Archer, Dilworth, Jobanputra, Thompson, McPartlin, Povey, Smith & Kelly, 1990) hydrazide complexes, with a wide range of coligands. The title complex, (1), can be compared to the only other examples of this type, $[M\mathrm{Br}_2(NNPh)(NNHPh)(PPh_3)_2]$ (M = Tc, Re), which were prepared by protonation of the parent



(1)

bis(diazenide) complex (Dilworth, Harrison, Walton & Schweda, 1985; Nicholson, de Vries, Davison & Jones, 1989).

In (1), the overall geometry around the central Re atom is distorted octahedral. The principal reason for the distortion is the small bite angle of the pyridinethiolato ligand [S—Re—N1 64.21 (9)°]. The phosphine ligands are bound *trans* with respect to each other in order to minimize steric interactions. The Re—P distances of 2.5051 (12) and 2.4933 (11) Å are unremarkable.

An immediately obvious feature of the structure is the absence of any steric effect due to the bulky silyl substituent on the pyridine ring, which is bound as a bidentate ligand despite the presence of the two bulky *trans* phosphine ligands.

The diazenide ligand is singly bent, with a nearly linear Re—N2—N3 angle of 172.4 (3)°. The Re—N2 and N2—N3 bond distances of 1.801 (4) and 1.228 (4) Å, respectively, are both indicative of a substantial proportion of multiple bonding.

The hydrazido(2−) ligand is bent at atom N4, with an Re—N4—N5 angle of 137.4 (3)°, and therefore only formally donates two electrons to give an overall electron count for the complex of 18. The Re—N4 bond length of 1.860 (3) Å nevertheless indicates some multiple bonding and the N4—N5 bond length of 1.288 (4) Å is shorter than a single bond (1.45 Å in free hydrazine) but longer than a double bond and indicates extensive delocalization within the Re—N4—N5 framework.

The geometries of both the hydrazido(2−) and diazenide ligands can be compared to those found in [ReBr$_2$(NNPh)(NNHPh)(PPh$_3$)$_2$] (Dilworth, Harrison, Walton & Schweda, 1985). In the bromo complex, the hydrazido(2−) ligand is slightly more bent, Re—N—N being 131.2 (1)°. This larger bending is stabilized by hydrogen bonding from the hydrazido(2−) proton to the bromide coligand. The absence of any electron density around the N3 atom in complex (1) that is attributable to an H atom is in contrast to atom N5 and therefore leads to the interpretation that the N4–N5 ligand is actually a hydrazido(2−) ligand protonated at N5 and that the N2–N3 ligand is actually a doubly bent diazenide ligand.

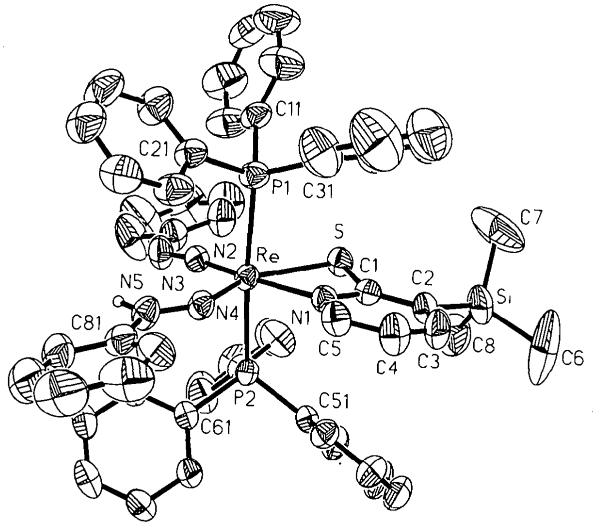


Fig. 1. The structure of the cation of (1). Displacement ellipsoids are plotted at the 50% probability level.

Experimental

Compound (1) was prepared by the reaction of [ReCl(NNPh)$_2$(PPh$_3$)$_2$] with the silylated pyridinethiol in ethanol under reflux and isolated as the stable orange tetraphenylborate salt by addition of sodium tetraphenylborate to the cooled reaction solution. Crystals of (1) suitable for an X-ray structure determination were obtained by slow recrystallization from a dichloromethane–methanol mixture. [ReCl(NNPh)$_2$(PPh$_3$)$_2$] was prepared according to the literature method of Dilworth *et al.* (1985). 2-SH-C_5H_3N was obtained commercially (Aldrich) and silylated using the literature procedure of Block, Gernon, Kang, Ofori-Okai & Zubieta (1991).

