Structures and Formation Mechanism of Novel Metal–Carbene Complexes Derived from Hypervalent Thiadiselenadiazapentalenes

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2,3,4,5-Tetrahydro-3,4-dimethylene-2,5-bis(4-chlorophenylimino)-6aλ^4-thia-1,6-diselena-3,4-diazapentalene (**6**), which contains a hypervalent sulfur atom, has been found to give novel complexes by treating with [$Pt(PPh_3)_4$], [$Pd(PPh_3)_4$], and [$RhCl(PPh_3)_3$]. X-Ray investigations have revealed that the resultant complexes are novel metal–carbene complexes: {1,1′-(perhydroimidazole-1,3-diyl-$\varkappa C^2$)bis[(4-chlorophenylimino)methaneselenolato-$\varkappa^2 SeSe'$]}(triphenylphosphine)platinum(II) (**8**), {1,1′-(perhydroimidazole-1,3-diyl-$\varkappa C^2$)bis[(4-chlorophenylimino)methaneselenolato-$\varkappa^2 SeSe'$]}(triphenylphosphine)palladium(II) (**9**), and *trans*(*P*,*P*′)-(chloro){(perhydroimidazole-1,3-diyl-$\varkappa C^2$)bis[(4-chrolophenylimino)methaneselenolato-$\varkappa^2 SeSe'$]}bis(triphenylphosphine)rhodium(III) (**10**). The central sulfur atom in **6** was substituted by a metal atom to form metal–selenium bonds in the resultant metallapentalene framework. The structure of complex (**11**), obtained from thiatetraazapentalene-2,5-diselone with [$Pd(PPh_3)_3$], was also determined by an X-ray analysis. This complex was also a metal–carbene complex with a metallapentalene framework: {1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(4-chlorophenylimino)methaneselenolato-$\varkappa^2 SeSe'$]}(triphenylphosphine)palladium(II) (**11**). The final *R* values are 0.038, 0.034, 0.046, and 0.032 for the 4494, 4234, 3919, and 4451 observed reflections for **8**, **9**, **10**, and **11**, respectively. The fact that similar metal–carbene complexes with a metallapentalene framework were obtained from both thiadiselenadiazapentalenes and thiatetraazapentalene-2,5-dithione/diselones confirms the previously proposed formation mechanism of these metal–carbene complexes.

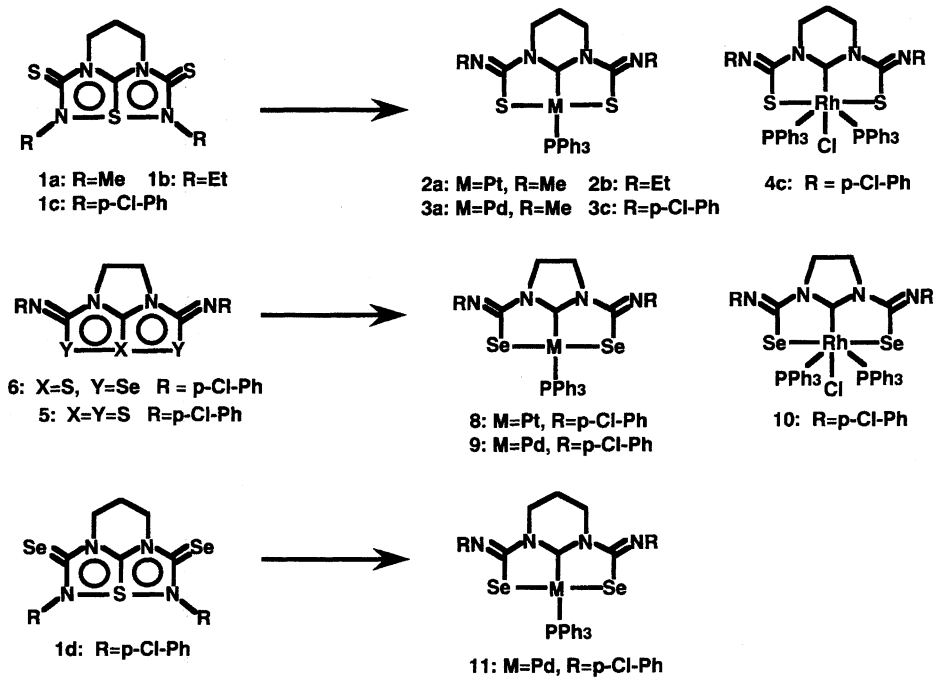
Novel metal–carbene complexes (**2**—**4**) with a metallapentalene framework were obtained from 6a-thia-1,3,4,6-tetraazapentalene-2,5-dithiones (**1**) by treating with [$Pt(PPh_3)_4$], [$Pd(PPh_3)_4$], and [$RhCl(PPh_3)_3$]. X-Ray investigations revealed that the central hypervalent sulfur atom in **1** was substituted by a metal atom, and that thioamide groups on one or both sides rotated to form metal–sulfur bonds in the resultant metallapentalene framework (Scheme 1).[1—3] From the results of the structures of these carbene complexes and MO calculations on frontier-orbital electron-densities of **1** and the related compounds, we proposed the formation mechanism of the metal–carbene complexes shown in Scheme 2.[4] In this mechanism, the weak hypervalent S–N bonds are easily cleaved after the central carbon atom of the pentalene framework is attacked by the nucleophilic metal reagent (A and B), and the S atoms of the thiocarbonyl groups work as a nucleophile (C). From a detailed examination of this formation mechanism, we noticed that the intermediate structure (B) of this Scheme may be equivalent to that of B′ in Scheme 3 derived from a trithiadiazapentalene (**1′**), since the thioamide moiety in B may be rotated in solutions. Thus, the same complex should be obtained from **1′** through the formation mechanism in the Scheme 3, if the sulfur atom of the thioamide moiety in B′ works as a nucleophilic ligand.

Compounds **5** and **6** were obtained from five-membered thioureas, although **1′** could not be synthesized from a six-membered thiourea from which **1** had been obtained.[5] A calculation of the frontier electron densities of **5** showed that large HOMO electron densities exist at the side sulfur atoms, while the corresponding densities were found at the sulfur atoms of the thiocarbonyl groups in the case of **1**.[6] This suggests that metal–carbene complexes should be obtained from **5** instead of **1′**. Recently, metal complexes, **8**—**10**, have been obtained from thiadiselenapentalene, **6**. Unfortunately, compound **5** is very unstable in solutions used to form the complexes. A Pd complex (**11**) was also obtained from a thiatetraazapentalene-2,5-diselone (**1d**). X-Ray analyses were performed on these complexes in order to investigate the structures and the formation mechanism.

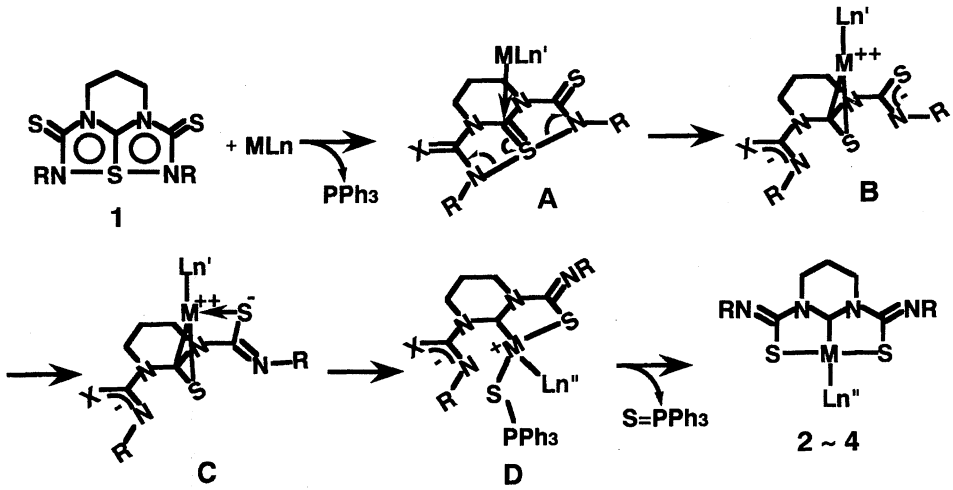
Experimental

Crystals of **8**—**11** for X-ray studies were grown from CH_2Cl_2/hexane solutions. Crystal data, details concerning data collection, and structure refinements are listed in Table 1. The intensity data were measured using a Rigaku diffractometer AFC-7R with a graphite monochromator. Absorption corrections were applied by the ψ-scan method for **8**—**10**, and by the numerical method for **11**.

