Crystal and Molecular Structures of Novel Metal–Carbene Complexes IV. Effect of Carbonyl Groups and Formation Mechanism

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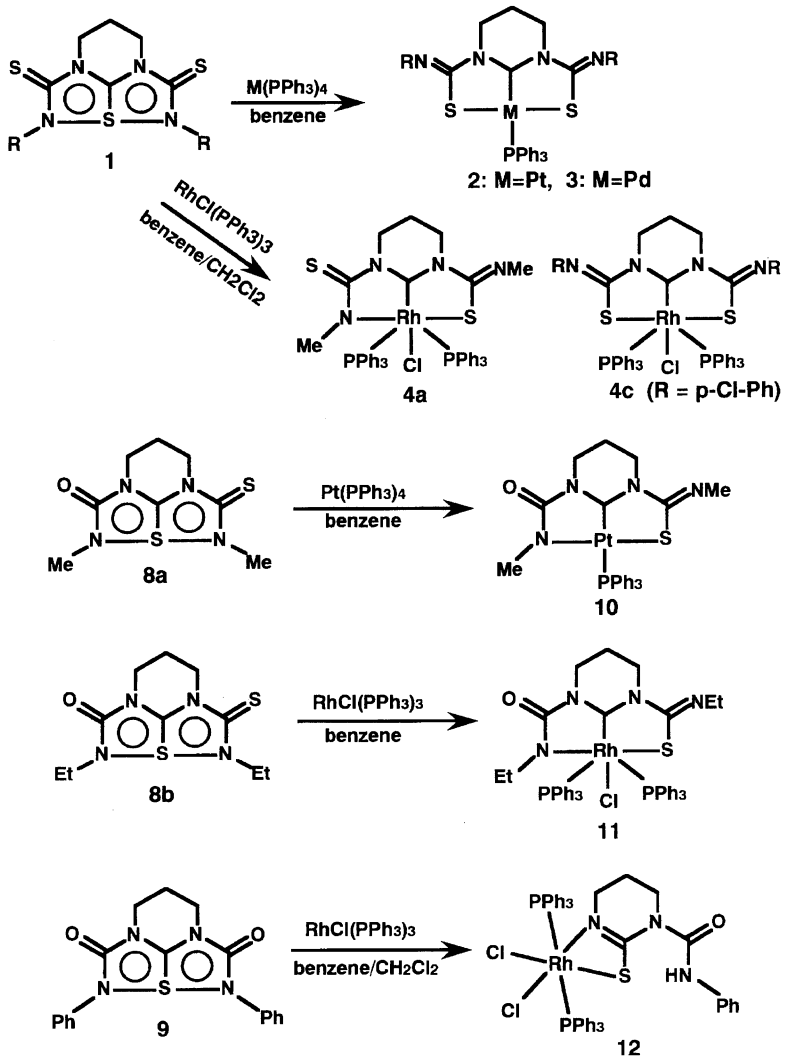
X-Ray structure analyses were carried out for the metal complexes obtained from 2,3,4,5-tetrahydro-1,6-dialkyl-3,4-trimethylene-5-thioxo-6aλ^4-thia-1,3,4,6-tetraazapentalene-2-ones (**8**) and 2,3,4,5-tetrahydro-1,6-diphenyl-3,4-trimethylene-6aλ^4-thia-1,3,4,6-tetraazapentalene-2,5-dione (**9**), in order to investigate the effect of the carbonyl groups on the formation of the metal–carbene complexes instead of thiocarbonyl groups. The structure analyses revealed that the Pt complex **10**, {[3-(methylcarbamoyl-$\varkappa N$) perhydropyrimidine-1-yl-$\varkappa C^2$] (methyliminomethanethiolato-$\varkappa S$)}(triphenylphosphine)platinum (II), and the Rh complex **11**, *trans*(*P*,*P*′)-(chloro) {[3-(ethylcarbamoyl-$\varkappa N$)perhydropyrimidine-1-yl-$\varkappa C^2$] (ethyliminomethanethiolato-$\varkappa S$)}bis(triphenylphosphine)rhodium(III), were obtained from the mono-carbonyl derivative **8**. They are metal–carbene complexes coordinated with S and N atoms; the oxygen atoms of the carbonyl groups remained without coordinating to a metal atom. Treating a bis-carbonyl derivative **9** with a Rh reagent, the resultant complex was a Rh complex, **12**, *trans*(*P*,*P*′)-dichlorobis(triphenylphosphine) [1,4,5,6-tetrahydro-1-(phenylcarbamoyl)-2-pyrimidinethiolato-$\varkappa N$,$\varkappa S$]rhodium(III), which was not a metal–carbene complex. The formation of the metal–carbene complexes required at least one thiocarbonyl group; the central metal was coordinated by at least one S atom. The formation mechanism of the metal–carbene complexes was proposed from the results of the structures of carbene complexes and MO calculations.