Crystal data

[Re($C_6H_5N_2$)($C_6H_6N_2$)-($C_8H_{12}NSSi$)($C_{18}H_{15}P$)$_2$]-($C_{24}H_{20}B$)
M_r = 1423.53
Monoclinic
$P2_1/n$
a = 13.922 (3) Å
b = 21.002 (2) Å
c = 24.866 (2) Å
β = 105.51 (1)°
V = 7005.8 (17) Å^3
Z = 4
D_x = 1.350 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11–18°
μ = 1.875 mm^{-1}
T = 293 (2) K
Block
0.25 × 0.25 × 0.15 mm
Dark red

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983; Walker, 1993)
$T_{\min}$ = 0.856, $T_{\max}$ = 1.000
14 006 measured reflections
13 693 independent reflections

8908 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int}$ = 0.0355
$\theta_{\max}$ = 25.97°
$h = -17 \rightarrow 16$
$k = 0 \rightarrow 25$
$l = 0 \rightarrow 30$
3 standard reflections
frequency: 120 min
intensity decay: insignificant

Refinement

Refinement on F^2
$R(F)$ = 0.0377
$wR(F^2)$ = 0.0700
S = 1.007

$w = 1/[\sigma^2(F_o^2) + (0.0199P)^2 + 2.9625P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$

13 691 reflections
827 parameters
H atoms refined as riding (*SHELXL*93; Sheldrick, 1993)

