Crystal and Molecular Structures of Novel Metal–Carbene Complexes I. {1,1′-(Perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(alkyl/arylimino)methanethiolato-$\varkappa^2SS'$]}(triphenylphosphine)–Pt/Pd Complexes

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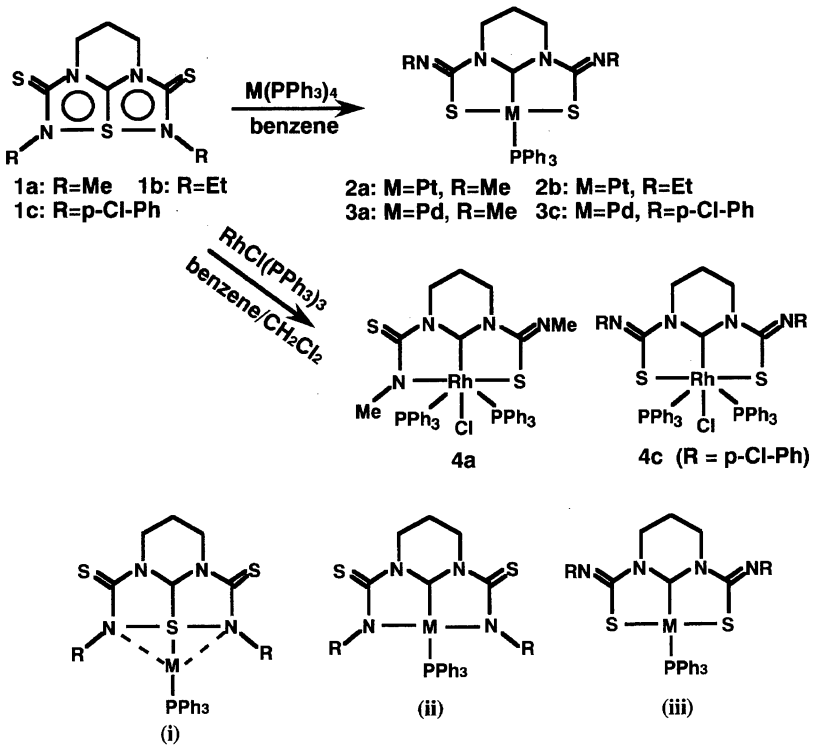
2,3,4,5-Tetrahydro-1,6-dialkyl-3,4-trimethylene-6aλ^4-thia-1,3,4,6-tetraazapentalene-2,5-dithiones (**1**), which contain a hypervalent sulfur atom, have been found to give novel complexes by treating with $Pt(PPh_3)_4$ and $Pd(PPh_3)_4$. X-Ray investigations have revealed that the resultant complexes are novel metal–carbene complexes: {1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(methylimino)methanethiolato-$\varkappa^2SS'$]}(triphenylphosphine)platinum(II) (**2a**), {1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(ethylimino)methanethiolato-$\varkappa^2SS'$]}(triphenylphosphine)platinum(II) (**2b**), {1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(methylimino)methanethiolato-$\varkappa^2SS'$]}(triphenylphosphine)palladium(II) (**3a**), {1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(4-chlorophenylimino)methanethiolato-$\varkappa^2SS'$]}(triphenylphosphine)palladium(II) (**3c**). The central sulfur atom in **1** was substituted by a metal atom and thioamide groups rotated to form metal–sulfur bonds in the resultant metallapentalene framework. The Pt and Pd atoms are four-coordinated by two S atoms, a C atom and a P atom in a square-planar configuration. The metallapentalene framework in each complex is planar. The *R* values are 0.042, 0.029, 0.046, and 0.054 for 4114, 5849, 5005, and 7106 observed reflections for **2a**, **2b**, **3a**, and **3c**, respectively.

Hypervalent sulfur compounds,[1] such as thiathiophthenes[2,3] and σ-sulfuranes,[4,5] provide great interest in structural chemistry and organic synthesis. We studied on the structural features of 6a-thiatetraazapentalene derivatives (**1**) which contain a hypervalent sulfur atom with a 12π conjugated system.[6—8] In the course of studying on the reactivity of **1**, novel metal–carbene complexes (**2**, **3**, and **4**) were obtained from **1** by treating with $Pt(PPh_3)_4$, $Pd(PPh_3)_4$, and $RhCl(PPh_3)_3$, respectively (Scheme 1).[9] At first, three possibilities of the complexes have been suggested: (i) hypervalent sulfur atoms coordinate the metal, (ii) nitrogen atoms coordinate the metal, and (iii) sulfur atoms of thiocarbonyl groups coordinate the metal. X-Ray investigations revealed that the resultant complex was the type (iii), so that the central sulfur atom in **1** was substituted by a metal atom, and thioamide groups rotated to form metal–sulfur bonds in the resultant metallapentalene framework. In this paper we describe the structures of some Pt complexes ({1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(methylimino)methanethiolato-$\varkappa^2SS'$]}(triphenylphosphine)platinum(II) (**2a**), {1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(ethylimino)methanethiolato-$\varkappa^2SS'$]}(triphenylphosphine)platinum(II) (**2b**)) and some Pd complexes ({1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(methylimino)methanethiolato-$\varkappa^2SS'$]}(triphenylphosphine)palladium(II) (**3a**), {1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(4-chlorophenylimino)methanethiolato-$\varkappa^2SS'$]}(triphenylphosphine)palladium(II) (**3c**)) derived from **1**. In following papers (II, III, and IV[10—12]), the structures of Pd complexes derived from **3**, the structures of Rh complexes **4** and a Cu complex, and the structures of Pt and Rh complexes derived from tetraazathiapentalenes with carbonyl groups, respectively, will be reported. A reaction mechanism for the formation of these novel metal–carbene complexes will also be discussed in paper IV.

Experimental

Crystals of **2a**, **2b**, and **3a** for X-ray studies were grown from CH_2Cl_2/hexane solutions. Crystals of **3c** were recrystallized from a $CHCl_3$/hexane solution. A specimen of **3c** was sealed in a thin glass capillary during intensity measurements because of being unstable in air. Crystal data, details of the data collection and structure refinements are listed in Table 1. The intensity data were collected using Rigaku diffractometers with graphite monochromators. For **2a**, **2b**, and **3a**, absorption corrections were applied numerically. The ψ-scan method was applied for an absorption correction of **3c**.