The structures were solved by the Patterson method and the direct method using the programs DIRDIF92[7] and SAPI91.[8] The positions of the H atoms, except for several terminal positions, were



Scheme 1.



Scheme 2.

obtained from D-maps. The remaining H atoms were located from calculations and included in the refinements with a constraint. The structures were refined by full-matrix least-squares with anisotropic temperature factors for non-H atoms and isotropic ones for H atoms. The function $\sum w(|F_o| - k|F_c|)^2$ was minimized. The final R values are 0.038, 0.034, 0.046, and 0.032 for 4494, 4234, 3919, and 4451 observed reflections for **8**, **9**, **10**, and **11**, respectively.

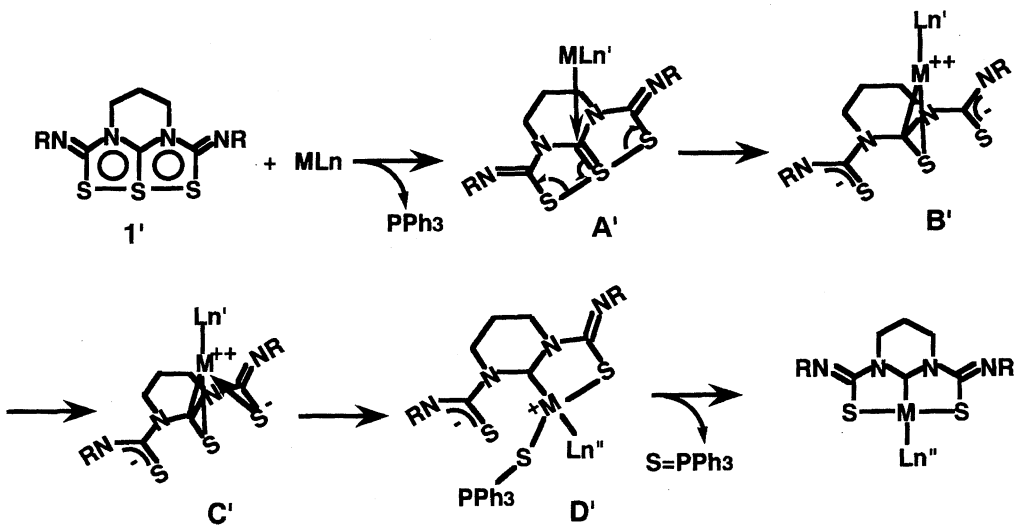
The atomic scattering factors were used from International Tables for X-Ray Crystallography.[9] The calculations of the refinements and structural geometry were performed using the programs teXsan,[10] UNICS III,[11] and ORTEP II.[12] The final atomic parameters are given in Table 2.[13]

Discussion

Molecular Structures. The molecular structures along with the atomic numbering are shown in Fig. 1. Selected bond distances and angles are listed in Table 3. Table 4 gives a comparison of the bond lengths and angles of these complexes, as well as those of the metallapentalene complexes, **2**—**4**.[2,3]

X-Ray analyses revealed that complexes (**8**—**11**) were also novel metal–carbene complexes coordinated by Se atoms: {1,1′-(perhydroimidazole-1,3-diyl-$\varkappa C^2$)bis[(4-chlorophenylimino)methaneselenolato-$\varkappa^2 SeSe'$]}(triphenylphosphine)-platinum(II) (**8**), {1,1′-(perhydroimidazole-1,3-diyl-$\varkappa C^2$)-bis[(4-chlorophenylimino)methaneselenolato-$\varkappa^2 SeSe'$]}(triphenylphosphine)palladium(II) (**9**), *trans*(*P*,*P*′)-(chloro)-{(perhydroimidazole-1,3-diyl-$\varkappa C^2$)bis[(4-chrolophenylimino)methaneselenolato-$\varkappa^2 SeSe'$]}bis(triphenylphosphine)-rhodium(III) (**10**), and {1,1′-(perhydropyrimidine-1,3-diyl-$\varkappa C^2$)bis[(4-chlorophenylimino)methaneselenolato-$\varkappa^2 SeSe'$]}(triphenylphosphine)palladium(II) (**11**).

In each complex, **8** and **9**, the central hypervalent sulfur atom of the thiadiselenadiazapentalene framework of **6** is substituted by the metal atom to form a square-planar config-



Scheme 3.