In previous papers, I and III,[1,2] we reported on the structures of novel metal–carbene complexes derived from 6a-thiatetraazapentalene derivatives (**1**), which contain a hypervalent sulfur atom.[3—5] In the Pt and Pd complexes, **2** and **3**, the central sulfur atom in **1** was substituted by a metal atom, and two thioamide groups rotated to form a square-planar coordination with two S atoms, a C atom of the pentalene and a P atom of the PPh_3 group (Scheme 1). In the case of the Rh complex, **4a**, only one thioamide group of the starting **1a** rotated to form a coordination of the S–M–N type, while two thioamide groups of **1c** rotated to form the complex of **4c** with a S–M–S type, like the Pt and Pd complexes. From the structures of these new metal–carbene complexes, it has been considered that at least one sulfur atom of the thioamide groups of the starting hypervalent compounds **1** is essential for the formation of these complexes. We then examined the effect the carbonyl groups instead of the thiocarbonyl groups. X-Ray structure analyses of three complexes, **10** obtained from **8a** with $Pt(PPh_3)_4$, **11** from **8b** with $RhCl(PPh_3)_3$, and **12** from **9** with $RhCl(PPh_3)_3$, were carried out to elucidate the coordination type of these complexes.

The structure analyses revealed that the Pt and Rh complexes, **10** and **11**, obtained from the mono-carbonyl derivatives **8** are metal–carbene complexes coordinated with sulfur and nitrogen: **10**, {[3-(methylcarbamoyl-$\varkappa N$)perhydropyrimidine-1-yl-$\varkappa C^2$] (methyliminomethanethiolato-$\varkappa S$)} (triphenylphosphine)platinum(II), and **11**, *trans*(*P*,*P*′)-(chloro){[3-(ethylcarbamoyl-$\varkappa N$)perhydropyrimidine-1-yl-$\varkappa C^2$](ethyliminomethanethiolato-$\varkappa S$)}bis(triphenylphosphine)rhodium(III). In these complexes the oxygen atoms of the carbonyl groups remained without coordinating to a metal atom. Upon treating a bis-carbonyl derivative **9** with a Rh reagent no metal–carbene complexes could be obtained. The resultant Rh complex **12** is *trans*(*P*,*P*′)-dichlorobis(triphenylphosphine) [1,4,5,6-tetrahydro-1-(phenylcarbamoyl)-2-pyrimidinethiolato-$\varkappa N$,$\varkappa S$]-rhodium(III), which has quite a different structure from those of the other metal–carbene complexes. We found that the formation of the metal–carbene complexes required at least one thiocarbonyl group, and that the central metal was coordinated by at least one S atom. No coordination of the N–M–N or O–M–O type has been observed.

Frontier electron densities were calculated on the tetraazathiapentalenes, **1**, **8**, and **9**, in order to investigate the difference in the reactivity among these compounds. In this paper we describe the structures of the complexes derived from tetraazathiapentalenes with carbonyl groups, and discuss the formation mechanism of the metal–carbene complexes based on the results of the structures of carbene complexes and MO calculations.



Scheme 1.

