Crystal and Molecular Structures of Novel Metal–Carbene Complexes II. Tris{1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(ethylimino)methanethiolato-$\varkappa^2SS'$]}tripalladium(II) and {1,1′-(Perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(methylimino)methanethiolato-$\varkappa^2SS'$]}(pyridine)palladium(II); Intensity Measurements Using Rapid X-Ray Diffractometers

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(Received March 13, 1996)

The crystal structures of tris{1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(ethylimino)methanethiolato-$\varkappa^2SS'$]} tripalladium(II) (**5b**) and {1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(methylimino)methanethiolato-$\varkappa^2SS'$]}(pyridine)-palladium(II) (**6a**) were determined by X-ray structure analyses. When {1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis-[(alkylimino)methanethiolato-$\varkappa^2SS'$]}(triphenylphosphine)palladium(II) (**3**) was treated with 18% HCl aq, a compound (**5**) was obtained with an elimination of the triphenylphosphine group. A reaction of **5** with pyridine gave a pyridine-coordinating metal–carbene complex (**6**). Complex **5** has a trimeric structure of the metal–pentalenes consisting of a cyclic $(Pd–S)_3$ framework. In the trimer, each Pd atom is coordinated by three S atoms and one C atom in a square-planar arrangement. Two of the S atoms belong to the same pentalene ring and one belongs to the next pentalene ring. The lengths of interpentalene Pd–S (2.38 Å) are significantly longer than those of intrapentalene Pd–S (2.28 Å). This difference suggests that a trimer is easily cleaved in pyridine to form a pyridine complex **6**. The trimeric structure is considered to show an intermediate-like structure of the ligand exchange reaction. Intensity data of **5** were measured by rapid X-ray diffractometers with imaging plates as a two-dimensional detector.

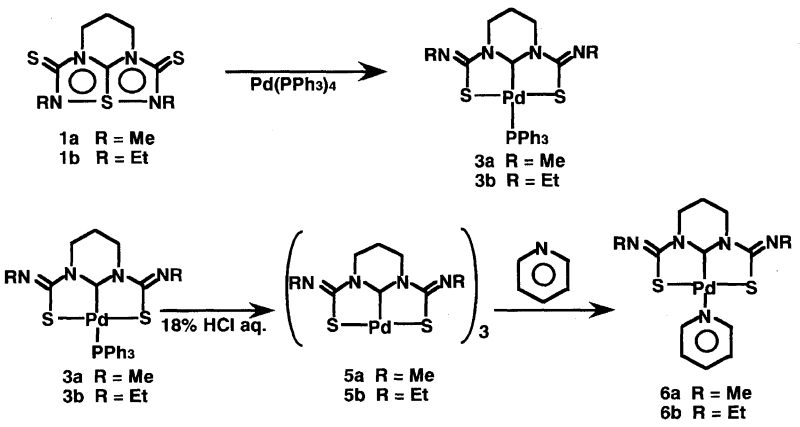
Recently, novel metal–carbene complexes were obtained from 6a-thiatetraazapentalene derivatives (**1**),[1] which contain a hypervalent sulfur atom[2] with a 12π conjugated system, by treating with $Pt(PPh_3)_4$ and $Pd(PPh_3)_4$. X-Ray investigations of these complexes revealed that the central sulfur atom in **1** was substituted by a metal atom, and that the thioamide groups on both sides rotated to form metal–sulfur bonds in the resultant metallapentalene framework.[3,4] When the Pd complexes (**3**) were treated with 18% HCl aq, compounds (**5**) were obtained with an elimination of the triphenylphosphine group. A reaction of **5** with pyridine gave pyridine-coordinating metal–carbene complexes (**6**) (Scheme 1). Compound **5** could be considered to be an intermediate-like state in the ligand-exchange reaction from **3** to **6**. An X-ray analysis was carried out to elucidate the structure of **5b** (R=Et). A structure analysis of **6a** (R=Me) was also carried out to compare the effects of a different ligand. The intensity data of **5b** couldn't be measured by a four-circle diffractometer, because the formed crystals were very unstable. A trimeric structure of **5b** was revealed using intensity data measured by rapid X-ray diffractometers with imaging plates as a two-dimensional detector.

Experimental

Since crystals of **5b-1** grown from a $CHCl_3$/hexane solution were very unstable in air, the specimens for intensity measurements were shielded in thin glass capillaries. At first the intensities of 10475 reflections, of which 6086 reflections were observed with $|F_o| \geq 3\sigma(F)$, were measured by a four-circle diffractometer with a Cu $K\alpha$ rotating anode. During the measurement, the intensities of the monitored reflections decreased to 0.67, and the structure analysis failed using these intensity data.

We then measured the diffraction intensities of **5b-1** using a rapid Weissenberg-type diffractometer (IPD-WAS)[5—7] with imaging plates[8,9] as a two-dimensional detector at RIKEN. The total time of the intensity measurements and processing data was 12 h. From the calculated density there are 24 monomer units of $C_{10}H_{16}N_4S_2Pd$ in the unit cell. The structure was solved by the direct method using the program MULTAN78.[10] Two independent trimers (**A** and **B**) consisting of a $(Pd–S)_3$ ring were obtained in a crystallographic asymmetric unit. During successive refinements it was revealed that crystals contained $CHCl_3$ as crystal solvents. The R value converged to 0.096. Hydrogen atoms were ignored in the structure refinements.

The quality of the crystals (**5b-2**) obtained from a benzene/hexane



Scheme 1.

Table 1. Crystal Data, Experimental Condition, and Details of Refinements

	5b-1	**5b-2**	**6a**
Chemical formula	$(C_{10}H_{16}N_4S_2Pd)_3$ $CHCl_3$	$(C_{10}H_{16}N_4S_2Pd)_3$ C_6H_6	$C_{13}H_{17}N_5S_2Pd$
F.W.	1207.83	1166.56	413.86
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	15.508(8)	14.179(1)	16.155(2)
b/Å	25.78(3)	26.447(1)	23.092(3)
c/Å	25.36(1)	29.148(1)	8.901(1)
β/°	107.18(3)	121.2(1)	105.72(1)
V/Å^3	9686(14)	9349.4(7)	3196.4(7)
Z	8	8	8
D_X/gcm^{-3}	1.657	1.658	1.720
$F(000)$	4832	4704	1664
Temperature	293	293	293
Crystal form	Plates	Prisms	Needles
Crystal color	Yellow	Yellow	Yellow
Crystal size/mm	0.15×0.60×0.40	0.20×0.20×0.40	0.12×0.24×0.37
Diffractometer	IPD-WAS	DIP3000	AFC-5R
Current/kV, mA	45, 50	45, 200	50, 150
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
λ/Å	0.71073	0.71073	0.71069
μ/mm^{-1}	1.541	1.426	1.397
Date collection method	Weissenberg	Weissenberg	Four-circle, 2θ–ω
$2\theta_{max}$/°	45	52.7	55
Scan width $\Delta\omega$/°	—	—	1.2+0.5tan θ
No. of standard reflections	—	—	3 (every 100 refs.)
Intesity variation	—	—	0.995—1.006
T_{max}, T_{min}	—	—	0.878, 0.683
Rotation axis	[0 1 1]	b	—
$\Delta\phi$/°	120	112	—
No. of IPs	40	28	—
Measurement time/h	12	7	—
Range of h k l	−17—17 −31—31 −31—31	−17—15 −15—29 −31—36	0—20 0—30 −11—11
No. of Reflections			
Measured	50341	46719	7820
Unique	14250	15615	7343
Observed [$F_o > 3\sigma(F)$]	10512	11013	5631
Refinement	10512	11013	5627
R_{int}	0.0541	0.0546	0.0269
No. of parameters	991	1267	543
R	0.0959	0.0733	0.0349
wR	0.1188	0.0840	0.0424
R_{all}	0.0959	0.0733	0.0356
S	11.14	8.07	1.077
$(\Delta/\sigma)_{max}$	0.04	0.09	0.03
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$	1.64, −2.76	0.795, −1.036	0.327, −0.613