The structures of **2a**, **2b**, **3a**, and **3c** were solved by the heavy-atom method preceded by the Patterson function to locate the metal atom using the program SHELXS86.[13] During the refinements, solvent molecules of CH_2Cl_2 and $CHCl_3$ were found in D-maps of **3a** and **3c**, respectively. The occupancy factors were set to the estimated value from the peak heights of the D-maps and measured densities. It was revealed that the central C atom (C(5)) of the cyclic methylene group of **3c** showed a disordered state, up and down sides of the pentalene plane. The occupancy factors were estimated from the height of the D-maps to be 0.7 : 0.3.



Scheme 1.

The positions of the H atoms, except several ones on terminal positions, were obtained from D-maps. The remaining H atoms were located from calculations, and were included in the refinements with restraint. The structures were refined by block-diagonal least-squares with anisotropic temperature factors for non-H atoms and isotropic ones for H atoms. The function $\Sigma w(|F_o|-k|F_c|)^2$ was minimized. The final R values are 0.040, 0.029, 0.046, and 0.054 for **2a**, **2b**, **3a**, and **3c**, respectively.

The atomic-scattering factors were used from the International Tables for X-Ray Crystallography.[14] All computation were performed on an IBM ES/3090-180s computer at the Information Processing Center of the University of Electro-Communications with the programs SHELXS86, UNICS III,[15] ORTEP II.[16] The final atomic parameters are given in Table 2.[17]

Discussion

Molecular Structures. The molecular structures with the atomic numbering are shown in Fig. 1. The selected bond distances and angles are listed in Table 3.

In each complex the sulfur atom of the tetraazathiapentalene framework of **1** is substituted by the Pt or Pd atom to form a square-planar configuration. The four coordination sites are occupied by a tridentate ligand containing a dithiapentalene framework and a PPh_3 ligand. In the tridentate ligand, two sulfur atoms resulted from rotations of the thioamide groups of **1**, as well as a carbon atom of the pentalene ring coordinate the central metal atom. The metallapentalene framework is planar and the molecule has an approximate mirror plane perpendicular to the pentalene framework, except for the phenyl groups of PPh_3. The maximum deviations from the plane defined by eight atoms of the pentalene ring, are 0.056(7), 0.113(5), 0.110(5), and 0.127(5) Å for **2a**, **2b**, **3a**, and **3c**, respectively.

The distances of Pt–S bonds in the complex (**2a**) are 2.284(2) and 2.279(2) Å and Pt–P is 2.304(2) Å, which are slightly shorter than those of the normal Pt complexes. The length of the Pt–C bond (2.001(8) Å) is similar to those of metallacyclic Pt–C bond, but significantly longer than those of the Pt–C bonds (1.8—1.9 Å) in metal–carbonyl complexes searched from Cambridge Structural Database.[18] This difference may be ascribed to that of d–π interactions resulting from the difference of Csp^2 and Csp. The angle of S–M–S is 169.45(8)°. The lengths of the C–N bonds in the pentalene are similar to the corresponding lengths of the starting tetraazathiapentalenes (**1**). The lengths of N(1)–C(3) and N(2)–C(3) bonds (inner bonds) are shorter than those of N(1)–C(1) and N(2)–C(2) bonds (outer bonds) in these complexes (**2** and **3**) and the starting tetraazathiapentalenes (**1**). On the other hand, the inner bonds are longer than the outer bonds in some thiapentalenes referred in Ref. 7.

The coordination geometry around the metal of **2b** is quite similar to that of **2a**, and also to those of Pd complexes (**3a** and **3c**), except for the M–P lengths. Significantly longer Pd–P distances are observed rather than Pt–P bonds.

In **2b**, the ethyl amide groups are nearly coplanar with the pentalene ring. The dihedral angles between the pentalene plane and the C(1)–N(3)–C(11)–C(12) and C(2)–N(4)–C(21)–C(22) planes are 9.8(4) and 15.1(1)°, respectively. For **3c**, 4-chlorophenyl rings were tilted against the pentalene ring with dihedral angles of 45.6(2) and 51.2(2)° for the C(11)—C(16) and C(21)—C(26) planes, respectively, because of the steric hindrance of $S\cdots H\text{–}C_{(p\text{-Cl-phenyl})}$.

The structural features show that these Pt and Pd complexes, obtained from the hypervalent tetraazathiapentalene derivatives, are quite novel metal–carbene complexes with

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

	2a	**2b**	**3a**	**3c**
	$C_{26}H_{27}N_4PPtS_2$	$C_{28}H_{31}N_4PPtS_2$	$C_{26}H_{27}N_4PPdS_2$ ·0.5(CH_2Cl_2)	$C_{36}H_{29}Cl_2N_4PPdS_2$ ·$CHCl_3$
F.W.	685.71	713.77	639.51	909.46
Color	Yellow	Yellow	Yellow	Yellow
Crystal shape	Prism	Prism	Prism	Pillar
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/a$	$P\bar{1}$	$P2_1/a$	$P\bar{1}$
a/Å	16.419(4)	12.061(2)	17.667(5)	12.919(3)
b/Å	10.415(2)	14.947(3)	11.001(2)	13.981(3)
c/Å	16.748(4)	9.189(2)	15.658(4)	11.936(3)
α/°	90.0	109.79(2)	90.0	101.09(2)
β/°	112.72(2)	107.17(3)	112.26(2)	73.50(2)
γ/°	90.0	65.37(1)	90.0	104.45(2)
V/Å^3	2641.7(9)	1393.9(5)	2817(1)	1984.5(9)
Z	4	2	4	2
D_x/g cm^{-3}	1.724	1.701	1.508	1.522
D_m/g cm^{-3}	—	—	1.523	1.523
μ/mm^{-1}	5.599	5.309	0.966	0.973
F(000)	1344	704	1300	916
Crystal size	0.25×0.20×0.35	0.14×0.18×0.28	0.20×0.30×0.20	0.45×0.35×0.35
Diffractometer	Rigaku-AFC5R	Rigaku-AFC4	Rigaku-AFC4	Rigaku-AFC4
Radiation	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
λ/Å	0.71069	0.71069	0.71069	0.71069
For cell parameters				
2θrange/°	25.36—34.69	26.05—34.90	25.64—34.02	25.22—34.77
No. of refs.	25	25	25	25
Temperature /K	293	293	293	293
Scan mode	2θ–ω	2θ–ω	2θ–ω	2θ–ω
Scan range 2θ/°	3.0—55.0	2.0—55.0	3.0—55.0	2.0—55.0
Scan width $\Delta\omega$/°	1.40+0.4tan θ	1.30+0.4tan θ	1.20+0.4tan θ	1.30+0.4tan θ
Scan speed /° min^{-1}	4	4	4	4
No. of standard refs. every 50 reflections	3	3	3	3
Variation of intensities	0.968—1.006	0.974—1.023	0.977—1.004	0.933—1.036
Range of h k l	−21—19 0—13 0—21	−15—15 −19—19 −12—0	−22—21 0—14 0—20	−18—18 0—19 −17—17
T_{min}, T_{max},	0.227, 0.398	0.432, 0.573	0.791, 0.810	0.940, 0.999
No. of reflections				
Measured	6465	7358	7105	10150
Unique	6071	6451	6465	9124
Observed ($\|F_o\| > 3\sigma(F)$)	4114	5849	5005	7106
Refinement[a)]	4111	5849	5004	7105
R_{int}	0.0473	0.0091	0.0363	0.0149
No. of parameters	407	449	450	575
S	1.3238	0.9998	1.3511	1.3739
$(\Delta/\sigma)_{max}$	0.066	0.026	0.111	0.090
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$	1.768, −1.151	0.631, −0.995	1.143, −0.590	1.187, −0.915
Weighting scheme[b)]	*1	*2	*3	*4
R	0.0402	0.0289	0.0456	0.0539
wR	0.0529	0.0361	0.0567	0.0690
R all observed	0.0416	0.0289	0.0459	0.054