$\Delta\rho_{\max} = 0.432$ e Å^{-3}
$\Delta\rho_{\min} = -0.680$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Re	0.328009 (13)	0.229929 (8)	0.069179 (7)	0.03583 (5)
S	0.15763 (8)	0.17821 (6)	0.04171 (4)	0.0434 (3)
P1	0.25043 (9)	0.32775 (6)	0.09719 (5)	0.0455 (3)
P2	0.39006 (8)	0.12761 (5)	0.04019 (4)	0.0364 (3)
Si	−0.02370 (10)	0.14909 (8)	−0.08470 (6)	0.0634 (4)
N1	0.2384 (2)	0.24904 (15)	−0.01543 (13)	0.0388 (9)
N2	0.3815 (2)	0.2016 (2)	0.13916 (14)	0.0428 (9)
N3	0.4284 (3)	0.1816 (2)	0.1851 (2)	0.0568 (11)
N4	0.4302 (2)	0.2763 (2)	0.05246 (13)	0.0405 (8)
N5	0.5209 (3)	0.2917 (2)	0.0771 (2)	0.0497 (10)
B	0.3689 (4)	0.3283 (2)	−0.2339 (2)	0.0413 (12)
C1	0.1569 (3)	0.2129 (2)	−0.0221 (2)	0.0375 (10)
C2	0.0840 (3)	0.2061 (2)	0.0736 (2)	0.0459 (11)
C3	0.1006 (4)	0.2438 (2)	−0.1160 (2)	0.0608 (15)
C4	0.1810 (3)	0.2846 (2)	−0.1087 (2)	0.0615 (14)
C5	0.2501 (3)	0.2858 (2)	−0.0579 (2)	0.0487 (12)
C6	−0.0773 (5)	0.1416 (4)	−0.1615 (3)	0.162 (4)
C7	−0.1141 (4)	0.1821 (3)	−0.0499 (4)	0.140 (3)
C8	0.0155 (4)	0.0696 (3)	−0.0553 (2)	0.088 (2)
C11	0.1898 (3)	0.3213 (2)	0.1535 (2)	0.0508 (12)
C12	0.1149 (4)	0.3613 (3)	0.1584 (3)	0.089 (2)
C13	0.0777 (5)	0.3584 (4)	0.2050 (3)	0.104 (2)
C14	0.1141 (5)	0.3146 (3)	0.2457 (3)	0.088 (2)
C15	0.1875 (5)	0.2752 (3)	0.2417 (3)	0.095 (2)
C16	0.2258 (4)	0.2788 (3)	0.1956 (2)	0.080 (2)
C21	0.3417 (3)	0.3909 (2)	0.1230 (2)	0.0485 (12)
C22	0.3581 (4)	0.4158 (2)	0.1757 (2)	0.069 (2)
C23	0.4282 (4)	0.4633 (3)	0.1942 (3)	0.086 (2)
C24	0.4844 (4)	0.4849 (3)	0.1609 (3)	0.080 (2)
C25	0.4723 (4)	0.4595 (2)	0.1090 (3)	0.072 (2)
C26	0.4012 (4)	0.4124 (2)	0.0902 (2)	0.0648 (15)
C31	0.1539 (4)	0.3643 (2)	0.0416 (2)	0.0582 (14)
C32	0.1681 (5)	0.4202 (3)	0.0157 (3)	0.097 (2)
C33	0.0913 (7)	0.4461 (4)	−0.0267 (4)	0.139 (3)
C34	0.0007 (7)	0.4158 (5)	−0.0413 (3)	0.127 (3)
C35	−0.0156 (5)	0.3606 (4)	−0.0169 (3)	0.103 (2)
C36	0.0616 (4)	0.3352 (3)	0.0251 (2)	0.079 (2)
C41	0.3821 (3)	0.0582 (2)	0.0838 (2)	0.0422 (11)
C42	0.2909 (4)	0.0405 (2)	0.0911 (2)	0.0668 (15)
C43	0.2828 (5)	−0.0129 (3)	0.1217 (3)	0.084 (2)
C44	0.3643 (5)	−0.0493 (3)	0.1452 (2)	0.083 (2)
C45	0.4546 (5)	−0.0326 (3)	0.1376 (2)	0.080 (2)
C46	0.4638 (4)	0.0209 (2)	0.1067 (2)	0.0597 (14)
C51	0.3344 (3)	0.1006 (2)	−0.0307 (2)	0.0363 (10)
C52	0.3306 (3)	0.1424 (2)	−0.0742 (2)	0.0448 (11)
C53	0.2896 (3)	0.1247 (2)	−0.1293 (2)	0.0545 (13)
C54	0.2545 (4)	0.0638 (3)	−0.1407 (2)	0.0628 (14)
C55	0.2602 (4)	0.0211 (2)	−0.0985 (2)	0.068 (2)
C56	0.2990 (3)	0.0395 (2)	−0.0439 (2)	0.0522 (12)
C61	0.5226 (3)	0.1331 (2)	0.0453 (2)	0.0375 (10)
C62	0.5627 (3)	0.1178 (2)	0.0020 (2)	0.0455 (11)
C63	0.6635 (3)	0.1254 (2)	0.0073 (2)	0.0540 (13)
C64	0.7248 (4)	0.1474 (2)	0.0565 (2)	0.0611 (14)
C65	0.6873 (3)	0.1614 (2)	0.1010 (2)	0.0584 (13)
C66	0.5873 (3)	0.1543 (2)	0.0955 (2)	0.0492 (12)
C71	0.3847 (4)	0.1396 (3)	0.2178 (2)	0.0594 (14)
C72	0.2846 (4)	0.1242 (3)	0.2047 (2)	0.0666 (15)
C73	0.2504 (5)	0.0840 (3)	0.2402 (3)	0.088 (2)
C74	0.3140 (6)	0.0594 (4)	0.2865 (3)	0.122 (3)
C75	0.4124 (6)	0.0739 (4)	0.2982 (3)	0.141 (4)
C76	0.4498 (4)	0.1144 (3)	0.2645 (2)	0.103 (2)
C81	0.5826 (4)	0.3280 (2)	0.0510 (2)	0.0523 (12)
C82	0.5454 (4)	0.3574 (2)	0.0011 (2)	0.067 (2)
C83	0.6084 (6)	0.3938 (3)	−0.0215 (3)	0.095 (2)
C84	0.7075 (6)	0.3997 (4)	0.0064 (4)	0.114 (3)
C85	0.7439 (5)	0.3700 (4)	0.0562 (3)	0.107 (3)
C86	0.6822 (4)	0.3333 (3)	0.0797 (2)	0.077 (2)
C101	0.2941 (3)	0.2664 (2)	−0.2520 (2)	0.0401 (9)
C102	0.3312 (4)	0.2058 (2)	−0.2588 (2)	0.0553 (13)
C103	0.2705 (5)	0.1524 (2)	−0.2735 (2)	0.069 (2)
C104	0.1699 (5)	0.1580 (3)	−0.2809 (2)	0.073 (2)
C105	0.1291 (4)	0.2160 (2)	−0.2741 (2)	0.0607 (14)
C106	0.1906 (3)	0.2689 (2)	−0.2603 (2)	0.0490 (10)
C111	0.4092 (3)	0.3541 (2)	−0.2870 (2)	0.0415 (11)
C112	0.4412 (3)	0.3123 (2)	−0.3223 (2)	0.0508 (12)
C113	0.4856 (4)	0.3327 (3)	−0.3627 (2)	0.0650 (15)
C114	0.4997 (4)	0.3962 (3)	−0.3697 (2)	0.070 (2)
C115	0.4692 (4)	0.4393 (3)	−0.3368 (2)	0.0647 (14)
C116	0.4242 (3)	0.4179 (2)	−0.2962 (2)	0.0524 (12)
C121	0.4692 (3)	0.3065 (2)	−0.1856 (2)	0.0411 (10)
C122	0.4645 (4)	0.2626 (2)	−0.1445 (2)	0.0639 (14)
C123	0.5468 (5)	0.2436 (3)	−0.1024 (2)	0.082 (2)
C124	0.6383 (4)	0.2694 (3)	−0.0997 (2)	0.083 (2)
C125	0.6464 (4)	0.3130 (3)	−0.1387 (2)	0.074 (2)
C126	0.5627 (3)	0.3317 (2)	−0.1805 (2)	0.0528 (12)
C131	0.3123 (3)	0.3848 (2)	−0.2091 (2)	0.0424 (11)
C132	0.2361 (3)	0.4221 (2)	−0.2435 (2)	0.0548 (13)
C133	0.1854 (4)	0.4686 (2)	−0.2234 (3)	0.076 (2)
C134	0.2075 (5)	0.4809 (3)	−0.1680 (3)	0.080 (2)
C135	0.2813 (5)	0.4465 (3)	−0.1322 (2)	0.071 (2)
C136	0.3322 (3)	0.3995 (2)	−0.1525 (2)	0.0526 (12)