Table 2. Positional Parameters and Equivalent Isotropic Temperature Factors (B_{eq}) for Non-H Atoms of **5b**

$$B_{eq} = 4/3 \sum_i \sum_j \beta_{ij} \boldsymbol{a}_i \cdot \boldsymbol{a}_j$$

(1) **5b-1**

Atom	x	y	z	B_{eq}/Å^2
Molecule A				
Pd(1A)	0.07464(10)	0.37054(6)	0.09911(7)	4.73(5)
Pd(2A)	0.12770(11)	0.28897(6)	0.00808(7)	4.82(5)
Pd(3A)	−0.08354 (10)	0.33187(6)	−0.01709(7)	4.76(5)
S(11A)	0.1831(3)	0.3688(2)	0.0532(2)	5.3(2)
S(12A)	−0.0154(4)	0.3637(3)	0.1549(3)	6.5(2)
S(21A)	0.0291(4)	0.3322(2)	−0.0648(2)	5.1(2)
S(22A)	0.2150(5)	0.2340(2)	0.0706(3)	6.9(2)
S(31A)	−0.0343(3)	0.4109(2)	0.0231(2)	5.6(2)
S(32A)	−0.1480(4)	0.2541(2)	−0.0472(3)	6.4(2)
N(11A)	0.2554(10)	0.3362(7)	0.1583(8)	5.9(6)
N(12A)	0.1511(13)	0.3305(7)	0.2097(7)	5.9(6)
N(13A)	0.3599(11)	0.3484(9)	0.1114(10)	8.1(8)
N(14A)	0.0477(17)	0.3262(8)	0.2597(8)	8.2(9)
N(21A)	0.0248(11)	0.2294(7)	−0.0873(7)	5.2(5)
N(22A)	0.1068(12)	0.1782(6)	−0.0119(7)	5.1(6)
N(23A)	−0.0347(14)	0.2795(8)	−0.1620(7)	6.9(7)
N(24A)	0.1871(14)	0.1297(7)	0.0625(8)	7.0(7)
N(31A)	−0.1885(12)	0.3814(8)	0.0461(8)	6.2(6)
N(32A)	−0.2344(12)	0.2967(7)	0.0201(9)	6.4(7)
N(33A)	−0.1468(13)	0.4662(7)	0.0653(9)	6.9(7)
N(34A)	−0.2897(13)	0.2160(8)	−0.0143(10)	8.2(8)
C(11A)	0.1684(14)	0.3418(7)	0.1623(9)	5.4(7)
C(12A)	0.2780(16)	0.3490(9)	0.1100(11)	6.5(8)
C(13A)	0.0619(15)	0.3374(8)	0.2149(11)	6.5(8)
C(14A)	0.3320(16)	0.3136(11)	0.2032(11)	7.8(9)
C(15A)	0.2932(17)	0.2797(10)	0.2428(12)	8.0(9)
C(16A)	0.2212(19)	0.3087(10)	0.2604(12)	8.6(10)
C(17A)	0.3809(18)	0.3592(14)	0.0586(15)	10.2(14)
C(18A)	0.4648(31)	0.3343(20)	0.0560(20)	16.2(24)
C(19A)	−0.0508(24)	0.3281(18)	0.2615(14)	13.2(18)
C(20A)	−0.0531(30)	0.3234(18)	0.3159(18)	14.3(21)
C(21A)	0.0815(13)	0.2261(8)	−0.0345(9)	5.7(7)
C(22A)	−0.0005(14)	0.2775(7)	−0.1124(8)	4.9(6)
C(23A)	0.1683(16)	0.1743(10)	0.0401(10)	6.5(8)
C(24A)	−0.0137(19)	0.1835(11)	−0.1228(10)	8.0(10)
C(25A)	−0.0183(17)	0.1377(8)	−0.0829(9)	6.2(8)
C(26A)	0.0727(17)	0.1279(9)	−0.0404(10)	6.8(8)
C(27A)	−0.0654(23)	0.3315(11)	−0.1893(11)	9.0(11)
C(28A)	−0.0183(37)	0.3394(17)	−0.2290(21)	15.6(24)
C(29A)	0.2560(20)	0.1241(14)	0.1179(13)	9.8(12)
C(30A)	0.3399(22)	0.1121(16)	0.1076(16)	11.9(16)
C(31A)	−0.1766(13)	0.3359(9)	0.0232(8)	5.1(6)
C(32A)	−0.1275(13)	0.4262(9)	0.0506(9)	5.4(7)
C(33A)	−0.2309(15)	0.2523(9)	−0.0137(10)	6.4(8)
C(34A)	−0.2583(20)	0.3876(12)	0.0795(15)	9.6(13)
C(35A)	−0.2768(24)	0.3333(13)	0.0954(15)	10.7(15)
C(36A)	−0.3034(19)	0.2965(11)	0.0515(14)	8.6(12)
C(37A)	−0.0877(19)	0.5128(11)	0.0686(13)	8.4(11)
C(38A)	−0.0513(26)	0.5261(17)	0.1237(15)	12.6(17)
C(39A)	−0.2901(22)	0.1702(11)	−0.0510(18)	11.6(16)
C(40A)	−0.3685(25)	0.1432(19)	−0.0673(19)	14.8(20)
Molecule B				
Pd(1B)	0.46863(11)	0.45403(7)	0.23218(7)	5.01(5)
Pd(2B)	0.41994(11)	0.53953(6)	0.31682(7)	4.53(5)
Pd(3B)	0.64143(11)	0.49723(7)	0.35111(8)	5.37(5)
S(11B)	0.3663(4)	0.4553(2)	0.2815(2)	5.1(2)
S(12B)	0.5521(5)	0.4588(3)	0.1725(3)	7.4(2)
S(21B)	0.5240(4)	0.5061(2)	0.3938(2)	4.8(2)
S(22B)	0.3287(5)	0.5860(2)	0.2469(3)	7.0(2)
S(31B)	0.5850(4)	0.4206(2)	0.3088(3)	5.8(2)
S(32B)	0.7195(5)	0.5690(3)	0.3898(4)	8.1(3)
N(11B)	0.2860(12)	0.4832(7)	0.1752(7)	5.6(6)
N(12B)	0.3842(13)	0.4990(8)	0.1225(8)	6.8(7)
N(13B)	0.1877(13)	0.4690(8)	0.2266(9)	7.1(7)
N(14B)	0.4918(17)	0.5114(11)	0.0763(9)	9.7(10)
N(21B)	0.5197(10)	0.6126(6)	0.4010(7)	4.9(5)
N(22B)	0.4375(12)	0.6518(7)	0.3213(7)	5.5(6)
N(23B)	0.5957(12)	0.5684(7)	0.4815(7)	5.4(6)
N(24B)	0.3599(17)	0.6889(8)	0.2343(10)	9.5(9)
N(31B)	0.7357(13)	0.4467(9)	0.2818(8)	7.6(8)
N(32B)	0.7999(14)	0.5244(9)	0.3191(10)	8.3(9)
N(33B)	0.6818(17)	0.3652(9)	0.2552(11)	9.4(10)
N(34B)	0.8673(17)	0.6021(13)	0.3653(15)	13.3(15)
C(11B)	0.3714(13)	0.4809(7)	0.1704(8)	4.7(6)
C(12B)	0.2690(14)	0.4695(8)	0.2265(8)	5.3(7)
C(13B)	0.4764(18)	0.4922(11)	0.1197(10)	7.4(9)
C(14B)	0.2078(16)	0.5043(10)	0.1302(11)	7.0(9)
C(15B)	0.2438(23)	0.5358(18)	0.0925(15)	12.8(16)
C(16B)	0.3148(20)	0.5186(14)	0.0739(11)	9.5(12)
C(17B)	0.1654(18)	0.4583(13)	0.2784(11)	8.3(11)
C(18B)	0.1023(30)	0.4970(21)	0.2822(17)	15.5(22)
C(19B)	0.5837(25)	0.5045(18)	0.0699(15)	13.2(19)
C(20B)	0.6238(35)	0.5520(23)	0.0559(23)	17.5(27)
C(21B)	0.4652(13)	0.6067(7)	0.3509(8)	4.5(6)
C(22B)	0.5539(13)	0.5647(7)	0.4339(9)	4.8(6)
C(23B)	0.3740(16)	0.6489(11)	0.2631(9)	6.8(8)
C(24B)	0.5517(16)	0.6628(8)	0.4268(9)	5.7(7)
C(25B)	0.5558(18)	0.6997(10)	0.3847(11)	7.6(10)
C(26B)	0.4637(17)	0.7058(8)	0.3398(10)	6.5(8)
C(27B)	0.6310(19)	0.5220(10)	0.5105(11)	7.7(9)
C(28B)	0.7027(21)	0.5361(12)	0.5616(12)	9.6(12)
C(29B)	0.3088(22)	0.6822(12)	0.1750(10)	10.1(11)
C(30B)	0.3703(25)	0.6768(18)	0.1395(13)	13.0(17)
C(31B)	0.7343(15)	0.4865(10)	0.3127(10)	6.7(8)
C(32B)	0.6726(17)	0.4053(10)	0.2781(11)	7.1(9)
C(33B)	0.8041(18)	0.5666(13)	0.3586(13)	9.2(11)
C(34B)	0.7995(21)	0.4381(15)	0.2486(15)	10.9(15)
C(35B)	0.8362(26)	0.4846(18)	0.2406(18)	13.3(19)
C(36B)	0.8729(24)	0.5243(15)	0.2912(17)	11.9(17)
C(37B)	0.6068(25)	0.3245(11)	0.2455(16)	10.8(16)
C(38B)	0.6277(33)	0.2815(17)	0.2166(19)	14.4(22)
C(39B)	0.8650(26)	0.6472(16)	0.4032(21)	16.1(22)
C(40B)	0.9284(32)	0.6789(18)	0.3964(22)	15.3(24)
$CHCl_3$				
C(51A)	0.6719(31)	0.7967(22)	0.0393(23)	17.0(25)
C1(1A)	0.7284(15)	0.8253(9)	0.0892(9)	25.7(13)
C1(2A)	0.5786(14)	0.7710(9)	0.0530(10)	25.1(13)
C1(3A)	0.7368(18)	0.7430(11)	0.0247(13)	31.5(17)
C(51B)	0.6812(33)	0.6348(20)	0.2530(22)	16.1(25)
C1(1B)	0.5899(14)	0.5910(8)	0.2212(9)	22.8(11)
C1(2B)	0.7422(16)	0.6321(10)	0.2083(10)	26.4(14)
C1(3B)	0.6262(18)	0.6908(11)	0.2494(11)	30.3(17)