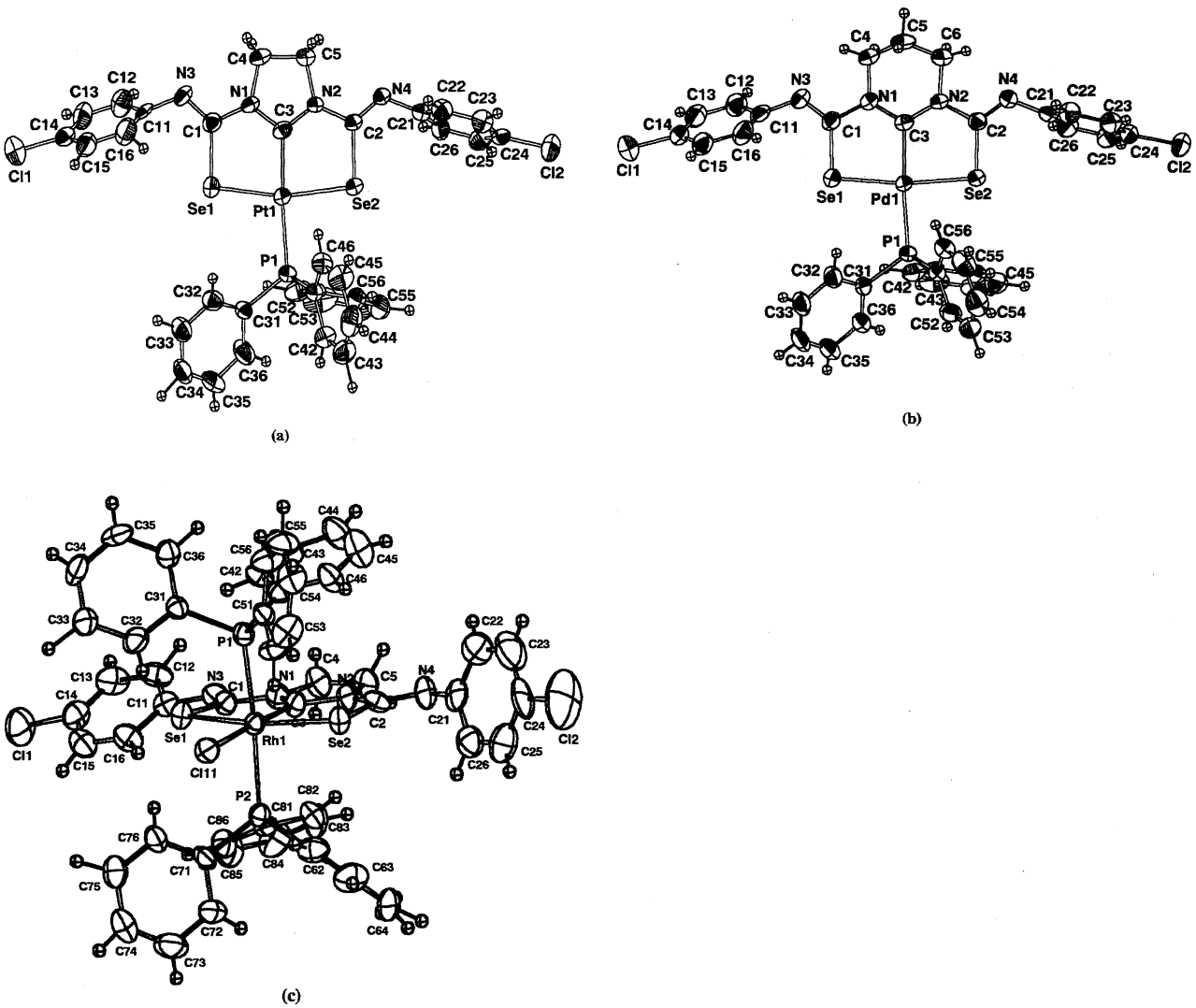


Fig. 1. ORTEP drawings of the molecules with the atom-numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å. (a) **8**, (b) **11**, and (c) **10**.

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

	8 $C_{35}H_{27}Cl_2N_4PPtSe_2$	**9** $C_{35}H_{27}Cl_2N_4PPdSe_2$	**11** $C_{36}H_{29}Cl_2N_4PPdSe_2$	**10** $C_{53}H_{42}Cl_3N_4P_2Se_2Ph$
F.W.	958.51	869.82	883.85	1164.07
Color	Yellow	Yellow	Yellow	Yellow
Crystal shape	Plate	Plate	Plate	Prism
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pbcn*	*Pbcn*	*Pbcn*	$P2_1/n$
a/Å	22.647(2)	22.662(3)	22.622(3)	16.820(2)
b/Å	17.664(3)	17.681(2)	17.726(2)	18.917(2)
c/Å	17.121(2)	17.108(2)	17.322(2)	15.063(2)
β/°	90.0	90.0	90.0	91.86(1)
V/Å^3	6849(1)	6854(1)	6945(1)	4790.0(9)
Z	8	8	8	4
D_x/g cm^{-3}	1.859	1.686	1.690	1.614
$F(000)$	3680	3424	3488	2328
Diffractometer	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R	Rigaku ACF7R
Radiation	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
λ/Å	0.71069	0.71069	0.71069	0.71069
μ/mm^{-1}	6.441	2.900	2.864	2.152
Crystal size/mm	0.59 × 0.23 × 0.02	0.45 × 0.20 × 0.05	0.20 × 0.05 × 0.25	0.21 × 0.07 × 0.06
Temperature/K	294	296	296	294
Cell dimensions				
2θ range/°	30.3—36.8	25.21—34.85	34.00—34.98	25.04—34.98
No. of refs.	25	23	24	24
Scan mode	2θ–ω	2θ–ω	2θ–ω	2θ–ω
Scan speed ω/° min^{-1}	16.0	16.0	16.0	16.0
Scan width $\Delta\omega$/°	1.15+0.30 tan θ	0.94+0.30 tan θ	1.26+0.30 tan θ	1.15+0.30 tan θ
$2\theta_{max}$/°	55.0	55.0	55.0	55.0
hkl_{min}—hkl_{max}	−29—0, −22—0, 0—22	0—29, 0—22, −22—0	0—29, 0—23, −22—0	−21—21, −24—0, 0—19
Standard refs.	3 (every 150 refs.)	3 (every 150 refs.)	3 (every 150 refs.)	3 (every 150 refs.)
Intensity variation	0.989—1.002	0.985—1.000	0.988—1.006	0.987—1.010
Measured refs.	8588	8582	8712	11770
Independent refs.	8588	8582	8712	11355
Observed refs. ($I > 3.0\sigma(I)$)	4494	4234	4451	3919
R_{int}	—	—	—	0.051
Absorption	ψ-scan	ψ-scan	ψ-scan	Numerical
T_{min}—T_{max}	0.2672—1.0000	0.7139—1.0000	0.7384—1.0000	0.8493—0.8888
Parameters refined	514	514	531	754
R	0.038	0.034	0.032	0.046
R_w	0.034	0.027	0.030	0.046
S	1.76	1.36	1.29	1.17
$(\Delta/\sigma)_{max}$	0.14	0.15	0.12	0.11
$(\Delta\rho)_{min}$, $(\Delta\rho)_{max}$/eÅ^{-3}	−1.21, 2.65	−0.40, 0.34	−0.44, 0.34	−0.52, 0.57
Least squares weight	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$

uration. The four coordination sites are occupied by a tridentate ligand containing a diselenapentalene framework and a PPh_3 ligand. 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 molecular feature of **11** is very similar to those of **8** and **9**, although **11** was synthesized from thiatetraazapentalene-2,5-diselone. The maximum deviations from the plane, defined by eight atoms of the pentalene ring, are 0.121(8), 0.116(5), and 0.096(3) Å for **8**, **9**, and **11**, respectively.

The distances of the Pt–Se bonds in the Pt-complex (**8**) are 2.4157(9) and 2.4350(9) Å. These lengths are longer than the Pt–S bonds in **2** by the difference in the covalent radii of Se and S. The lengths of the Pt–P (2.319(2) Å) and Pt–C (1.981(9) Å) bonds are similar to those of the corresponding bonds of **2** (2.310 and 1.997 Å for Pt–P and Pt–C, respectively). The angle of Se–M–Se is 166.71(3)°, which is smaller than that of **2**. For the Pd-complex (**9**), a similar geometry is observed. For the other Pd-complex **11**, which has a perhydropyrimidine moiety instead of the perhydroimidazole moiety in **8** and **9**, the lengths of Pd–Se bonds (2.3800(6) and 2.4018(6) Å) are slightly shorter than those of **9**. This difference is related to that of the bond angles, C–N–C and Pd–C–N (δ, and ε in Table 4), between **9** and **11**. These innerpentalene angles closely relate to the outer five and six-membered rings.

In the Rh-complex **10**, the central sulfur atom of the thiadiselenadiazapentalene framework of **6** is substituted by the Rh atom as in the case of Pt and Pd complexes, **8** and **9**. The Rh atom is coordinated by Se, Se, C, and Cl atoms