Experimental

The crystals of **10** and **12** for X-ray studies were grown from $CHCl_3$ solutions. A crystal of **10** was coated with epoxy resin. A crystal, **11**, grown from CH_2Cl_2, was sealed in a thin glass capillary. Crystal data, details of data collection and structure refinements are listed in Table 1. For **10** and **12**, the intensity data were measured using Rigaku diffractometers with graphite monochromators. Absorption corrections were applied numerically. For **11**, the intensities were measured using a rapid X-ray diffractometer,[6] MacScience DIP-3000, with imaging plates as a two-dimensional detector.

The structures were solved by the heavy-atom method preceded by the Patterson function to locate the metal atom using the program SHELXS86.[7] During the refinements of **10** and **12**, molecules of $CHCl_3$ were found in D-maps as crystal solvents. In an asymmetric unit there was one $CHCl_3$ for **10** and two for **12**. From D-maps of **11**, CH_2Cl_2 molecules were found. Although the refinement converged to an R value of 0.07, one large peak remained in the D-maps, being about 2.8 Å from the O atom of the carbonyl group. After the assignment of this peak to a water oxygen, the R value was dropped to 0.04. The densities of these crystals could not be measured, because only very few single crystals were obtained. For all of the structures, the positions of the H atoms, except for several on the terminal positions, were obtained from D-maps. The remaining H atoms were located from calculations, and were included in the refinements with restraining. 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 $\sum w(|F_o|-k|F_c|)^2$ was minimized. The final R values were 0.0415, 0.0403, and 0.0886 for **10**, **11**, and **12**, respectively. The atomic scattering factors were used from the International Tables for X-Ray Crystallography.[8] All of the computations were performed with the programs SHELXS86, UNICS III,[9] ORTEP II.[10] The final atomic parameters are given in Table 2.[11]

Discussion

Structures of 10 and 11. The molecular structures of **10** and **11** with the atomic numbering are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are listed in Table 3. In complex **10**, the sulfur atom of the tetraazathiapentalene framework of **8** is substituted by the Pt atom. The coordination mode of complex **10** is not an O–M–S type, but an N–M–S type. Only the thiocarbonyl group rotated to form a Pt–S bond, while the carbonyl group remained uncoordinated, so that the N atom of the amide group coor-

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

	10	**11**	**12**
	$C_{26}H_{27}N_4OPSPt$ $CHCl_3$	$C_{46}H_{46}ClN_4OP_2SRh$ $CH_2Cl_2 \cdot H_2O$	$C_{47}H_{42}Cl_2N_3OP_2SRh$ $2CHCl_3$
F.W.	789.02	1006.22	1171.45
Color	Yellow	Yellow	Orange
Crystal shape	Plate	Prism	Pillar
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	Pn	$P2_1/n$
a/Å	12.263(1)	15.984(1)	22.353(4)
b/Å	13.306(2)	9.949(1)	14.013(4)
c/Å	12.029(2)	14.854(1)	16.313(7)
α/°	129.813(8)	90.0	90.0
β/°	90.61(3)	100.94(11)	94.56(3)
γ/°	91.86(3)	90.0	90.0
V/Å^3	1505.6(4)	2319.2(9)	5094(3)
Z	2	2	4
D_x/gcm^{-3}	1.741	1.441	1.528
μ/mm^{-1}	5.123	0.682	0.894
F(000)	772	1036	2376
Crystal size	$0.16 \times 0.35 \times 0.38$	$0.16 \times 0.40 \times 0.13$	$0.50 \times 0.125 \times 0.125$
Diffractometer	Rigaku-AFC5R	Mac-Science DIP3000	Rigaku-AFC5R
Radiation	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$
λ/Å	0.71073	0.71073	0.71069
Temperature /K	293	296	296
Scan mode	ω–2θ	Weissenberg	ω–2θ
$2\theta_{max}$/°	55.0	52.7	55.0
Scan width $\triangle\omega$/°	$1.30+0.5\tan\theta$	—	$1.30+0.5\tan\theta$
Scan speed /° min^{-1}	4	—	4
Rotation axis	—	c	—
$\triangle\phi$/°	—	181	—
No. of IPs	—	20	—
No. of standard refs.	3 every 50 reflections	—	3 every 100 reflections
Variation of intensities	0.934—1.000	—	0.971—1.000
Range of $h\ k\ l$	−15—15 −17—13 0—15	−19—19 −12—11 −16—8	−29—28 0—18 0—21
T_{max}, T_{min}	0.4588, 0.1875	—	0.956, 0.911
No. of reflections			
Measured	7461	14890	12468
Unique	6908	4688	11698
Observed ($\lvert F_o \rvert > 3\sigma(F)$)	6264	4297	5974
Refinement	6264	4297	5974
R_{int}	0.0110	0.035	0.027
No. of parameters	448	742	763
S	1.457	1.754	1.586
$(\Delta/\sigma)_{max}$	0.440	0.171	0.047
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$	1.649, −1.202	0.689, −0.813	1.350, −1.274
Weighting scheme[a)]	*1	*2	*3
R	0.0415	0.0403	0.0886
wR	0.0614	0.0484	0.0867