Table 2. (Continued)

(2) **5b-2**

Atom	x	y	z	B_{eq}/Å^2
Molecule A				
Pd(1A)	0.10817(8)	0.36141(4)	0.10829(4)	3.54(3)
Pd(2A)	0.20672(8)	0.28157(4)	0.05343(4)	3.76(4)
Pd(3A)	−0.05108(8)	0.32496(4)	−0.02060(4)	3.33(3)
S(11A)	0.2629(3)	0.35933(14)	0.10185(15)	4.34(13)
S(12A)	−0.0279(3)	0.35276(18)	0.12661(15)	5.09(15)
S(21A)	0.1098(3)	0.32301(14)	−0.02663(14)	3.95(13)
S(22A)	0.2895(4)	0.22812(17)	0.12440(17)	6.36(19)
S(31A)	−0.0007(3)	0.40082(12)	0.02312(13)	3.66(12)
S(32A)	−0.1264(3)	0.25017(14)	−0.06179(15)	4.38(14)
N(11A)	0.3128(9)	0.3291(4)	0.2001(4)	4.2(4)
N(12A)	0.1656(9)	0.3238(4)	0.2112(4)	4.6(4)
N(13A)	0.4607(10)	0.3370(5)	0.1894(6)	5.8(5)
N(14A)	0.0185(12)	0.3192(6)	0.2226(5)	6.6(6)
N(21A)	0.1167(9)	0.2225(4)	−0.0428(4)	3.9(5)
N(22A)	0.1895(11)	0.1739(4)	0.0327(5)	5.1(5)
N(23A)	0.0614(11)	0.2734(5)	−0.1182(5)	5.6(6)
N(24A)	0.2644(18)	0.1276(6)	0.1107(7)	9.5(10)
N(31A)	−0.2038(9)	0.3740(4)	0.0027 (5)	4.1 (4)
N(32A)	−0.2539(8)	0.2922(5)	−0.0293(4)	4.2(4)
N(33A)	−0.1541(10)	0.4550(5)	0.0313(6)	5.3(6)
N(34A)	−0.3121(10)	0.2141(5)	−0.0675(6)	6.0(6)
C(11A)	0.2034(11)	0.3349(4)	0.1804(5)	3.8(5)
C(12A)	0.3588(12)	0.3404(5)	0.1694 (5)	4.4(5)
C(13A)	0.0495(13)	0.3295(5)	0.1920(5)	4.3(6)
C(14A)	0.3907(14)	0.3092(7)	0.2560(7)	6.9(7)
C(15A)	0.3295(17)	0.2755(8)	0.2708(8)	8.1(9)
C(16A)	0.2305(15)	0.3045(7)	0.2685(6)	5.9(7)
C(17A)	0.5102(14)	0.3470(8)	0.1593(8)	7.4(9)
C(18A)	0.5416(27)	0.2965(8)	0.1397(13)	12.6(19)
C(19A)	−0.1054(20)	0.3251(14)	0.2049(10)	12.4(15)
C(20A)	−0.1418(27)	0.2749(18)	0.2019(20)	18.6(30)
C(21A)	0.1660(10)	0.2197(5)	0.0101(5)	3.9(5)
C(22A)	0.0907(11)	0.2689(6)	−0.0679(5)	4.3(5)
C(23A)	0.2473(16)	0.1697(6)	0.0906(7)	6.4(8)
C(24A)	0.0810(15)	0.1780(6)	−0.0782(6)	5.6(8)
C(25A)	0.0561(15)	0.1359(6)	−0.0519(7)	5.8(8)
C(26A)	0.1574(17)	0.1266(6)	0.0030(7)	6.7(9)
C(27A)	0.0349(24)	0.3225(7)	−0.1435(7)	9.5(13)
C(28A)	0.0526(26)	0.3208(15)	−0.1891(12)	14.1(18)
C(29A)	0.3228(29)	0.1232(9)	0.1706(9)	12.8(17)
C(30A)	0.3811(38)	0.0894(13)	0.1908(13)	19.3(25)
C(31A)	−0.1834(10)	0.3325(6)	−0.0147(5)	4.0(5)
C(32A)	−0.1275(11)	0.4156(6)	0.0196(5)	4.0(5)
C(33A)	−0.2412(10)	0.2495(5)	−0.0546(6)	4.0(5)
C(34A)	−0.3028(13)	0.3803(7)	0.0056(8)	6.3(8)
C(35A)	−0.3350(13)	0.3326(7)	0.0191(8)	6.0(8)
C(36A)	−0.3515(12)	0.2938(7)	−0.0227(9)	6.7(8)
C(37A)	−0.0721(17)	0.4988(8)	0.0523(11)	8.7(13)
C(38A)	−0.1066(24)	0.5367(10)	0.0748(14)	12.2(19)
C(39A)	−0.3056(15)	0.1688(7)	−0.0933(9)	7.6(9)
C(40A)	−0.4097(17)	0.1588(9)	−0.1430(8)	8.2(10)
Molecule B				
Pd(1B)	0.54685(8)	0.45342(4)	0.28271(4)	3.67(4)
Pd(2B)	0.45475(8)	0.53799(4)	0.33492(4)	3.51(4)
Pd(3B)	0.72560(8)	0.50354(4)	0.41768(4)	3.58(4)
S(11B)	0.4033(3)	0.45461(13)	0.29805(14)	4.01(13)
S(12B)	0.6676(3)	0.45609(19)	0.25395(16)	5.51(16)
S(21B)	0.5610(3)	0.50916(13)	0.42074(13)	3.78(12)