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

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

(1) **8** (M=Pt)					(2) **9** (M=Pd)				
Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Pt(1)	0.083690(15)	0.197193(17)	0.11287(2)	2.573(7)	Pd(1)	0.083698(16)	0.19728(2)	0.11280(3)	2.731(8)
Se(1)	0.04862(4)	0.32629(5)	0.11694(6)	3.33(2)	Se(1)	0.04808(2)	0.32592(3)	0.11667(4)	3.42(1)
Se(2)	0.09588(4)	0.06034(5)	0.11862(6)	3.45(2)	Se(2)	0.09618(2)	0.06061(3)	0.11929(4)	3.71(1)
Cl(1)	−0.06031(15)	0.67802(15)	0.1405(2)	6.6(1)	Cl(1)	−0.06080(8)	0.67755(9)	0.14020(13)	6.62(5)
Cl(2)	0.10846(13)	−0.32091(13)	0.10991(18)	5.27(7)	Cl(2)	0.10859(7)	−0.32108(8)	0.10982(11)	5.36(4)
P(1)	0.18152(10)	0.21587(12)	0.07784(14)	2.77(5)	P(1)	0.18190(6)	0.21661(7)	0.07671(9)	2.82(3)
N(1)	−0.0422(3)	0.2231(4)	0.1473(4)	3.1(2)	N(1)	−0.04187(18)	0.2231(2)	0.1478(3)	3.1(1)
N(2)	−0.0208(3)	0.1031(4)	0.1462(4)	2.9(2)	N(2)	−0.02083(18)	0.1034(2)	0.1465(3)	3.1(1)
N(3)	−0.0756(3)	0.3454(4)	0.1521(5)	4.0(2)	N(3)	−0.0755(2)	0.3441(2)	0.1524(3)	3.9(1)
N(4)	−0.0107(3)	−0.0249(4)	0.1394(4)	3.1(2)	N(4)	−0.01052(17)	−0.0251(2)	0.1396(3)	3.2(1)
C(1)	−0.0324(4)	0.3013(5)	0.1418(5)	3.1(2)	C(1)	−0.0316(2)	0.3014(3)	0.1422(3)	3.2(1)
C(2)	0.0135(4)	0.0381(5)	0.1362(5)	2.8(2)	C(2)	0.0143(2)	0.0384(3)	0.1369(3)	2.9(1)
C(3)	0.0006(4)	0.1726(5)	0.1387(5)	2.8(2)	C(3)	0.0012(2)	0.1730(3)	0.1398(3)	2.9(1)
C(4)	−0.0999(4)	0.1869(6)	0.1615(7)	4.0(3)	C(4)	−0.0997(3)	0.1876(4)	0.1639(4)	4.4(2)
C(5)	−0.0858(5)	0.1027(5)	0.1555(7)	3.8(2)	C(5)	−0.0860(2)	0.1022(3)	0.1576(4)	3.8(1)
C(11)	−0.0686(4)	0.4244(5)	0.1480(6)	3.3(2)	C(11)	−0.0694(2)	0.4242(3)	0.1479(4)	3.7(1)
C(12)	−0.0755(6)	0.4668(6)	0.2150(6)	4.5(3)	C(12)	−0.0756(3)	0.4657(4)	0.2151(4)	4.7(2)
C(13)	−0.0720(5)	0.5433(6)	0.2133(7)	4.5(3)	C(13)	−0.0716(3)	0.5431(4)	0.2130(4)	5.0(2)
C(14)	−0.0620(4)	0.5799(5)	0.1429(6)	3.9(3)	C(14)	−0.0630(3)	0.5789(3)	0.1435(4)	4.2(2)
C(15)	−0.0559(5)	0.5401(6)	0.0746(7)	5.0(3)	C(15)	−0.0564(3)	0.5396(4)	0.0737(4)	5.0(2)
C(16)	−0.0595(5)	0.4618(6)	0.0779(7)	5.0(3)	C(16)	−0.0602(3)	0.4607(4)	0.0766(4)	5.0(2)
C(21)	0.0219(4)	−0.0927(5)	0.1303(5)	3.0(2)	C(21)	0.0218(2)	−0.0930(3)	0.1308(3)	3.1(1)
C(22)	0.0142(4)	−0.1355(5)	0.0631(6)	3.5(2)	C(22)	0.0139(2)	−0.1361(3)	0.0635(3)	3.3(1)
C(23)	0.0411(5)	−0.2062(6)	0.0569(5)	3.6(2)	C(23)	0.0408(3)	−0.2061(3)	0.0566(4)	4.1(2)
C(24)	0.0782(4)	−0.2318(4)	0.1166(5)	2.8(2)	C(24)	0.0762(2)	−0.2314(3)	0.1165(4)	3.4(1)
C(25)	0.0855(5)	−0.1887(6)	0.1838(6)	4.0(2)	C(25)	0.0853(3)	−0.1891(3)	0.1841(3)	3.9(1)
C(26)	0.0590(5)	−0.1183(5)	0.1908(6)	3.7(2)	C(26)	0.0587(3)	−0.1191(3)	0.1907(4)	3.6(1)
C(31)	0.2123(4)	0.3096(5)	0.0604(5)	3.2(2)	C(31)	0.2133(2)	0.3097(3)	0.0591(3)	3.0(1)
C(32)	0.1818(5)	0.3614(6)	0.0162(6)	3.6(3)	C(32)	0.1819(3)	0.3622(3)	0.0164(4)	3.9(2)
C(33)	0.2058(6)	0.4296(6)	−0.0077(6)	4.4(3)	C(33)	0.2071(3)	0.4286(4)	−0.0078(4)	4.8(2)
C(34)	0.2648(6)	0.4441(6)	0.0111(6)	4.6(3)	C(34)	0.2656(4)	0.4446(4)	0.0105(4)	5.1(2)
C(35)	0.2963(6)	0.3940(7)	0.0547(10)	5.9(4)	C(35)	0.2970(3)	0.3934(4)	0.0536(5)	5.6(2)
C(36)	0.2715(5)	0.3267(6)	0.0809(7)	5.0(3)	C(36)	0.2713(3)	0.3267(4)	0.0786(5)	4.9(2)
C(41)	0.1997(4)	0.1681(4)	−0.0135(5)	2.8(2)	C(41)	0.2006(2)	0.1685(3)	−0.0140(3)	2.7(1)
C(42)	0.2587(5)	0.1641(6)	−0.0379(6)	3.8(3)	C(42)	0.2586(3)	0.1639(3)	−0.0405(4)	3.8(1)
C(43)	0.2725(5)	0.1303(6)	−0.1106(7)	5.0(3)	C(43)	0.2714(3)	0.1306(4)	−0.1116(4)	5.2(2)
C(44)	0.2266(7)	0.1024(6)	−0.1551(7)	5.3(3)	C(44)	0.2259(4)	0.1026(4)	−0.1570(4)	5.3(2)
C(45)	0.1697(6)	0.1069(7)	−0.1306(7)	4.7(3)	C(45)	0.1686(3)	0.1070(4)	−0.1314(4)	4.7(2)
C(46)	0.1563(4)	0.1401(6)	−0.0608(6)	3.4(2)	C(46)	0.1568(3)	0.1401(4)	−0.0610(4)	3.7(1)
C(51)	0.2268(4)	0.1737(5)	0.1526(5)	3.0(2)	C(51)	0.2267(2)	0.1746(3)	0.1534(3)	3.3(1)
C(52)	0.2326(5)	0.2112(6)	0.2248(6)	4.4(3)	C(52)	0.2489(3)	0.1019(3)	0.1464(4)	4.0(2)
C(53)	0.2619(6)	0.1763(9)	0.2851(6)	6.3(4)	C(53)	0.2779(3)	0.0678(4)	0.2086(5)	5.1(2)
C(54)	0.2844(6)	0.1043(8)	0.2778(8)	5.9(4)	C(54)	0.2841(3)	0.1057(5)	0.2772(5)	6.0(2)
C(55)	0.2780(5)	0.0659(6)	0.2084(7)	4.9(3)	C(55)	0.2626(4)	0.1770(6)	0.2852(4)	6.3(2)
C(56)	0.2494(5)	0.1010(5)	0.1459(6)	3.7(3)	C(56)	0.2335(3)	0.2120(4)	0.2240(4)	4.4(2)

to form an equatorial metallapentalene plane, and is coordinated by two PPh_3 groups apically. The maximum deviations from the best plane defined with eight atoms of the pentalene ring are 0.190(9) Å. The distance of the Rh–C bond is 1.941(9) Å, which is slightly longer than those of **4**, but shorter than those of the Pt–C and Pd–C bonds. Since the distances of the Rh–Se bonds (2.500(1) and 2.486(1) Å) are longer than those of the Pt/Pd–Se bonds of **8**, **9**, and **11**, the difference between the Rh–C and Pt/Pd–C lengths shows the trans influence[14,15] of the ligands: Cl for **10**, and PPh_3 for **8**, **9**, and **11**. The same tendency was also observed between **4** (Rh-complexes) and **2** or **3** (Pt/Pd-complexes).