Table 2. *Selected geometric parameters (Å, °)*

Re—N2	1.801 (4)	N1—C1	1.338 (5)
Re—N4	1.860 (3)	N1—C5	1.352 (5)
Re—N1	2.177 (3)	N2—N3	1.228 (4)
Re—P2	2.4933 (11)	N3—C71	1.440 (6)
Re—P1	2.5051 (12)	N4—N5	1.288 (4)
Re—S	2.5311 (12)	N5—C81	1.429 (5)
S—C1	1.743 (4)	C1—C2	1.414 (5)
Si—C7	1.843 (6)	C2—C3	1.385 (6)
Si—C8	1.845 (6)	C3—C4	1.383 (6)
Si—C6	1.863 (6)	C4—C5	1.369 (6)
Si—C2	1.881 (4)		
N2—Re—N4	104.20 (14)	C7—Si—C2	108.0 (3)
N2—Re—N1	167.59 (13)	C8—Si—C2	112.2 (2)
N4—Re—N1	87.84 (13)	C6—Si—C2	106.8 (3)
N2—Re—P2	84.76 (11)	C1—N1—C5	120.2 (3)
N4—Re—P2	92.37 (11)	C1—N1—Re	105.2 (2)
N1—Re—P2	91.88 (9)	C5—N1—Re	134.6 (3)
N2—Re—P1	95.75 (11)	N3—N2—Re	172.4 (3)
N4—Re—P1	92.61 (11)	N2—N3—C71	122.3 (4)
N1—Re—P1	86.52 (9)	N5—N4—Re	137.4 (3)
P2—Re—P1	174.71 (4)	N4—N5—C81	123.4 (4)
N2—Re—S	103.57 (11)	N1—C1—C2	123.2 (4)
N4—Re—S	151.86 (10)	N1—C1—S	109.1 (3)
N1—Re—S	64.21 (9)	C2—C1—S	127.7 (3)
P2—Re—S	85.66 (4)	C3—C2—C1	114.0 (4)
P1—Re—S	89.10 (4)	C3—C2—Si	122.8 (3)
C1—S—Re	80.97 (14)	C1—C2—Si	123.2 (3)
C7—Si—C8	108.7 (3)	C4—C3—C2	123.3 (4)
C7—Si—C6	112.1 (4)	C5—C4—C3	118.4 (4)
C8—Si—C6	109.0 (3)	N1—C5—C4	120.6 (4)