S(22B)	0.3631(4)	0.58023(16)	0.25655(15)	6.06(18)
S(31B)	0.6744(3)	0.42821(13)	0.37195(14)	3.90(13)
S(32B)	0.8048(3)	0.57527(16)	0.46479(17)	4.99(16)
N(11B)	0.3302(9)	0.4768(4)	0.1945(4)	4.3(4)
N(12B)	0.4656(10)	0.4829(5)	0.1742(4)	4.8(5)
N(13B)	0.1955(10)	0.4647(5)	0.2144(5)	4.8(5)
N(14B)	0.6017(12)	0.4849(7)	0.1527(5)	6.8(7)
N(21B)	0.5375(9)	0.6114(4)	0.4206(4)	3.7(4)
N(22B)	0.4562(10)	0.6466(4)	0.3376(4)	4.7(5)
N(23B)	0.6123(10)	0.5721(4)	0.5038(4)	4.5(5)
N(24B)	0.3750(16)	0.6815(5)	0.2534(5)	8.1(8)
N(31B)	0.8737(9)	0.4566(4)	0.3889(5)	4.1(5)
N(32B)	0.9340(9)	0.5354(4)	0.4317(5)	4.5(5)
N(33B)	0.8222(11)	0.3765(5)	0.3563(6)	5.8(6)
N(34B)	0.9925(11)	0.6116(5)	0.4751(6)	6.3(7)
C(11B)	0.4376(11)	0.4733(5)	0.2084(5)	3.8(5)
C(12B)	0.2975(11)	0.4657(5)	0.2294(5)	4.0(5)
C(13B)	0.5787(13)	0.4764(7)	0.1877(6)	5.2(6)
C(14B)	0.2430(13)	0.4979(6)	0.1413(6)	5.2(6)
C(15B)	0.2965(14)	0.5269(7)	0.1177(7)	6.0(7)
C(16B)	0.3893(16)	0.5029(7)	0.1180(6)	6.6(8)
C(17B)	0.1572(14)	0.4571(9)	0.2500(8)	7.2(8)
C(18B)	0.0390(18)	0.4746(13)	0.2275(12)	11.6(15)
C(19B)	0.7167(17)	0.4753(12)	0.1642(9)	9.8(12)
C(20B)	0.7165(22)	0.4470(11)	0.1204(12)	11.2(16)
C(21B)	0.4864(11)	0.6065(4)	0.3678(5)	3.9(5)
C(22B)	0.5733(10)	0.5673(5)	0.4544(5)	3.5(5)
C(23B)	0.3988(14)	0.6418(6)	0.2793(5)	5.4(6)
C(24B)	0.5631(15)	0.6610(5)	0.4482(5)	5.3(7)
C(25B)	0.5718(17)	0.7007(6)	0.4137(6)	6.4(8)
C(26B)	0.4755(16)	0.7002(5)	0.3581(6)	5.6(7)
C(27B)	0.6558(16)	0.5273(7)	0.5377(6)	6.1(8)
C(28B)	0.7048(14)	0.5411(7)	0.5964(6)	5.7(7)
C(29B)	0.3229(25)	0.6769(8)	0.1935(7)	11.2(13)
C(30B)	0.4065(29)	0.6769(13)	0.1779(10)	13.3(18)
C(31B)	0.8587(11)	0.4967(6)	0.4132(5)	4.2(5)
C(32B)	0.7966(12)	0.4166(5)	0.3724(6)	4.3(6)
C(33B)	0.9186(13)	0.5776(6)	0.4590(6)	5.1(6)
C(34B)	0.9680(12)	0.4519(6)	0.3809(8)	5.6(7)
C(35B)	1.0021(14)	0.5046(8)	0.3759(8)	6.5(8)
C(36B)	1.0300(13)	0.5363(6)	0.4234(8)	6.3(8)
C(37B)	0.7403(16)	0.3343(7)	0.3334(9)	7.1(9)
C(38B)	0.7906(24)	0.2889(13)	0.3269(17)	15.7(24)
C(39B)	0.9795(15)	0.6548(8)	0.4997(9)	7.2(9)
C(40B)	1.0521(23)	0.6984(8)	0.5010(13)	11.5(18)
C_6H_6				
C(51A)	0.6035(19)	0.6049(11)	0.0883(11)	11.2(13)
C(52A)	0.6373(19)	0.6539(12)	0.0866(14)	13.4(16)
C(53A)	0.6441(17)	0.6658(10)	0.0427(14)	11.5(16)
C(54A)	0.6221(20)	0.6318(15)	0.0021(12)	13.7(17)
C(55A)	0.5830(21)	0.5827(15)	0.0041(15)	15.1(20)
C(56A)	0.5750(20)	0.5697(12)	0.0490(15)	13.7(18)
C(51B)	0.6830(26)	0.5996(11)	0.2928(15)	13.3(20)
C(52B)	0.7411(32)	0.6362(13)	0.3353(12)	14.4(21)
C(53B)	0.8281(34)	0.6661(12)	0.3340(15)	15.2(26)
C(54B)	0.8352(42)	0.6662(14)	0.2956(18)	20.0(36)
C(55B)	0.7831(43)	0.6257(21)	0.2499(18)	21.3(34)
C(56B)	0.7065(33)	0.6011(11)	0.2539(15)	15.0(24)

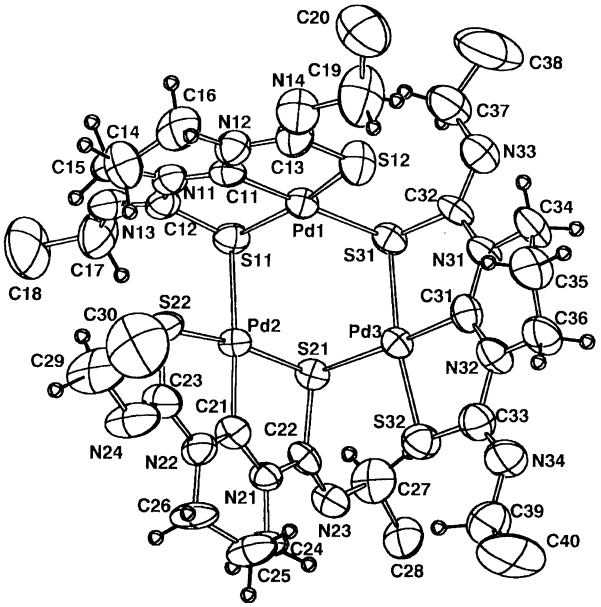


Fig. 1. ORTEP drawing of **5b-2** (Molecule **B**) with the atom-numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å.