a) Three reflections (−201, −111, 110) for **2a**, one (110) for **3a** and one (220) for **3c**, which were considered to be affected by extinction effects, were omitted from the refinements. b) *1 : $w=1/\{\sigma(F)^2+0.00089|F_o|^2\}$, *2 : $w=1/\{\sigma(F)^2+0.00059|F_o|^2\}$, *3 : $w=1/\{\sigma(F)^2+0.00065|F_o|^2\}$, *4 : $w=1/\{\sigma(F)^2+0.00376|F_o|+0.00065|F_o|^2\}$.

a metallapentalene framework. According to Cambridge Structural Database,[18] only two examples of Pd–carbene complexes having a central Pd–C bond of the metallapentalene framework have been found, [1,8-bis(diphenylphosphino)-9-anthryl]chloropalladium(II)[19] and {2,6-bis[(2,4,6-tri-*t*-butylphenyl)phosphinomethylene]phenyl-κ^2P,P'}chloropalladium(II).[20] In these complexes the Pd atom is also coordinated by two *endo*-cyclic P atoms and an *exo*-cyclic Cl atom. Two other examples with a metallapentalene framework are Pt complexes with a central Pt–N bond, where the

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

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

Atom	x	y	z	B_{eq}/Å^2
(1) **2a**				
Pt(1)	0.38106(2)	0.50200(3)	0.31700(2)	2.86(1)
S(1)	0.33778(15)	0.70468(20)	0.26623(12)	4.40(7)
S(2)	0.41956(13)	0.31195(18)	0.38933(12)	3.88(6)
P(1)	0.41126(12)	0.44563(19)	0.19822(12)	3.13(5)
N(1)	0.3314(3)	0.6811(6)	0.4245(3)	3.28(18)
N(2)	0.3703(4)	0.4789(5)	0.4863(4)	3.17(17)
N(3)	0.2984(4)	0.8840(6)	0.3626(4)	3.95(2)
N(4)	0.4171(4)	0.2804(6)	0.5487(4)	4.28(2)
C(1)	0.3204(4)	0.7667(7)	0.3559(4)	3.54(2)
C(2)	0.4032(4)	0.3532(7)	0.4841(4)	3.41(2)
C(3)	0.3579(4)	0.5581(7)	0.4205(4)	3.04(19)
C(4)	0.3183(6)	0.7324(8)	0.5012(5)	4.8(3)
C(5)	0.2914(5)	0.6242(9)	0.5449(5)	5.0(3)
C(6)	0.3571(5)	0.5193(7)	0.5653(5)	3.7(2)
C(11)	0.2887(7)	0.9732(7)	0.2936(7)	5.5(4)
C(21)	0.4528(6)	0.1528(9)	0.5471(6)	5.6(3)
C(31)	0.3139(5)	0.4088(7)	0.1021(4)	3.5(2)
C(32)	0.3170(6)	0.3284(11)	0.0371(6)	6.6(4)
C(33)	0.2435(7)	0.3171(13)	−0.0391(6)	8.2(4)
C(34)	0.1664(6)	0.3801(11)	−0.0524(5)	6.5(3)
C(35)	0.1613(6)	0.4470(11)	0.0154(7)	6.6(4)
C(36)	0.2349(6)	0.4652(9)	0.0904(6)	5.5(3)
C(41)	0.4679(5)	0.5736(7)	0.1633(5)	3.3(2)
C(42)	0.4555(6)	0.5886(8)	0.0779(5)	4.9(3)
C(43)	0.5073(7)	0.6815(9)	0.0575(6)	6.4(4)
C(44)	0.5664(6)	0.7526(9)	0.1213(6)	6.1(4)
C(45)	0.5774(5)	0.7384(7)	0.2069(6)	4.8(3)
C(46)	0.5262(5)	0.6498(7)	0.2278(5)	3.9(2)
C(51)	0.4839(5)	0.3065(7)	0.2116(4)	3.5(2)
C(52)	0.4565(6)	0.1858(7)	0.2252(6)	4.7(3)
C(53)	0.5133(7)	0.0818(9)	0.2406(6)	6.1(4)
C(54)	0.5960(7)	0.0968(9)	0.2419(7)	6.7(4)
C(55)	0.6253(6)	0.2142(9)	0.2285(7)	6.6(4)
C(56)	0.5684(6)	0.3222(8)	0.2122(6)	5.4(3)
(2) **2b**				
Pt(1)	0.02858(1)	0.21357(1)	0.15119(2)	2.09(1)
S(1)	−0.10902(11)	0.34241(9)	0.03674(15)	3.17(4)
S(2)	0.13264(11)	0.07871(9)	0.26264(14)	3.05(4)
P(1)	0.19227(10)	0.26426(8)	0.17866(13)	2.36(3)
N(1)	−0.2288(3)	0.2267(3)	0.0430(5)	3.13(14)
N(2)	−0.1090(3)	0.0982(3)	0.1689(4)	2.68(12)
N(3)	−0.3448(4)	0.3507(4)	−0.0939(6)	4.45(18)
N(4)	0.0143(4)	−0.0344(3)	0.2848(5)	3.14(14)