In these complexes (**8**—**11**) and the starting compound (**6**), the lengths of the N(1)–C(3) and N(2)–C(3) bonds (**e** in Table 4) are shorter than those of the N(1)–C(1) and N(2)–C(2) bonds (**d**). The same tendency is also observed in the complexes (**2**—**4**) and the starting tetraazathiapentalenes (**1**).

The dihedral angles between pentalene plane and the phen-

Table 2. (Continued)

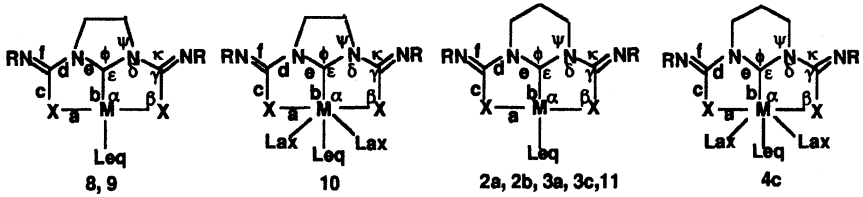
(3) **10** (M=Rh)					(4) **11** (M=Pd)				
Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Rh(1)	0.39430(5)	0.17116(4)	0.27048(5)	2.25(2)	Pd(1)	0.078677(14)	0.194785(18)	0.10968(2)	2.609(7)
Se(1)	0.40574(7)	0.21635(5)	0.42633(7)	2.99(3)	Se(1)	0.04826(2)	0.32316(3)	0.11629(3)	3.46(1)
Se(2)	0.39320(7)	0.15845(6)	0.10615(7)	3.08(3)	Se(2)	0.09479(2)	0.06087(3)	0.11161(4)	4.46(1)
Cl(11)	0.38141(15)	0.04586(13)	0.29744(17)	3.02(6)					
Cl(1)	0.3674(2)	0.41069(19)	0.8263(2)	5.9(1)	Cl(1)	−0.05772(8)	0.68093(8)	0.14375(11)	6.57(5)
Cl(2)	0.4090(4)	0.1263(3)	−0.3261(3)	11.6(2)	Cl(2)	0.11295(7)	−0.32341(8)	0.11021(10)	5.30(4)
P(1)	0.53416(16)	0.15415(13)	0.26705(17)	2.47(6)	P(1)	0.17732(5)	0.21572(7)	0.07754(7)	2.72(3)
P(2)	0.25310(16)	0.17952(14)	0.28056(17)	2.50(6)					
N(1)	0.4049(5)	0.3243(4)	0.3015(5)	3.0(2)	N(1)	−0.04692(16)	0.2242(2)	0.1495(2)	3.1(1)
N(2)	0.4007(5)	0.2985(4)	0.1604(5)	3.0(2)	N(2)	−0.02510(16)	0.0976(2)	0.1411(2)	3.1(1)
N(3)	0.4035(5)	0.3697(4)	0.4392(5)	2.9(2)	N(3)	−0.07211(17)	0.3485(2)	0.1569(3)	4.0(1)
N(4)	0.4026(5)	0.2885(5)	0.0096(6)	3.9(2)	N(4)	−0.00627(17)	−0.0290(2)	0.1404(2)	3.6(1)
C(1)	0.4023(6)	0.3139(5)	0.3931(7)	2.7(2)	C(1)	−0.0314(2)	0.3017(3)	0.1441(3)	3.2(1)
C(2)	0.3998(6)	0.2567(5)	0.0830(7)	2.9(3)	C(2)	0.0153(2)	0.0362(3)	0.1329(3)	2.9(1)
C(3)	0.4012(6)	0.2713(5)	0.2438(6)	2.6(2)	C(3)	−0.0064(2)	0.1696(2)	0.1378(2)	2.7(1)
C(4)	0.4090(8)	0.3953(6)	0.2604(8)	3.7(3)	C(4)	−0.1092(3)	0.2072(4)	0.1694(4)	4.9(2)
C(5)	0.4071(7)	0.3763(6)	0.1621(8)	3.6(3)	C(5)	−0.1279(2)	0.1371(4)	0.1288(4)	5.2(2)
C(11)	0.3951(6)	0.3726(5)	0.5337(7)	3.0(3)	C(6)	−0.0883(3)	0.0743(3)	0.1500(4)	5.3(2)
C(12)	0.4293(7)	0.4321(6)	0.5768(9)	3.8(3)	C(11)	−0.0642(2)	0.4271(3)	0.1526(3)	3.6(1)
C(13)	0.4222(8)	0.4434(7)	0.6648(9)	4.4(3)	C(12)	−0.0728(3)	0.4694(3)	0.2181(4)	4.5(2)
C(14)	0.3823(7)	0.3959(6)	0.7137(7)	3.9(3)	C(13)	−0.0699(3)	0.5470(3)	0.2158(4)	4.6(2)
C(15)	0.3499(7)	0.3362(6)	0.6752(8)	4.0(3)	C(14)	−0.0593(2)	0.5828(3)	0.1473(4)	4.1(1)
C(16)	0.3559(7)	0.3254(6)	0.5851(8)	3.9(3)	C(15)	−0.0514(3)	0.5422(3)	0.0810(4)	4.9(2)
C(21)	0.4036(8)	0.2468(6)	−0.0683(8)	3.8(3)	C(16)	−0.0542(3)	0.4640(3)	0.0842(4)	4.7(2)
C(22)	0.4731(9)	0.2425(9)	−0.1166(11)	5.9(5)	C(21)	0.0280(2)	−0.0952(2)	0.1312(3)	3.1(1)
C(23)	0.4729(11)	0.2062(10)	−0.1958(11)	7.4(5)	C(22)	0.0207(2)	−0.1371(3)	0.0651(3)	3.7(1)
C(24)	0.4060(11)	0.1730(8)	−0.2266(8)	5.9(4)	C(23)	0.0476(2)	−0.2071(3)	0.0586(3)	3.9(1)
C(25)	0.3396(10)	0.1770(8)	−0.1821(9)	5.6(4)	C(24)	0.0817(2)	−0.2335(2)	0.1175(3)	3.3(1)
C(26)	0.3377(8)	0.2139(7)	−0.1023(8)	4.4(3)	C(25)	0.0902(2)	−0.1924(3)	0.1833(3)	4.2(1)
C(31)	0.5846(6)	0.1316(5)	0.3733(6)	2.5(2)	C(26)	0.0630(2)	−0.1225(3)	0.1900(3)	3.9(1)
C(32)	0.5466(7)	0.0925(7)	0.4358(9)	4.0(3)	C(31)	0.2077(2)	0.3094(2)	0.0589(3)	3.0(1)
C(33)	0.5833(7)	0.0714(6)	0.5154(8)	4.3(3)	C(32)	0.1756(2)	0.3596(3)	0.0141(3)	3.8(1)
C(34)	0.6587(8)	0.0928(7)	0.5327(8)	4.1(3)	C(33)	0.2004(3)	0.4269(3)	−0.0098(3)	4.4(2)
C(35)	0.6997(6)	0.1325(6)	0.4728(9)	3.9(3)	C(34)	0.2575(3)	0.4449(3)	0.0113(4)	4.8(2)
C(36)	0.6629(7)	0.1529(6)	0.3921(7)	3.4(3)	C(35)	0.2895(3)	0.3974(3)	0.0572(4)	4.6(2)
C(41)	0.5790(6)	0.2366(5)	0.2355(7)	2.7(2)	C(36)	0.2651(2)	0.3291(3)	0.0802(3)	3.9(1)
C(42)	0.5959(6)	0.2891(6)	0.2967(7)	3.4(3)	C(41)	0.2235(2)	0.1771(2)	0.1543(3)	2.9(1)
C(43)	0.6208(8)	0.3558(6)	0.2739(8)	4.3(3)	C(42)	0.2340(2)	0.2189(3)	0.2212(3)	3.9(1)
C(44)	0.6372(8)	0.3693(7)	0.1870(9)	5.2(4)	C(43)	0.2658(3)	0.1881(4)	0.2808(3)	4.9(2)
C(45)	0.6216(10)	0.3179(8)	0.1233(9)	5.8(4)	C(44)	0.2862(3)	0.1159(4)	0.2766(4)	5.0(2)
C(46)	0.5926(7)	0.2517(7)	0.1467(7)	4.0(3)	C(45)	0.2753(3)	0.0732(3)	0.2126(4)	4.8(2)
C(51)	0.5744(6)	0.0868(5)	0.1918(6)	2.7(2)	C(46)	0.2438(2)	0.1038(3)	0.1508(3)	3.6(1)
C(52)	0.5300(6)	0.0338(5)	0.1529(8)	3.2(3)	C(51)	0.1989(2)	0.1683(2)	−0.0113(3)	2.8(1)
C(53)	0.5656(8)	−0.0143(6)	0.0999(8)	4.4(3)	C(52)	0.2581(2)	0.1599(3)	−0.0332(3)	4.0(1)
C(54)	0.6448(8)	−0.0119(6)	0.0834(9)	4.3(3)	C(53)	0.2740(3)	0.1280(3)	−0.1024(4)	4.8(2)
C(55)	0.6890(7)	0.0401(7)	0.1224(8)	4.6(3)	C(54)	0.2301(4)	0.1029(3)	−0.1510(3)	5.3(2)
C(56)	0.6555(7)	0.0886(7)	0.1773(8)	3.9(3)	C(55)	0.1719(3)	0.1108(3)	−0.1314(4)	5.0(2)
C(61)	0.1970(6)	0.1582(6)	0.1780(6)	2.9(2)	C(56)	0.1562(2)	0.1424(3)	−0.0619(3)	3.7(1)
C(62)	0.2110(7)	0.0924(6)	0.1430(9)	4.1(3)					
C(63)	0.1696(8)	0.0685(7)	0.0653(9)	5.1(4)					
C(64)	0.1170(8)	0.1123(9)	0.0223(7)	5.0(4)					
C(65)	0.1039(8)	0.1790(9)	0.0572(9)	5.4(4)					
C(66)	0.1439(7)	0.2020(6)	0.1327(8)	3.8(3)					
C(71)	0.2053(6)	0.1194(5)	0.3574(6)	3.0(3)					
C(72)	0.1256(7)	0.1052(7)	0.3457(8)	4.3(3)					
C(73)	0.0856(8)	0.0614(8)	0.4050(10)	5.3(4)					
C(74)	0.1258(9)	0.0314(7)	0.4728(8)	4.5(4)					
C(75)	0.2056(8)	0.0464(6)	0.4887(8)	3.9(3)					
C(76)	0.2438(7)	0.0893(6)	0.4298(8)	3.7(3)					
C(81)	0.2189(5)	0.2663(5)	0.3151(6)	2.5(2)					
C(82)	0.2208(7)	0.3226(6)	0.2576(7)	3.4(3)					
C(83)	0.1992(8)	0.3903(6)	0.2851(8)	4.3(3)					
C(84)	0.1727(8)	0.3993(6)	0.3698(10)	4.7(4)					
C(85)	0.1727(8)	0.3447(8)	0.4272(8)	5.0(4)					
C(86)	0.1950(7)	0.2775(6)	0.4010(7)	3.5(3)					