solution was considered to be better than that of **5b-1** for the structure analysis. Intensity data of **5b-2** were also measured by a rapid Weissenberg-type diffractometer with imaging plates (MacScience-DIP3000) at the Univ. of Electro-Communications using a crystal shielded in a thin glass capillary. The structure was solved by the same method. Benzene molecules were contained as crystal solvents. The positions of the hydrogen atoms of the methylene groups were obtained from calculation, and were included in the refinement. The H atoms of the terminal methyl groups and benzenes were not located because of the large thermal motion of these groups. The final R value was 0.073 for 11013 reflections. In these structure analyses, absorption corrections were not applied. $\sum w(|F_c|-k^{-1}|F_o|)^2$ was minimized, where $w=1$.

The total time for an intensity measurement of **5b-1** or **5b-2** using

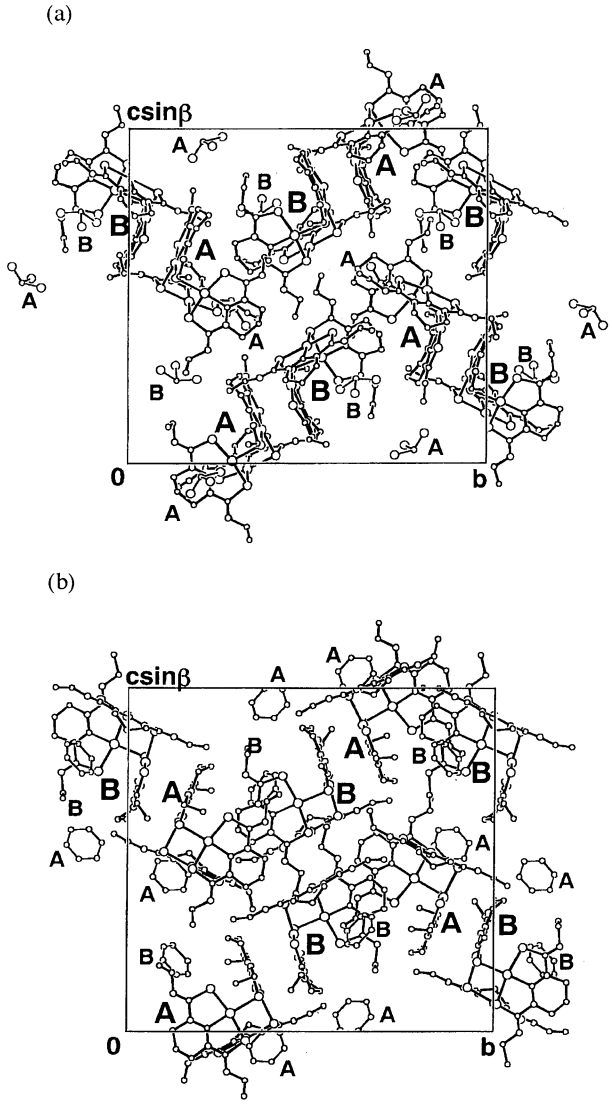


Fig. 2. Projections of the crystal structures of **5b** viewed along the a axis. (a) **5b-1** and (b) **5b-2**.

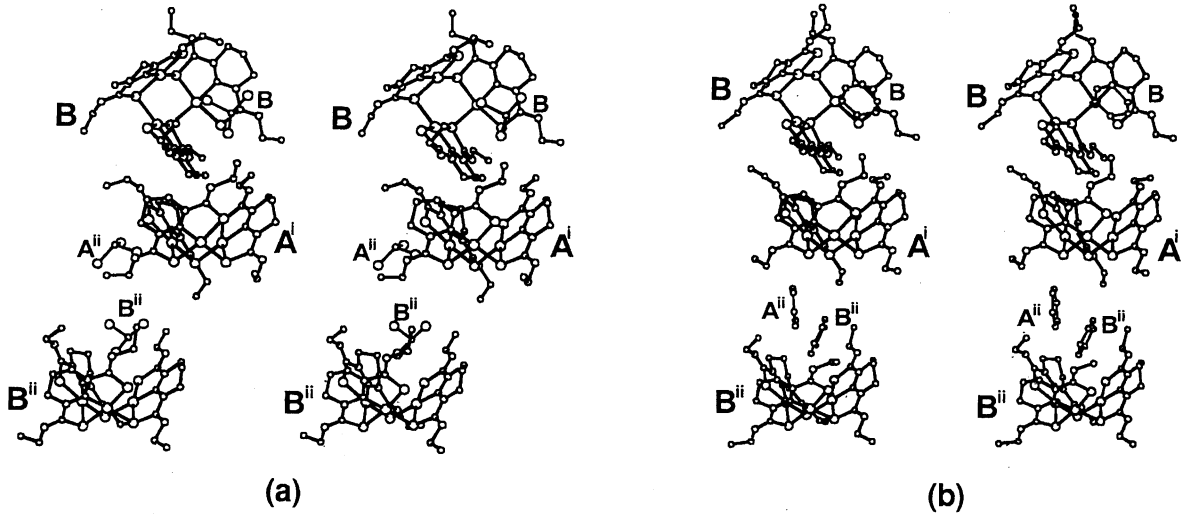


Fig. 3. Stereoscopic view of the arrangement of **5b** and crystal solvents. (a) **5b-1**, (b) **5b-2**. Symmetry code: (None=x, y, z), (i=$1/2-x$, $1/2+y$, $1/2-z$) and (ii=$x-1/2$, $3/2-y$, $z+1/2$).

a four-circle diffractometer with a rotating-anode was estimated to be about 7—10 d because the volume of a unit cell of a monoclinic system was very large. Using rapid diffractometers, intensities of more than 10400 independent reflections could be measured within 12 h in the laboratory.

Intensity data of **6a** were measured using a four-circle diffractometer (AFC-5R) with a graphite monochromator. Absorption corrections were applied numerically. The structure was solved by a direct method using the program MULTAN78.[10] There are two independent molecules (**A** and **B**) in an asymmetric unit. During the refinement it was revealed that one of the C atoms, C(5B), of the cyclic methylene group of the molecule **B** shows a disordered state, up and down the sides of the pentalene plane. The occupancy factors were estimated from the heights of the Fourier maps to be 0.6 : 0.4. Some H atoms were located from the D-maps, and the positional parameters of remaining H atoms were assumed from the calculation, which were included in the refinements. The structures were refined using block-diagonal least-squares with anisotropic temperature factors for non-H atoms and isotropic ones for H. $\sum w(|F_c|-k^{-1}|F_o|)^2$ was minimized, where $w=1\{\sigma^2(F)+0.00056|F_o|^2\}$. The final R value was 0.0349, for 5627 observed reflections.