C(1)	−0.2413(4)	0.3097(4)	−0.0132(6)	3.23(16)
C(2)	0.0081(4)	0.0397(3)	0.2409(5)	2.55(14)
C(3)	−0.1187(4)	0.1758(3)	0.1181(5)	2.47(14)
C(4)	−0.3403(5)	0.1990(5)	0.0101(8)	4.8(2)
C(5)	−0.3340(5)	0.1550(5)	0.1357(8)	4.5(2)
C(6)	−0.2148(4)	0.0679(4)	0.1547(6)	3.55(18)
C(11)	−0.3583(6)	0.4365(5)	−0.1491(9)	5.8(3)
C(12)	−0.4751(8)	0.4665(7)	−0.2562(12)	8.6(4)
C(21)	0.1349(5)	−0.0923(4)	0.3619(6)	3.54(18)
C(22)	0.1284(5)	−0.1794(4)	0.4021(6)	3.92(19)
C(31)	0.2231(4)	0.2527(3)	−0.0096(5)	2.67(14)
C(32)	0.1694(4)	0.1982(4)	−0.1445(5)	3.13(16)
C(33)	0.1962(5)	0.1831(4)	−0.2901(6)	3.83(18)
C(34)	0.2760(5)	0.2249(4)	−0.2996(7)	4.3(2)
C(35)	0.3310(5)	0.2789(4)	−0.1669(7)	4.4(2)
C(36)	0.3064(5)	0.2923(4)	−0.0213(6)	3.67(19)
C(41)	0.3446(4)	0.1936(3)	0.2761(5)	2.77(15)
C(42)	0.4181(5)	0.2366(4)	0.4019(6)	3.75(18)
C(43)	0.5286(5)	0.1745(5)	0.4742(7)	4.7(2)
C(44)	0.5665(5)	0.0723(5)	0.4200(8)	5.2(3)
C(45)	0.4968(5)	0.0289(4)	0.2893(9)	5.7(3)
C(46)	0.3871(5)	0.0888(4)	0.2201(7)	4.4(2)
C(51)	0.1583(4)	0.3964(3)	0.2859(5)	2.9(15)
C(52)	0.1140(5)	0.4736(4)	0.2084(6)	3.79(19)
C(53)	0.0792(7)	0.5740(4)	0.2920(8)	5.2(3)
C(54)	0.0900(6)	0.5976(4)	0.4525(8)	5.1(2)
C(55)	0.1312(6)	0.5242(5)	0.5291(7)	4.9(2)
C(56)	0.1641(5)	0.4229(4)	0.4476(6)	3.81(19)
(3) **3a**				
Pd(1)	0.08266(2)	0.10296(3)	0.18133(2)	2.94(1)
S(1)	0.21877(8)	0.06754(13)	0.26473(8)	4.33(4)
S(2)	−0.04496(7)	0.14584(12)	0.07621(7)	3.73(3)
P(1)	0.04465(7)	0.07051(10)	0.30677(7)	3.05(3)
N(1)	0.1974(2)	0.1169(4)	0.0876(2)	3.76(11)
N(2)	0.0641(2)	0.1649(3)	−0.0063(2)	3.09(10)
N(3)	0.3258(2)	0.0551(5)	0.1780(3)	5.61(16)
N(4)	−0.0694(2)	0.2019(3)	−0.1007(2)	3.53(11)
C(1)	0.2553(3)	0.0787(5)	0.1752(3)	4.03(14)
C(2)	−0.0200(3)	0.1743(4)	−0.0205(3)	3.08(12)
C(3)	0.1188(3)	0.1320(4)	0.0762(3)	3.08(12)
C(4)	0.2266(3)	0.1325(6)	0.0107(3)	5.7(2)
C(5)	0.1743(3)	0.2242(6)	−0.0557(3)	5.74(19)
C(6)	0.0865(3)	0.1872(5)	−0.0868(3)	4.46(16)
C(11)	0.3876(4)	0.0127(8)	0.2661(4)	8.2(3)
C(21)	−0.1558(3)	0.2147(5)	−0.1162(3)	4.50(16)
C(31)	−0.0627(3)	0.0342(4)	0.2840(3)	3.26(12)
C(32)	−0.0864(3)	−0.0739(5)	0.3111(3)	4.14(15)
C(33)	−0.1685(3)	−0.0979(5)	0.2928(4)	5.05(18)
C(34)	−0.2271(3)	−0.0129(6)	0.2475(4)	5.33(19)
C(35)	−0.2044(3)	0.0958(5)	0.2197(4)	4.87(17)
C(36)	−0.1224(3)	0.1198(4)	0.2383(3)	4.01(15)
C(41)	0.0634(3)	0.2037(4)	0.3818(3)	3.35(13)
C(42)	0.1152(3)	0.2935(5)	0.3742(4)	4.63(17)
C(43)	0.1304(4)	0.3952(5)	0.4298(5)	5.9(2)
C(44)	0.0939(4)	0.4078(5)	0.4928(4)	5.51(19)
C(45)	0.0415(4)	0.3194(5)	0.5002(3)	5.05(18)
C(46)	0.0258(3)	0.2195(4)	0.4450(3)	4.27(16)
C(51)	0.0997(3)	−0.0560(4)	0.3787(3)	3.23(12)
C(52)	0.1113(3)	−0.1595(4)	0.3346(3)	4.09(15)
C(53)	0.1479(4)	−0.2617(5)	0.3833(4)	5.3(2)
C(54)	0.1753(3)	−0.2609(5)	0.4782(4)	4.99(18)
C(55)	0.1658(3)	−0.1591(5)	0.5237(3)	4.77(17)
C(56)	0.1284(3)	−0.0568(5)	0.4749(3)	3.87(14)
C(9)[a]	−0.0010(15)	0.4799(12)	0.0523(12)	14.4(10)
Cl(1)[a]	0.0799(4)	0.4753(5)	0.0282(6)	18.2(4)
Cl(2)[a]	0.0450(7)	0.4978(12)	0.1684(9)	25.9(8)

a) Occupancy factor: 0.5.