Table 3. Selected Bond Lengths (l) and Bond Angles (θ)

	8	**9**	**11**	**10**
M	Pt	Pd	Pd	Rh
L_{eq}	P	P	P	Cl
L_{ax}				P
Lengths	l/Å	l/Å	l/Å	l/Å
M(1)–Se(1)	2.4157(9)	2.4143(7)	2.3800(6)	2.500(1)
M(1)–Se(2)	2.4350(9)	2.4355(7)	2.4018(6)	2.486(1)
M(1)–L_{eq}(1)	2.319(2)	2.335(1)	2.330(1)	2.416(3)
M(1)–L_{ax}(1)				2.377(3)
M(1)–L_{ax}(2)				2.390(3)
M(1)–C(3)	1.981(9)	1.974(5)	2.034(4)	1.941(9)
Se(1)–C(1)	1.933(9)	1.908(5)	1.903(5)	1.913(9)
Se(2)–C(2)	1.930(8)	1.920(5)	1.887(5)	1.90(1)
N(1)–C(1)	1.40(1)	1.406(6)	1.422(5)	1.40(1)
N(1)–C(3)	1.33(1)	1.325(6)	1.349(5)	1.33(1)
N(1)–C(4)	1.48(1)	1.480(7)	1.482(6)	1.48(1)
N(2)–C(2)	1.40(1)	1.409(6)	1.429(5)	1.41(1)
N(2)–C(3)	1.328(9)	1.332(6)	1.345(5)	1.36(1)
N(2)–C(5)	1.48(1)	1.489(6)	1.497(6)	1.48(1)
N(3)–C(1)	1.26(1)	1.260(6)	1.259(5)	1.26(1)
N(3)–C(11)	1.41(1)	1.425(6)	1.408(6)	1.44(1)
N(4)–C(2)	1.242(9)	1.258(5)	1.260(5)	1.26(1)
N(4)–C(21)	1.41(1)	1.413(6)	1.416(5)	1.41(1)
C(4)–C(5)	1.52(1)	1.546(8)	1.488(9)	1.52(2)
C(5)–C(6)			1.476(8)	
Angles	θ/°	θ/°	θ/°	θ/°
Se(1)–M(1)–Se(2)	166.71(3)	166.48(3)	171.16(2)	164.97(5)
Se(1)–M(1)–L_{eq}(1)	100.80(6)	100.84(4)	97.83(3)	100.50(7)
Se(1)–M(1)–L_{ax}(1)				91.18(7)
Se(1)–M(1)–L_{ax}(2)				87.94(7)
Se(1)–M(1)–C(3)	83.6(2)	83.2(1)	85.7(1)	81.8(3)
Se(2)–M(1)–L_{eq}(1)	92.48(6)	92.67(4)	90.88(3)	94.28(7)
Se(2)–M(1)–L_{ax}(1)				86.59(7)
Se(2)–M(1)–L_{ax}(2)				95.42(7)
Se(2)–M(1)–C(3)	83.2(2)	83.3(1)	85.6(1)	83.5(3)
L_{eq}(1)–M(1)–L_{ax}(1)				88.00(9)
L_{eq}(1)–M(1)–L_{ax}(2)				87.67(9)
L_{eq}(1)–M(1)–C(3)	175.1(2)	175.6(1)	176.5(1)	177.2(3)
L_{ax}(1)–M(1)–L_{ax}(2)				175.35(9)
L_{ax}(1)–M(1)–C(3)				93.6(3)
L_{ax}(2)–M(1)–C(3)				90.8(3)
M(1)–Se(1)–C(1)	95.9(3)	96.2(2)	95.5(1)	94.8(3)
M(1)–Se(2)–C(2)	95.7(2)	95.6(1)	95.0(1)	95.2(3)
C(1)–N(1)–C(3)	122.6(8)	122.0(4)	121.1(4)	122.5(8)
C(1)–N(1)–C(4)	125.4(7)	125.2(4)	116.6(4)	123.0(9)
C(3)–N(1)–C(4)	112.0(7)	112.8(4)	122.4(4)	114.4(8)
C(2)–N(2)–C(3)	123.1(8)	122.1(4)	121.1(4)	123.6(8)
C(2)–N(2)–C(5)	124.3(7)	124.3(4)	114.3(4)	125.0(9)
C(3)–N(2)–C(5)	112.2(7)	113.4(4)	124.6(4)	111.3(9)
C(1)–N(3)–C(11)	121.2(8)	120.7(5)	123.3(4)	125.2(9)
C(2)–N(4)–C(21)	121.5(7)	121.5(4)	122.5(4)	117.6(9)
Se(1)–C(1)–N(1)	113.0(6)	113.3(4)	116.3(3)	113.1(7)
Se(1)–C(1)–N(3)	128.7(7)	130.0(4)	127.3(4)	131.5(8)
N(1)–C(1)–N(3)	118.3(8)	116.7(5)	116.3(4)	115.2(8)
Se(2)–C(2)–N(2)	112.9(6)	113.5(3)	116.9(3)	113.4(7)
Se(2)–C(2)–N(4)	128.1(6)	128.4(4)	127.0(4)	129.3(8)
N(2)–C(2)–N(4)	119.0(8)	118.1(4)	116.1(4)	117.3(9)
M(1)–C(3)–N(1)	124.9(6)	125.2(4)	121.4(3)	127.2(7)
M(1)–C(3)–N(2)	124.8(6)	125.2(4)	121.1(3)	124.2(7)
N(1)–C(3)–N(2)	110.2(8)	109.5(4)	117.4(4)	108.6(8)
N(1)–C(4)–C(5)	103.1(8)	102.9(4)	109.3(5)	101.1(8)
N(2)–C(5)–C(4)	102.2(7)	101.2(4)	110.2(5)	104.6(9)
C(4)–C(5)–C(6)			109.8(5)	