The programs used were *CADSHEL* (Kopf & Rübcke, 1993) for data reduction, *SHELXS*86 (Sheldrick, 1990*a*) for structure solution, *SHELXTL-Plus* (Sheldrick, 1990*b*) and *SHELXL*93 (Sheldrick, 1993) for structure refinement.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1129). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5,5-Bis(dimethylphenylphosphine)-4,6-dithia-5-pallada-*arachno*-nonaborane

George Ferguson,[a] Donogh E. McCarthy,[b] Trevor R. Spalding[b] and John D. Kennedy[c]

[a]*Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1,* [b]*Department of Chemistry, University College, Cork, Ireland, and* [c]*School of Chemistry, University of Leeds, Leeds LS2 9JT, England. E-mail: george@x-ray.chembio.uoguelph.ca*

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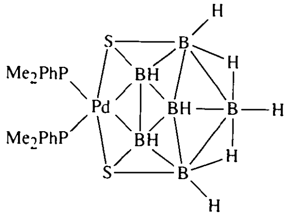
Abstract

The title compound $[5,5\text{-}(PMe_2Ph)_2\text{-}arachno\text{-}5,4,6\text{-}PdS_2B_6H_8]$ contains a nine-vertex PdS_2B_6 cage with the Pd atom η^4-bonded to two S and two B atoms. The Pd—S distances are notably asymmetric at 2.3588 (14) and 2.6759 (15) Å, whereas the interatomic distances of symmetry-related pairs of Pd—B, S—B and B—B atoms indicate symmetric bonding. The two *exo* cage dimethylphenylphosphine ligands are attached to the Pd atom with Pd—P 2.2986 (15) and 2.2876 (13) Å. Bridging H atoms in the $S_2B_6H_8$ moiety are asymmetrically bonded.

Comment

There is much current interest in transition element derivatives of thia-boranes containing more than one S atom (Mazighi, Carroll & Sneddon, 1992; Murphy *et al.*, 1994; Murphy, 1994). The title compound, (1), is the first monomeric PdS_2B_6 complex to be structurally characterized.



(1)

The X-ray analysis shows that the Pd atom in (1) is bonded to two PMe_2Ph ligands as well as to a S_2B_2 section of the $S_2B_6H_8$ cage (Fig. 1). The nine-vertex cage structure can be described in terms of Wade's rules as a variation of $[arachno\text{-}B_9H_{15}]$ with the $Pd(PMe_2Ph)_2$ unit equivalent to BH and each S to BH_2 (Wade, 1976). The *exo*-cage Pd—P distances of 2.2986 (15) and 2.2876 (13) Å may be compared with previously reported Pd—PMe_2Ph distances in palladaheteroborane cages, such as 2.311 (3) and 2.327 (3) Å in $[3,3\text{-}(PMe_2Ph)_2\text{-}closo\text{-}3,2,1\text{-}PdAs_2B_9H_9]$,

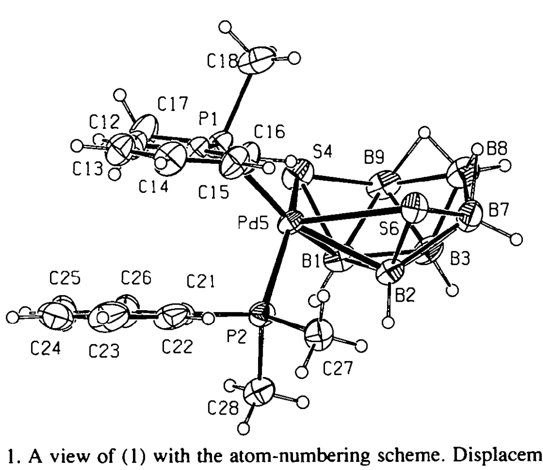


Fig. 1. A view of (1) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.