(4) **3c**				
Pd(1)	−0.06389(3)	0.27398(3)	−0.11211(3)	3.49(1)
S(1)	0.03488(11)	0.15093(10)	−0.17966(10)	4.62(4)
S(2)	−0.15324(11)	0.39901(10)	−0.01178(10)	4.66(4)
P(1)	−0.12864(9)	0.24486(8)	−0.28184(9)	3.29(3)
N(1)	0.0620(3)	0.2354(4)	0.0357(3)	5.13(14)
N(2)	−0.0386(3)	0.3576(3)	0.1244(3)	4.68(13)
N(3)	0.1575(4)	0.1116(4)	−0.0498(3)	5.35(15)
N(4)	−0.1574(4)	0.4610(3)	0.2209(3)	5.15(14)
C(1)	0.0911(4)	0.1611(4)	−0.0607(4)	4.58(15)
C(2)	−0.1186(4)	0.4127(4)	0.1225(4)	4.32(14)
C(3)	−0.0082(4)	0.2900(4)	0.0311(4)	4.31(14)
C(4)	0.1064(6)	0.2448(7)	0.1403(5)	8.5(3)
C(5)[a]	0.0376(8)	0.2921(6)	0.2462(7)	6.5(3)
C(6)	−0.0008(5)	0.3741(5)	0.2338(4)	6.4(2)
Cl(1)	0.3344(2)	−0.2131(2)	−0.3867(2)	9.3(9)

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Cl(2)	−0.4734(2)	0.7271(2)	0.3376(3)	11.08(10)	C(36)	0.0814(4)	0.2539(4)	−0.4256(4)	4.90(16)
C(11)	0.1954(4)	0.0359(4)	−0.1353(4)	4.58(15)	C(41)	−0.2496(4)	0.1442(3)	−0.2684(4)	3.96(13)
C(12)	0.2426(4)	0.0457(4)	−0.2543(4)	4.83(16)	C(42)	−0.2624(4)	0.0752(4)	−0.1939(5)	5.29(18)
C(13)	0.2836(4)	−0.0308(4)	−0.3308(4)	5.14(17)	C(43)	−0.3569(5)	−0.0010(4)	−0.1787(6)	6.8(2)
C(14)	0.2805(5)	−0.1164(4)	−0.2903(5)	5.48(18)	C(44)	−0.4340(5)	−0.0086(5)	−0.2394(7)	7.5(3)
C(15)	0.2349(5)	−0.1294(4)	−0.1733(6)	6.3(2)	C(45)	−0.4218(5)	0.0579(5)	−0.3140(7)	7.1(3)
C(16)	0.1925(5)	−0.0530(4)	−0.0969(5)	5.63(19)	C(46)	−0.3299(4)	0.1356(4)	−0.3286(5)	5.69(19)
C(21)	−0.2353(4)	0.5199(4)	0.2372(4)	4.96(16)	C(51)	−0.1735(4)	0.3453(3)	−0.3207(3)	3.60(12)
C(22)	−0.3183(5)	0.5161(5)	0.3427(5)	6.6(2)	C(52)	−0.2606(4)	0.3820(4)	−0.2420(4)	4.68(16)
C(23)	−0.3924(5)	0.5762(5)	0.3725(6)	7.6(3)	C(53)	−0.2971(5)	0.4581(4)	−0.2679(5)	5.63(19)
C(24)	−0.3839(5)	0.6445(4)	0.2986(6)	6.8(2)	C(54)	−0.2492(5)	0.4982(4)	−0.3720(5)	5.55(19)
C(25)	−0.3051(5)	0.6493(4)	0.1940(6)	6.7(2)	C(55)	−0.1624(5)	0.4615(4)	−0.4505(4)	5.48(18)
C(26)	−0.2316(5)	0.5865(4)	0.1658(5)	6.07(19)	C(56)	−0.1244(4)	0.3854(3)	−0.4257(4)	4.21(14)
C(31)	−0.0269(4)	0.2062(3)	−0.4130(3)	3.62(12)	Cl(11)	0.4425(3)	−0.2083(2)	−0.0220(3)	14.5(13)
C(32)	−0.0542(4)	0.1283(4)	−0.4981(4)	4.70(15)	Cl(12)	0.5548(3)	−0.2978(2)	−0.2421(2)	14.00(14)
C(33)	0.0277(6)	0.0978(4)	−0.5919(5)	6.3(2)	Cl(13)	0.4981(3)	−0.3945(3)	−0.0400(3)	18.2(2)
C(34)	0.1336(5)	0.1448(5)	−0.6035(5)	6.7(2)	C(60)	0.4660(6)	−0.3152(5)	−0.1081(8)	9.5(3)
C(35)	0.1627(5)	0.2236(5)	−0.5210(5)	6.4(2)	C(5b)[b)]	0.0992(14)	0.3378(13)	0.2180(16)	5.2(3)

Occupancy factor: a) 0.7, b) 0.3.