Table 4. Comparison of the Mean Bond Lengths and Angles of the Metallapentalenes

	8	**9**	**11**	**10**	**2a**	**2b**	**3a**	**3c**	**4c-1**	**4c-2**
Ref.					2	2	2	2	3	3
M	Pt	Pd	Pd	Rh	Pt	Pt	Pd	Pd	Rh	Rh
X	Se	Se	Se	Se	S	S	S	S	S	S
L_{eq}	PPh_3	PPh_3	PPh_3	Cl	PPh_3	PPh_3	PPh_3	PPh_3	Cl	Cl
L_{ax}				$(PPh_3)_2$					$(PPh_3)_2$	$(PPh_3)_2$
R	*p*-Cl-Ph	*p*-Cl-Ph	*p*-Cl-Ph	*p*-Cl-Ph	Me	Et	Me	*p*-Cl-Ph	*p*-Cl-Ph	*p*-Cl-Ph
a(M–X)/Å	2.425	2.425	2.391	2.493	2.282	2.287	2.288	2.287	2.343	2.345
b(M–C)/Å	1.981	1.974	2.034	1.941	2.001	1.992	2.005	1.990	1.930	1.933
c(X–C)/Å	1.932	1.914	1.890	1.91	1.760	1.757	1.757	1.743	1.703	1.736
d(N–C)/Å	1.40	1.408	1.426	1.41	1.416	1.426	1.425	1.434	1.441	1.432
e(N–C)/Å	1.33	1.329	1.347	1.35	1.345	1.340	1.339	1.345	1.366	1.371
f(N–C)/Å	1.25	1.259	1.260	1.26	1.279	1.269	1.261	1.273	1.295	1.286
M–L_{eq}/Å	2.319	2.335	2.330	2.416	2.304	2.315	2.331	2.333	2.442	2.429
M–L_{ax}/Å				2.384					2.389	2.393
S–M–X/°	166.7	166.5	171.2	165.0	169.5	168.9	169.3	169.1	168.2	166.9
α(X–M–C)/°	83.4	83.3	85.7	82.7	84.7	84.5	84.6	84.6	84.2	83.5
β(M–X–C)/°	95.8	95.9	95.3	95.0	99.0	99.2	99.0	99.3	97.9	97.9
γ(X–C–N)/°	113.0	113.4	116.6	113.3	116.5	115.7	116.2	116.2	117.5	116.0
δ(C–N–C)/°	122.9	122.1	121.1	123.1	119.6	119.8	119.9	119.1	117.5	117.3
ε(M–C–N)/°	124.9	125.2	121.1	124.2	120.2	120.6	120.1	120.6	122.2	123.0
C–M–L_{eq}/°	175.1	175.6	176.5	177.2	177.5	176.3	178.3	176.5	177.0	175.9
S–M–L_{eq}/°	96.7	96.8	94.4	97.4	95.3	95.5	95.4	95.5	95.9	96.5
ϕ(N–C–N)/°	110.2	109.5	117.4	108.5	119.6	118.8	119.8	118.8	115.6	114.1
ψ(C–N–C)/°	112.1	113.1	123.5	112.9	122.4	123.3	122.5	123.3	125.4	125.8
$\varkappa$(N–C–N)/°	118.7	117.4	116.2	116.3	118.5	117.8	116.6	115.2	112.7	114.6



8, 9 10 2a, 2b, 3a, 3c,11 4c

yl groups of **8** are 111.4(3) and 77.5(3)° for C(11)—C(16) and C(21)—C(26), respectively. The corresponding angles are 110.8(2) and 77.4(2)° for **9**, 113.8(2) and 78.9° for **11**, and 153.2(3) and 70.8(4)° for **10**.

Crystal Structures. Crystals of **8**, **9**, and **11** are isomorphous with each other. The crystal structure of **9** is shown in Fig. 2. Figure 3 shows the molecular overlapping in the crystals of **9** and **11**. It is very interesting whether or not the *exo*-pentalene perhydroimidazole rings of **8** and **9** or the perhydropyrimidine ring of **11** affect the molecular packing. The crystal structure of **11** is different from that of **3c**, the sulfur derivative of **11**. Crystals of **8**—**11** are very stable, and contain no crystal solvents, while crystals of **3c** are unstable, and $CHCl_3$ molecules are loosely included among PPh_3 groups as crystal solvents.[2] The metallapentalene framework is overlapped with the other pentalene at the

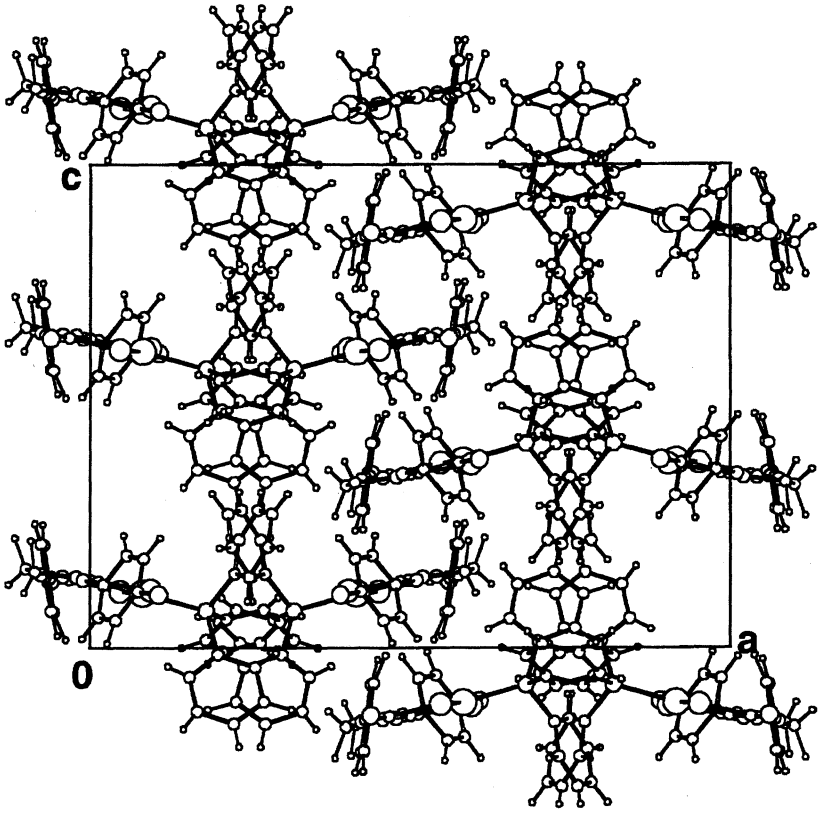


Fig. 2. Projection of the crystal structure of **9** viewed along the *b* axis.