Crystal data as well as details of the data collection and structure refinement are listed in Table 1. The atomic scattering factors were used from the International Tables for X-Ray Crystallography.[11] All of the computations were performed using the programs UNICS III[12] and ORTEP II.[13] The final atomic parameters are given in Tables 2 and 3 for **5** and **6**, respectively.[14]

Discussion

Structures of 5b-1 and 5b-2. For both crystals, there are two independent trimer units (**A** and **B**) in an asymmetric unit. The molecular structure of **5b-2** (**B**) with the atomic numbering is shown in Fig. 1. Selected bond distances, bond angles and torsion angles are listed in Table 4. Each trimer consists of a cyclic $(Pd–S)_3$ framework. In the trimer, each Pd atom is coordinated by three S atoms and one C atom in a square-planar arrangement, just like the starting carbene-complex **3**.[4] Two of these three S atoms belong to the same pentalene ring; the other belongs to the next pentalene ring. In other words, the PPh_3 group of the starting molecule **3** is replaced by one of the S atoms bridging the neighboring Pd to form a $(Pd–S)_3$ ring. The bridging S atom is three-coordinated with two Pd atoms and one C atom located at the apex of a pyramidal structure. A conformation of $(Pd–S)_3$ is a chair form with endocyclic torsion angles of about ±(78—94)°. The torsion angles of $S_{exocyclic}–Pd–S_{bridging}–C_{exocyclic}$, such as S(12)–Pd(1)–S(31)–C(32), are within 11°. Thus, the shape of the trimer molecule is like a cage with a base of three S atoms. The dihedral angles between pentalene planes in the trimeric unit are 74.4(2)—89.0(2)°. A similar cage-like trimer structure has been observed for 2,2′-dimercaptodiethyl-sulfide-palladium(II).[15] The conformations of the terminal ethyl groups (torsion angles of $C–N–CH_2–CH_3$) are different from each other.

The lengths of the Pd–C bonds (mean value: 1.97 Å) are slightly shorter than those of the PPh_3 complexes **3** (2.00 Å), but slightly longer than that of the pyridine complex **6a** (1.94 Å). The distances of intrapentalene Pd–S bonds (mean value, 2.26 Å) consisting the hexagon, such as Pd(1)–S(11) and Pd(2)–S(21), are slightly longer than those of intrapentalene Pd–S (mean, 2.30 Å), such as Pd(1)–S(12) and Pd(2)–S(22), which are not included in the hexagon. This may reflect the difference in the coordination number of these S atoms. The mean value of the intrapentalene Pd–S lengths is 2.28 Å, which is the same as those of the PPh_3 complexes **3** and the pyridine complex **6a**.

The distances of the interpentalene Pd–S bonds (2.39 Å) are significantly longer than those of the intrapentalene Pd–S bonds. This difference suggests that the trimer cleaved easily

Table 3. Positional Parameters and Equivalent Isotropic Temperature Factors (B_{eq}) for Non-H Atoms of **6a**

Atom	x	y	z	B_{eq}/Å^2
Pd(1A)	0.19982(2)	0.13992(1)	0.49033(3)	3.07(1)
S(1A)	0.26937(6)	0.22686(4)	0.54532(13)	3.74(3)
S(2A)	0.14837(7)	0.04889(5)	0.42015(15)	4.30(3)
N(1A)	0.36779(19)	0.15152(13)	0.4393(4)	3.13(8)
N(2A)	0.3058(2)	0.06096(14)	0.3737(4)	3.34(9)
N(3A)	0.4207(2)	0.24396(15)	0.4758(4)	3.95(10)
N(4A)	0.2430(2)	−0.02776(16)	0.3059(5)	4.87(12)
N(11A)	0.0878(2)	0.16800(14)	0.5454(4)	3.51(9)
C(1A)	0.3606(2)	0.21001(16)	0.4836(4)	3.14(10)
C(2A)	0.2349(3)	0.02200(18)	0.3597(5)	3.73(11)
C(3A)	0.3007(2)	0.11490(16)	0.4289(4)	2.92(9)
C(4A)	0.4474(3)	0.13473(18)	0.4010(5)	3.88(12)
C(5A)	0.4603(3)	0.07051(19)	0.4254(5)	4.15(12)
C(6A)	0.3820(3)	0.03843(18)	0.3313(5)	3.95(12)
C(7A)	0.4150(3)	0.3044(2)	0.5202(6)	5.24(16)
C(8A)	0.1734(3)	−0.0688(2)	0.2971(7)	6.19(19)
C(12A)	0.0906(3)	0.20311(19)	0.6668(5)	4.06(12)
C(13A)	0.0171(3)	0.2239(2)	0.6990(6)	4.83(14)
C(14A)	−0.0617(3)	0.2096(2)	0.6045(6)	5.03(15)
C(15A)	−0.0659(3)	0.1732(2)	0.4789(6)	4.95(15)
C(16A)	0.0097(3)	0.15359(19)	0.4535(6)	4.37(13)
Pd(1B)	0.34775(2)	0.07794(1)	0.86762(3)	3.07(1)
S(1B)	0.37029(7)	−0.00717(5)	0.75490(14)	4.07(3)
S(2B)	0.30555(7)	0.15582(5)	0.98741(13)	4.10(3)
N(1B)	0.2158(2)	−0.00877(15)	0.8155(4)	4.00(10)
N(2B)	0.1801(2)	0.07611(15)	0.9219(4)	3.92(10)
N(3B)	0.2550(2)	−0.09455(17)	0.7226(6)	5.53(14)
N(4B)	0.1462(2)	0.15973(18)	1.0299(4)	4.72(12)
N(11B)	0.4678(2)	0.11317(14)	0.8650(4)	3.34(10)
C(1B)	0.2761(3)	−0.04272(18)	0.7599(5)	3.97(12)
C(2B)	0.2030(3)	0.13224(18)	0.9844(5)	3.71(11)
C(3B)	0.2370(2)	0.04501(17)	0.8682(5)	3.34(10)
C(4B)	0.1314(3)	−0.0355(2)	0.8033(7)	6.11(18)
C(51B)[a]	0.0663(4)	0.0122(4)	0.8017(10)	5.33(26)
C(6B)	0.0941(3)	0.0537(2)	0.9183(8)	6.07(18)
C(7B)	0.3161(4)	−0.1303(2)	0.6690(9)	7.47(23)
C(8B)	0.1668(3)	0.2172(2)	1.0927(6)	5.63(16)
C(12B)	0.5377(3)	0.07911(18)	0.8811(5)	4.08(12)
C(13B)	0.6158(3)	0.1009(2)	0.8738(6)	4.61(13)
C(14B)	0.6244(3)	0.1592(2)	0.8528(6)	4.79(14)
C(15B)	0.5530(3)	0.19443(19)	0.8369(6)	4.72(14)
C(16B)	0.4768(3)	0.17021(18)	0.8432(5)	3.75(11)
C(52B)[b]	0.0862(9)	−0.0096(6)	0.8985(17)	6.0(3)

Occupancy factors: a) 0.6, b) 0.4.