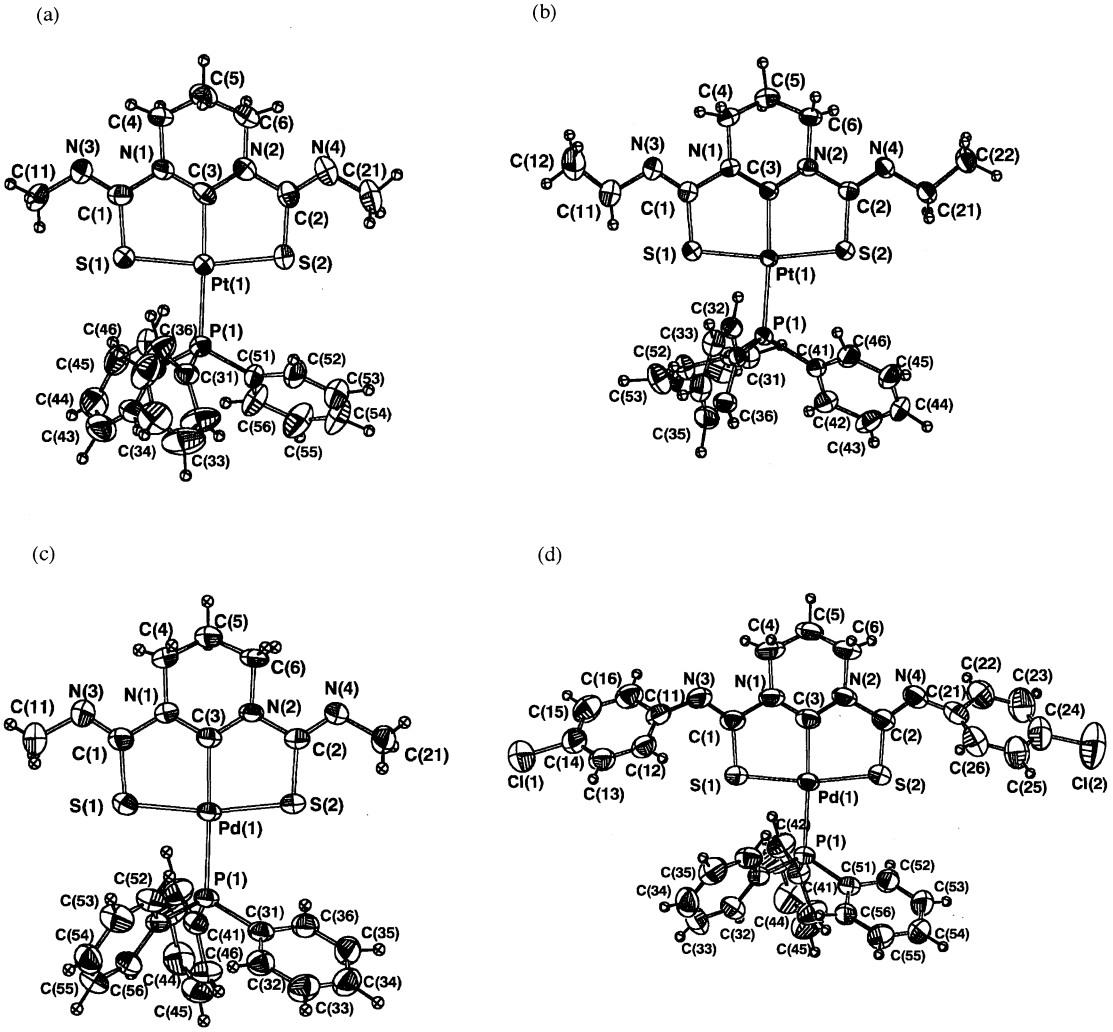


Fig. 1. ORTEP drawings with the atom-numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å. (a) **2a**, (b) **2b**, (c) **3a**, and (d) **3c**.

Pt atom is also coordinated by an *endo*-cyclic C atom and two (*endo*- and *exo*-cyclic) N atoms.[21] In these complexes,

Table 3. Bond Lengths (l) and Bond Angles (θ) of Non-H Atoms

	2a	**2b**	**3a**	**3c**
M	Pt	Pt	Pd	Pd
Lengths	l/Å	l/Å	l/Å	l/Å
M(1)–S(1)	2.284(2)	2.290(1)	2.294(1)	2.284(1)
M(1)–S(2)	2.279(2)	2.284(1)	2.281(1)	2.289(1)
M(1)–P(1)	2.304(2)	2.315(1)	2.331(1)	2.333(1)
M(1)–C(3)	2.001(8)	1.992(5)	2.005(5)	1.990(5)
S(1)–C(1)	1.756(8)	1.749(6)	1.757(6)	1.738(5)
S(2)–C(2)	1.763(8)	1.764(6)	1.757(5)	1.747(5)
N(1)–C(1)	1.409(9)	1.436(8)	1.429(5)	1.426(6)
N(1)–C(3)	1.363(10)	1.338(5)	1.340(6)	1.340(8)
N(1)–C(4)	1.482(11)	1.486(9)	1.490(8)	1.488(9)
N(2)–C(2)	1.422(9)	1.416(5)	1.420(6)	1.442(8)
N(2)–C(3)	1.327(9)	1.341(7)	1.337(5)	1.349(6)
N(2)–C(6)	1.481(11)	1.482(8)	1.478(7)	1.479(7)
N(3)–C(1)	1.291(10)	1.268(6)	1.256(7)	1.275(8)
N(3)–C(11)	1.442(12)	1.466(11)	1.474(7)	1.400(7)
N(4)–C(2)	1.267(10)	1.270(8)	1.266(5)	1.271(6)
N(4)–C(21)	1.456(11)	1.457(6)	1.457(7)	1.404(8)
C(4)–C(5)	1.500(13)	1.481(12)	1.491(8)	1.469(10)
C(5)–C(6)	1.481(12)	1.496(7)	1.496(8)	1.404(13)
C(4)–C(5b)				1.452(19)
C(6)–C(5b)				1.454(22)
Angles	θ/°	θ/°	θ/°	θ/°
S(1)–M(1)–S(2)	169.45(8)	168.94(5)	169.26(5)	169.06(5)
S(1)–M(1)–P(1)	93.09(8)	91.95(5)	93.94(5)	92.58(5)
S(1)–M(1)–C(3)	85.2(2)	84.43(14)	84.45(14)	84.33(15)
S(2)–M(1)–P(1)	97.45(8)	99.07(5)	96.79(5)	98.29(5)
S(2)–M(1)–C(3)	84.2(2)	84.56(14)	84.82(14)	84.77(15)
P(1)–M(1)–C(3)	177.5(2)	176.27(14)	178.25(14)	176.46(15)
M(1)–S(1)–C(1)	98.7(3)	99.36(19)	99.03(18)	99.35(19)
M(1)–S(2)–C(2)	99.2(3)	99.07(17)	99.01(16)	99.22(18)
C(1)–N(1)–C(3)	119.9(6)	119.8(4)	119.6(4)	119.1(5)
C(1)–N(1)–C(4)	117.6(6)	117.6(5)	117.9(4)	118.0(5)
C(3)–N(1)–C(4)	122.4(6)	122.6(5)	122.4(4)	122.8(5)
C(2)–N(2)–C(3)	119.3(6)	119.8(4)	120.1(4)	119.0(4)
C(2)–N(2)–C(6)	118.2(6)	116.2(4)	117.2(4)	117.1(5)
C(3)–N(2)–C(6)	122.4(6)	124.0(4)	122.6(4)	123.8(5)
C(1)–N(3)–C(11)	119.2(8)	117.6(6)	118.1(6)	123.7(5)
C(2)–N(4)–C(21)	118.2(7)	117.3(4)	118.3(4)	123.6(5)
S(1)–C(1)–N(1)	116.9(5)	115.5(4)	116.1(4)	116.4(4)
S(1)–C(1)–N(3)	124.5(6)	127.0(5)	128.1(4)	127.9(5)
N(1)–C(1)–N(3)	118.7(7)	117.5(5)	115.8(5)	115.6(5)
S(2)–C(2)–N(2)	116.1(5)	115.9(3)	116.2(3)	115.9(4)
S(2)–C(2)–N(4)	125.6(6)	126.0(4)	126.4(4)	129.3(4)
N(2)–C(2)–N(4)	118.3(7)	118.1(4)	117.4(4)	114.8(5)
M(1)–C(3)–N(1)	119.1(5)	120.6(4)	120.4(3)	120.7(4)
M(1)–C(3)–N(2)	121.2(6)	120.6(3)	119.8(3)	120.5(4)
N(1)–C(3)–N(2)	119.6(7)	118.8(4)	119.8(4)	118.8(5)
N(1)–C(4)–C(5)	108.7(7)	109.6(6)	109.2(5)	111.1(7)
C(4)–C(5)–C(6)	109.9(8)	110.8(6)	109.6(5)	117.4(9)
N(2)–C(6)–C(5)	110.4(7)	109.9(5)	110.3(5)	111.7(7)
N(3)–C(11)–C(12)		111.1(7)		124.7(5)
N(3)–C(11)–C(16)				117.3(5)
N(4)–C(21)–C(22)		111.1(5)		116.2(5)
N(4)–C(21)–C(26)				126.0(5)
C(4)–C(5b)–C(6)				115.3(13)
N(1)–C(4)–C(5b)				113.9(10)
N(2)–C(6)–C(5b)				113.1(9)