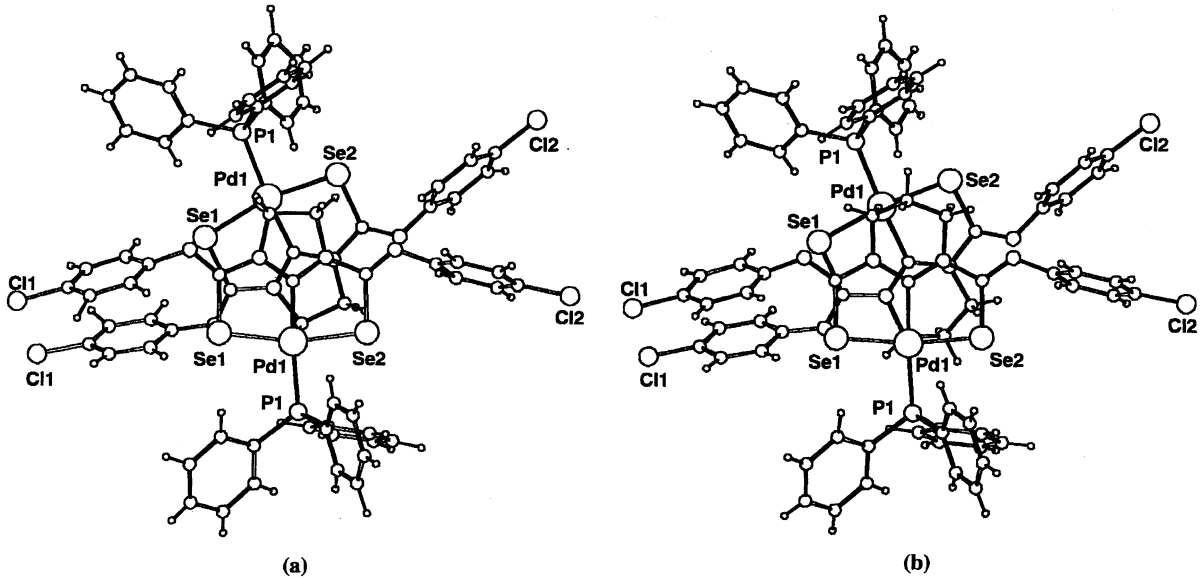
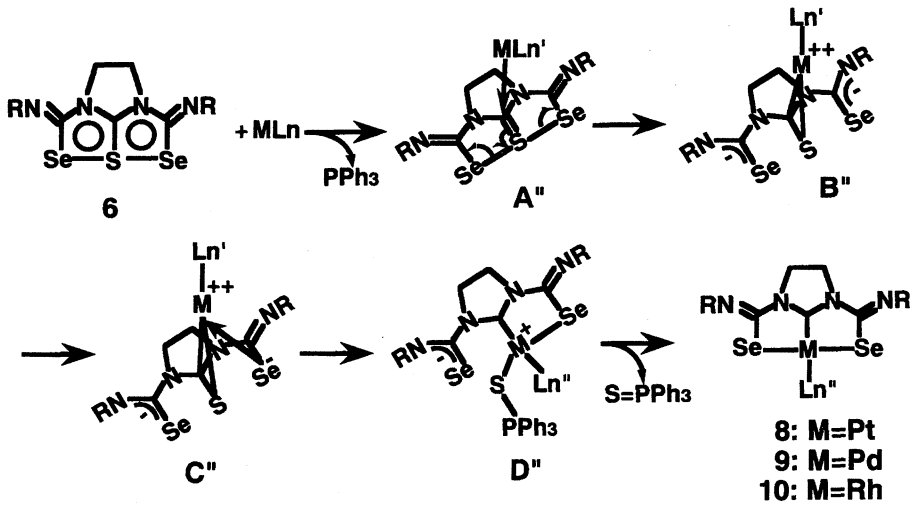


Fig. 3. Overlappings of the molecules. (a) **9** and (b) **11**.



Scheme 4.

position of $(-x, y, 1/2-z)$, with the interplanar distances of 3.715(10), 3.705(6), and 3.845(5) Å for **8**, **9**, and **11**, respectively. This overlapping mode is quite different from that of **3c**, where a metallapentalene framework only slightly overlaps the other one at the center of symmetry with interplanar distances of 3.731(5) Å.

The crystal structure of **10** is shown in Fig. 4. In this case, crystals are also very stable and no crystal solvents are found in the crystals, while unstable crystals of **4c**, the sulfur and pyrimidine derivative of **10**, include CH_2Cl_2 molecules as crystal solvents.[3]

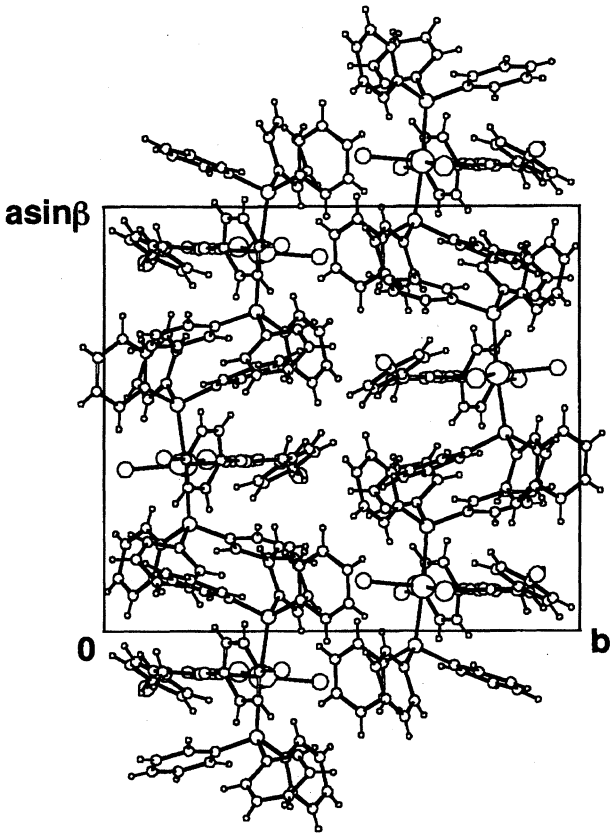


Fig. 4. Projection of the crystal structure of **10** viewed along the *c* axis.

Formation Mechanism of Metal–Carbene Complexes. The structure analyses revealed that the complexes (**8**, **9**, and **10**) obtained from the thiadiselenadiazapentalene derivative (**6**) were metal–carbene complexes with a metallapentalene framework. The structural feature of these complexes are very similar to those of the metal-carbene complexes (**2**—**4** and **11**) obtained from thiatetraazapentalene-2,5-dithione/diselones (**1**).

Based on the structures of these carbene complexes and MO calculations of the frontier-orbital electron-densities of **5** (the related compound of **6**), the formation mechanism of the metal–carbene complexes are shown in Scheme 4, as in Scheme 3. In this mechanism, the weak hypervalent Se–S bonds are easily cleaved after the central carbon atom of the pentalene framework is attacked by the nucleophilic metal reagent (A″ and B″), and the Se atom of the selenoamide group works as a nucleophile (C″). The intermediate state, B″, should be essentially equivalent to that of B in Scheme 2. The fact that similar metal–carbene complexes (**8**—**10**) have been obtained from the thiadiselenadiazapentalene derivative (**6**) confirms the previously proposed formation mechanism of the metal–carbene complexes (**2**—**4**) from thiatetraazapentalene-2,5-dithiones (**1**).[4]

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