Table 4. Selected Bond Lengths (l), Bond Angles (θ), and Torsion Angles (τ) of **5b**

	5b-1		**5b-2**	
Molecule	**A**	**B**	**A**	**B**
Lengths	l/Å	l/Å	l/Å	l/Å
Pd(1)–S(11)	2.311(7)	2.294(7)	2.297(5)	2.299(5)
Pd(1)–S(12)	2.270(8)	2.266(8)	2.264(5)	2.264(6)
Pd(1)–S(31)	2.393(5)	2.389(6)	2.379(3)	2.368(3)
Pd(1)–C(11)	1.962(19)	1.952(18)	1.949(11)	1.972(11)
Pd(2)–S(11)	2.387(6)	2.401(6)	2.386(4)	2.395(4)
Pd(2)–S(21)	2.307(5)	2.301(5)	2.283(3)	2.281(3)
Pd(2)–S(22)	2.255(6)	2.258(6)	2.267(4)	2.254(4)
Pd(2)–C(21)	1.962(20)	1.971(18)	1.961(14)	1.989(12)
Pd(3)–S(21)	2.401(7)	2.388(7)	2.377(5)	2.385(5)
Pd(3)–S(31)	2.306(6)	2.295(6)	2.284(3)	2.296(4)
Pd(3)–S(32)	2.270(6)	2.269(8)	2.273(4)	2.269(4)
Pd(3)–C(31)	2.001(23)	1.982(28)	1.981(17)	1.965(18)
S(11)–C(12)	1.802(23)	1.765(19)	1.789(13)	1.797(12)
S(12)–C(13)	1.770(23)	1.727(25)	1.745(12)	1.756(14)
S(21)–C(22)	1.824(20)	1.805(20)	1.796(16)	1.783(14)
S(22)–C(23)	1.780(25)	1.767(27)	1.761(16)	1.731(15)
S(31)–C(32)	1.824(24)	1.798(31)	1.790(17)	1.752(19)
S(32)–C(33)	1.738(28)	1.722(35)	1.745(18)	1.710(22)
Angles	θ/°	θ/°	θ/°	θ/°
S(11)–Pd(1)–S(12)	170.3(3)	170.8(3)	169.5(2)	170.7(2)
S(11)–Pd(1)–S(31)	92.8(2)	92.3(2)	93.2(1)	92.3(1)
S(11)–Pd(1)–C(11)	86.0(7)	86.4(6)	85.5(5)	86.5(5)
S(12)–Pd(1)–S(31)	96.8(2)	96.9(3)	96.8(2)	97.0(2)
S(12)–Pd(1)–C(11)	84.6(7)	84.5(7)	84.7(5)	84.3(5)
S(31)–Pd(1)–C(11)	176.2(7)	178.6(6)	175.0(5)	178.5(5)
S(11)–Pd(2)–S(21)	91.6(2)	93.2(2)	91.7(2)	93.4(1)
S(11)–Pd(2)–S(22)	98.5(2)	96.8(2)	98.1(2)	96.9(2)
S(11)–Pd(2)–C(21)	175.5(7)	176.1(7)	175.2(5)	174.2(5)
S(21)–Pd(2)–S(22)	169.9(2)	169.9(2)	170.0(2)	169.6(2)
S(21)–Pd(2)–C(21)	84.9(7)	83.5(6)	85.5(5)	85.4(5)
S(22)–Pd(2)–C(21)	85.0(7)	86.5(7)	84.7(5)	84.5(5)
S(21)–Pd(3)–S(31)	91.4(2)	93.3(2)	91.5(1)	93.1(1)
S(21)–Pd(3)–S(32)	98.5(2)	96.1(3)	98.5(2)	96.4(2)
S(21)–Pd(3)–C(31)	176.8(7)	176.4(8)	175.5(4)	177.8(5)
S(31)–Pd(3)–S(32)	170.1(3)	170.1(3)	170.0(2)	170.2(2)
S(31)–Pd(3)–C(31)	85.6(7)	83.2(8)	84.3(4)	84.7(5)
S(32)–Pd(3)–C(31)	84.6(7)	87.4(8)	85.7(4)	85.7(5)
Pd(1)–S(11)–Pd(2)	92.7(2)	89.8(2)	91.7(2)	90.3(1)
Pd(1)–S(11)–C(12)	98.5(9)	98.0(8)	97.5(6)	95.7(5)
Pd(2)–S(11)–C(12)	103.5(9)	103.2(2)	103.9(6)	103.5(5)
Pd(1)–S(12)–C(13)	100.4(10)	98.8(10)	99.4(6)	99.6(6)
Pd(2)–S(21)–Pd(3)	90.2(2)	95.1(2)	91.6(1)	94.8(2)
Pd(2)–S(21)–C(22)	97.7(7)	99.4(8)	96.0(5)	97.9(5)
Pd(3)–S(21)–C(22)	104.6(7)	103.4(8)	104.4(5)	104.8(5)
Pd(2)–S(22)–C(23)	98.9(9)	100.9(10)	99.8(8)	100.2(7)
Pd(1)–S(31)–Pd(3)	92.0(2)	99.3(2)	92.5(1)	103.0(2)
Pd(1)–S(31)–C(32)	103.7(8)	102.3(9)	104.2(5)	104.4(6)
Pd(3)–S(31)–C(32)	99.4(8)	99.1(9)	98.3(5)	97.7(6)
Pd(3)–S(32)–C(33)	100.1(9)	98.9(12)	99.1(6)	99.6(6)
Torsions	τ/°	τ/°	τ/°	τ/°
S(31)–Pd(1)–S(11)–Pd(2)	−85.3(2)	85.9(2)	−85.48(15)	83.35(15)
Pd(1)–S(11)–Pd(2)–S(21)	89.1(2)	−91.9(2)	88.65(15)	−93.44(15)
S(11)–Pd(2)–S(21)–Pd(3)	−88.5(2)	88.1(2)	−88.60(15)	89.85(15)
Pd(2)–S(21)–Pd(3)–S(31)	91.0(2)	−81.1(2)	90.11(15)	−79.47(15)
S(21)–Pd(3)–S(31)–Pd(1)	−87.8(2)	80.1(2)	−86.43(14)	78.47(16)
Pd(3)–S(31)–Pd(1)–S(11)	87.3(2)	−87.4(2)	88.09(15)	−84.78(16)
S(12)–Pd(1)–S(31)–C(32)	9.1(8)	−9.6(9)	10.4(5)	−6.4(6)
S(22)–Pd(2)–S(11)–C(12)	7.8(9)	−10.9(8)	8.1(6)	−10.9(5)
S(32)–Pd(3)–S(21)–C(22)	10.1(8)	0.9(8)	7.3(5)	3.0(5)

Table 5. Selected Bond Lengths (l) and Angles (θ) of **6a**

Molecule	**A**	**B**
Lengths	l/Å	l/Å
Pd(1)–S(1)	2.288(1)	2.280(1)
Pd(1)–S(2)	2.284(1)	2.287(1)
Pd(1)–N(11)	2.102(4)	2.109(3)
Pd(1)–C(3)	1.942(4)	1.946(4)
S(1)–C(1)	1.751(4)	1.739(4)
S(2)–C(2)	1.743(5)	1.738(4)
N(1)–C(1)	1.421(5)	1.440(6)
N(1)–C(3)	1.358(5)	1.339(5)
N(1)–C(4)	1.469(6)	1.473(6)
N(2)–C(2)	1.434(5)	1.419(5)
N(2)–C(3)	1.349(5)	1.352(6)
N(2)–C(6)	1.477(6)	1.473(6)
N(3)–C(1)	1.264(5)	1.264(6)
N(3)–C(7)	1.459(6)	1.461(8)
N(4)–C(2)	1.265(6)	1.269(6)
N(4)–C(8)	1.455(7)	1.443(7)
N(11)–C(12)	1.342(6)	1.352(5)
N(11)–C(16)	1.346(5)	1.345(5)
Angles	θ/°	θ/°
S(1)–Pd(1)–S(2)	170.81(5)	170.48(5)
S(1)–Pd(1)–N(11)	94.8(1)	94.1(1)
S(1)–Pd(1)–C(3)	85.4(1)	85.5(1)
S(2)–Pd(1)–N(11)	94.3(1)	95.3(1)
S(2)–Pd(1)–C(3)	85.4(1)	85.2(1)
N(11)–Pd(1)–C(3)	177.2(1)	179.5(1)
Pd(1)–S(1)–C(1)	98.3(1)	98.7(2)
Pd(1)–S(2)–C(2)	98.6(2)	98.6(1)
C(1)–N(1)–C(3)	119.2(3)	119.5(4)
C(1)–N(1)–C(4)	117.2(3)	116.5(4)
C(3)–N(1)–C(4)	123.6(3)	123.9(4)
C(2)–N(2)–C(3)	119.0(3)	119.5(3)
C(2)–N(2)–C(6)	117.2(3)	118.3(4)
C(3)–N(2)–C(6)	123.7(3)	122.2(4)
C(1)–N(3)–C(7)	118.2(4)	117.6(5)
C(2)–N(4)–C(8)	117.0(4)	118.2(4)
Pd(1)–N(11)–C(12)	122.1(3)	121.3(3)
Pd(1)–N(11)–C(16)	120.4(3)	121.0(3)
C(12)–N(11)–C(16)	117.4(4)	117.7(4)
S(1)–C(1)–N(1)	115.9(3)	115.5(3)
S(1)–C(1)–N(3)	127.1(3)	128.0(4)
N(1)–C(1)–N(3)	116.9(4)	116.5(4)
S(2)–C(2)–N(2)	115.9(3)	116.0(3)
S(2)–C(2)–N(4)	127.9(4)	127.4(3)
N(2)–C(2)–N(4)	116.2(4)	116.6(4)
Pd(1)–C(3)–N(1)	120.7(3)	120.7(3)
Pd(1)–C(3)–N(2)	121.0(3)	120.5(3)
N(1)–C(3)–N(2)	118.3(3)	118.8(4)