the Pd–C and Pt–C distances are 2.006—2.041 Å.

Crystal Structures. The crystal structures of **2a**, **2b**, **3a**, and **3c** are shown in Figs. 2, 3, 4, and 5, respectively. Figure 6 shows the molecular overlapping in crystals of **2a**, **2b**, **3a**, and **3c**.

Although the cell dimensions of **2a** and **3a** are very similar, two crystals are not isomorphous, as shown in Figs. 2 and 4. It is very interesting that the molecular packings of **2a** and **3a** are quite different from each other, in spite of having the same molecular dimensions. In crystals of **2a** and **3a**, the metallapentalene frameworks are overlapped with each other, related by the center of symmetry, although the interplanar distance of **3a** (3.498(4) Å) is significantly shorter than that of **2a** (3.712(8) Å). Pd and S atoms in **3a** are closely overlapping to the N atoms to form a dimer-like contact with the intermolecular distances of 3.560(4) and 3.567(4) Å for Pd(1)···N(4^{i}) and S(2)···N (2^{i}) (i=$-x$, $-y$, $-z$), respectively. In the crystal structure of **3a**, solvent molecules with an occupancy factor of 0.5 lie near to the center of symmetry, so that the disordered CH_2Cl_2 molecules are located between the dimer-like pentalene planes. In the Pt complex, **2a**, no such short contacts were observed, and no crystal solvents

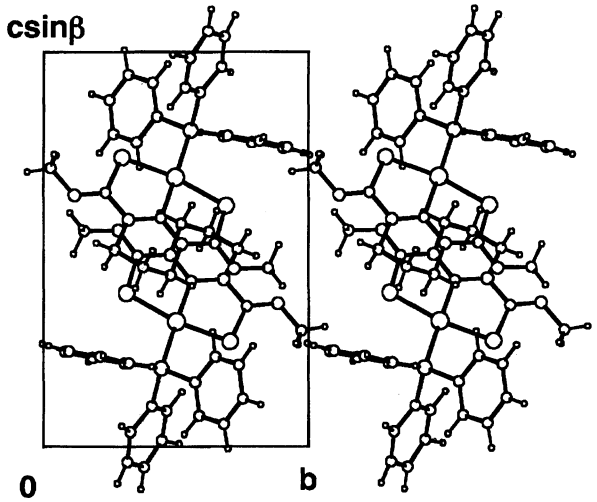


Fig. 2. Projection of the crystal structure of **2a** viewed along the *a* axis within the range x=0.25—0.75.

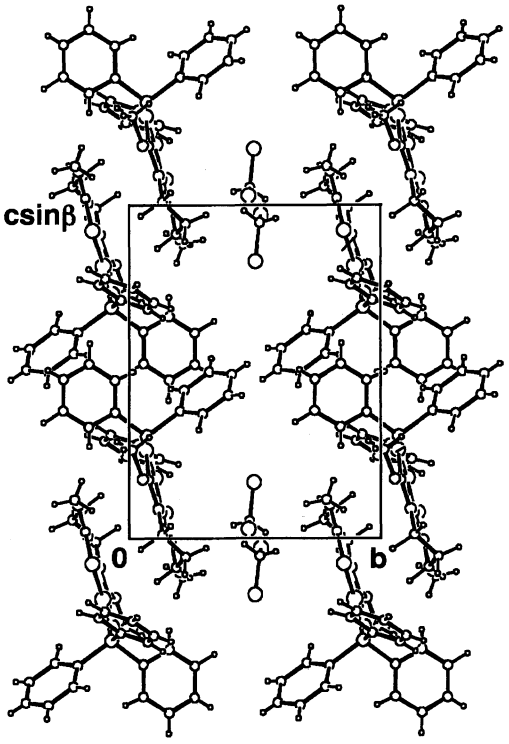


Fig. 4. Projection of the crystal structure of **3a** viewed along the *a* axis within the range x=−0.25—0.25.

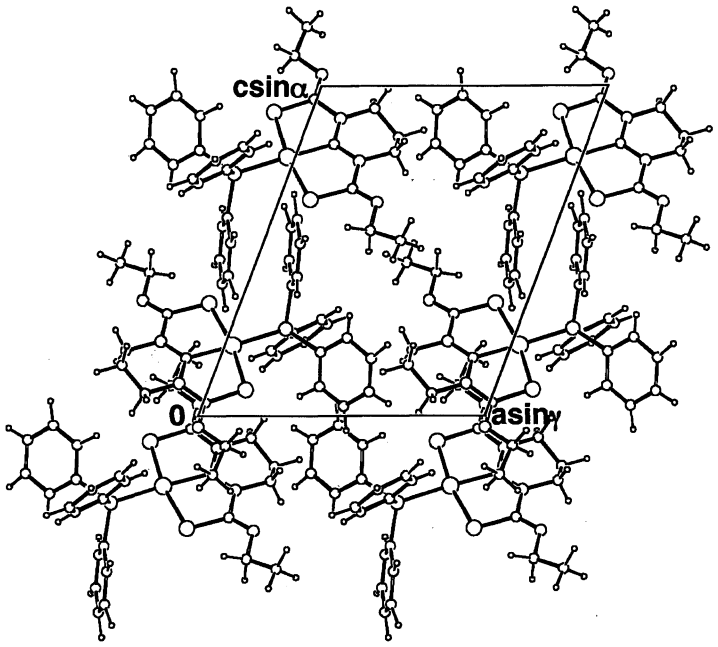


Fig. 3. Projection of the crystal structure of **2b** viewed along the *b* axis.