in pyridine to form a pyridine complex. The trimeric structure may be considered to show an intermediate structure of the ligand-exchange reaction.

The crystal structures of **5b-1** and **5b-2** are shown in Fig. 2. Stereoscopic views of the relationships between the trimer molecules and solvent molecules are shown in Fig. 3. In both crystals, one of the pentalene rings (Pd(2B)—) of the **B** trimer is included in the trimer cage ($\mathbf{A}^{i}$, i=$1/2-x$, $1/2+y$, $1/2-z$). This guest pentalene ring is almost parallel to one of the pentalene rings (Pd(2A)—) of the host trimer. The dihedral angles of the guest pentalene (Pd(2B)—) and the host pentalene (Pd(2A)—) planes are 175.3(3) and 172.1(2)°, for **5b-1** and **5b-2**, respectively. The solvent molecule **B** is included in the trimer cage (**B**), while another solvent molecule ($\mathbf{A}^{ii}$, ii=$x-1/2$, $3/2-y$, $z+1/2$) is not included in the trimer cage ($\mathbf{A}^{i}$). A unit consisting of the solvent molecule **B**, the trimer **B** and the trimer $\mathbf{A}^{i}$ of **5b-1** is the same as that of **5b-2**. The solvent molecule **A** fills between these units, although the locations are different between crystals of **5b-1** and **5b-2**. This difference is related to the slight deviation from the isomorphous crystal structures of **5b-1** and **5b-2**, as shown in Fig. 2. The intermolecular distances are the van der Waals' type. The instability of the crystals is ascribed to a collapse of the crystal lattice upon withdrawing the solvent molecules. Collapsed powders can be recrystallized again from the solvents.

Structure of 6a. There are two independent molecules (**A** and **B**) in an asymmetric unit. The molecular structure of **6a**(**A**) with the atomic numbering is shown in Fig. 4. Selected bond distances and angles are listed in Table 5. Two independent molecules are similar, except for the disordered state of a cyclic methylene group of the molecule **B**. The structural feature of the pentalene framework is in good agreement with those coordinated by the PPh_3 group and **5**. The Pd–S lengths (2.280—2.288 Å) are equivalent with those of **3**, and slightly shorter than the sum of the covalent radii of Pd and S (2.32 Å). Two Pd–S bonds in the pentalene plane are equivalent with each other, while these bonds of **5b** are significantly different because of the formation of a trimer ring. The distances of Pd–C (1.942 and 1.946 Å) are shorter than those of **3**, **5** and the sum of the covalent radii of Pd and C (2.05

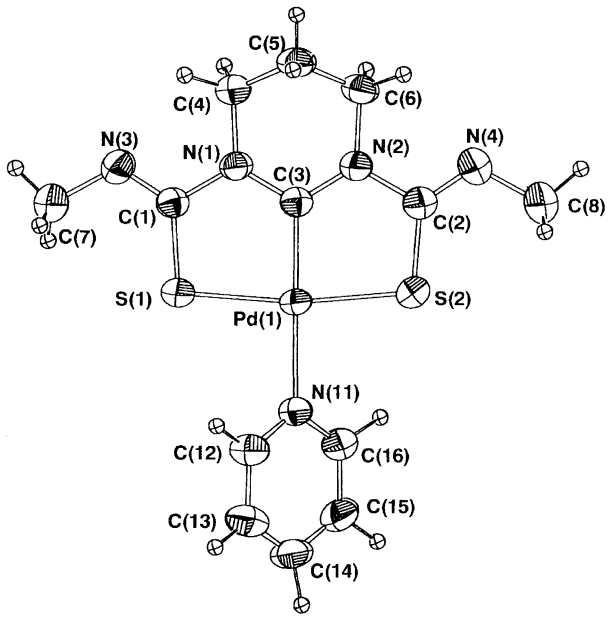


Fig. 4. ORTEP drawing of **6a** (Molecule **A**) with the atom-numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å.

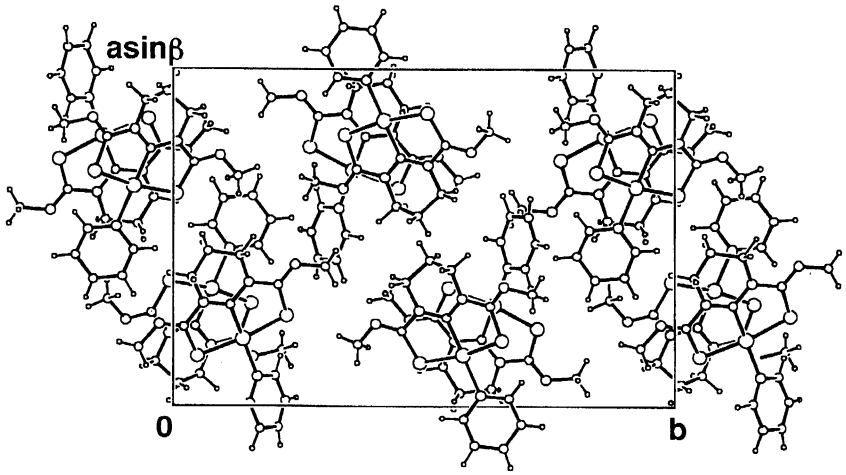


Fig. 5. Projection of the crystal structure of **6a** viewed along the *c* axis.

Å). The shortening of the lengths of Pd–C compared with those of PPh_3 complexes is explained by the trans influence of the ligands.[16,17] The Pd–N distances (2.102 and 2.109 Å) are longer than the covalent Pd–N length (1.98 Å) and the Pd–N lengths of some other Pd-pyridine complexes (1.98—2.04 Å) according to Cambridge Structural Database.[18] The maximum deviations from the metallapentalene planes are 0.078(3) and 0.112(4) Å for the **A** and **B** molecules, respectively. The dihedral angles between the pentalene plane and the pyridine plane are 138.9(1) and 146.3(1)°, for **A** and **B**, respectively.

The molecular packing in the crystal is shown in Fig. 5. Molecules **A** and **B** overlap with a separation of 3.689(4) Å.

This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas No. 04217103 and for Developmental Scientific Research No. 04504002 from the Ministry of Education, Science and Culture.

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