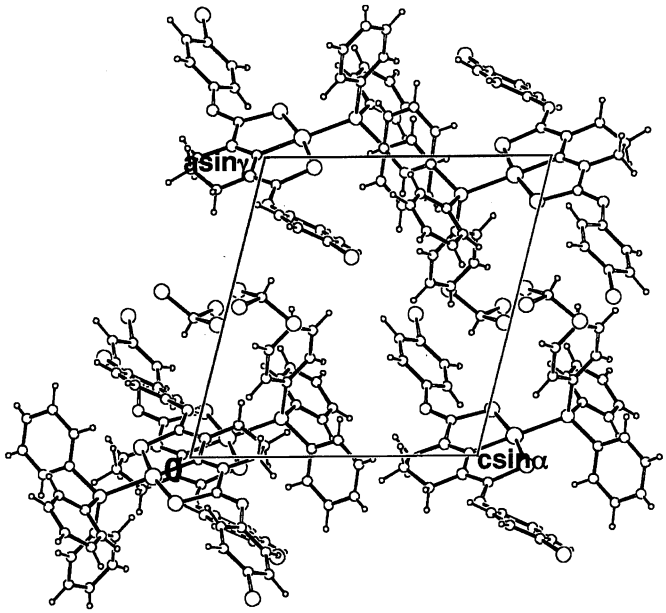


Fig. 5. Projection of the crystal structure of **3c** viewed along the *b* axis.

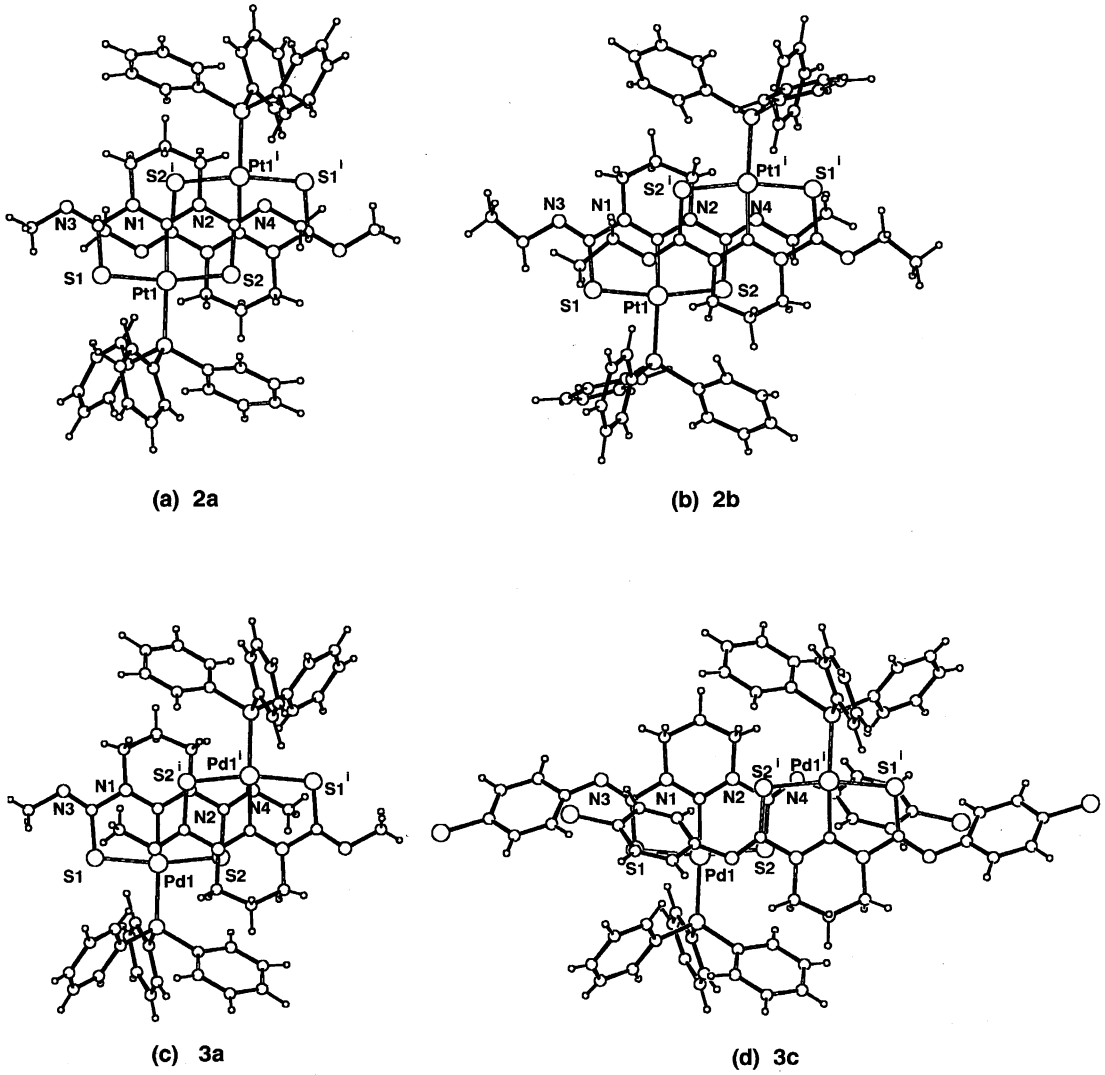


Fig. 6. Overlappings of the metallapentalene planes. (a) **2a** (i=1−*x*, 1−*y*, 1−*z*), (b) **2b** (i=−*x*, −*y*, −*z*), (c) **3a** (i=−*x*, −*y*, −*z*), and (d) **3c** (i=−*x*, −*y*, −*z*).

were observed. The difference in these crystal structures, **2a** and **3a**, may be ascribed to that of the sizes of the lobes of lone-paired electrons of Pt and Pd perpendicular to the metallapentalene plenes.

In the ethyl derivative, **2b**, one of the ethyl groups, C(2)–N-(4)–C(21)–C(22), overlaps with the pentalene plane related to the center of symmetry. The interplanar distance between the pentalene rings is 3.739(6) Å.

In **3c**, a metallapentalene framework only slightly overlaps the other one because of the steric effect of non-conjugated *p*-Cl–phenyl groups. The interplanar distances between the pentalene rings is 3.731(5) Å. In crystals, $CHCl_3$ molecules are loosely included as crystal solvents among PPh_3 groups. The unstability of crystals of **3c** may be ascribed to a collapse of the crystal lattice upon gradually withdrawing the solvent molecules.

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