a) *1: $w = 1.2379/\{\sigma(F)^2 + 0.001552|F_o|^2\}$, *2: $w = 1$, *3: $w = 1/\{\sigma(F)^2 + 0.00067|F_o|^2\}$.

dinates the Pt atom like the Rh complex **4a**. The length of the Pt–S bond is 2.281(1) Å, which is the same as those of Pt–pentalene complexes, **2**. The length of the Pt–C bond, 1.961(8) Å, is slightly shorter than those of **2**, as shown in Table 4 of Part III.[2)] The metallapentalene framework is planar with the maximum deviations from the plane, 0.061(5) Å.

The Rh atoms in **11** is also coordinated by S and N atoms following a rotation of the thiocarbonyl group. The structural feature is similar to that of **4a**. The maximum deviation from

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) **10**				
Pt(1)	0.21028(2)	0.12415(2)	0.16837(2)	3.11(1)
S(1)	0.17162(14)	−0.09582(14)	−0.00328(16)	4.07(5)
P(1)	0.27494(12)	0.12082(14)	0.34769(15)	3.22(5)
O(1)	0.1804(5)	0.4680(4)	0.2418(6)	6.33(9)
N(1)	0.1161(4)	0.0235(5)	−0.1114(5)	4.13(9)
N(2)	0.1436(4)	0.2497(5)	0.0615(5)	4.30(9)
N(3)	0.0864(5)	−0.1991(5)	−0.2674(5)	4.92(9)
N(4)	0.2282(4)	0.3219(4)	0.2740(5)	4.02(8)
C(1)	0.1205(4)	−0.1018(5)	−0.1449(5)	3.73(9)
C(2)	0.1860(5)	0.3562(5)	0.2027(6)	4.57(9)
C(3)	0.1500(4)	0.1293(5)	0.0206(5)	3.61(9)
C(4)	0.0720(5)	0.0299(6)	−0.2190(6)	5.26(9)
C(5)	0.1155(6)	0.1480(7)	−0.1935(7)	6.03(9)
C(6)	0.0999(6)	0.2686(6)	−0.0391(7)	6.12(9)
C(7)	0.0863(6)	−0.3247(6)	−0.3034(7)	6.37(10)
C(8)	0.2800(6)	0.4260(6)	0.4156(6)	5.19(9)
C(11)	0.2414(4)	−0.0300(5)	0.3182(5)	3.50(8)
C(12)	0.1662(5)	−0.0370(5)	0.3978(5)	4.06(9)
C(13)	0.1387(5)	−0.1562(5)	0.3644(6)	4.67(9)
C(14)	0.1883(5)	−0.2682(5)	0.2547(6)	5.22(9)
C(15)	0.2645(6)	−0.2613(5)	0.1761(7)	6.02(9)
C(16)	0.2904(5)	−0.1421(5)	0.2064(6)	4.59(9)
C(21)	0.4232(5)	0.1384(5)	0.3726(6)	4.02(9)
C(22)	0.4851(5)	0.1743(6)	0.3047(7)	5.56(9)
C(23)	0.5958(6)	0.1903(7)	0.3262(8)	7.34(10)
C(24)	0.6481(6)	0.1676(7)	0.4039(8)	7.51(10)
C(25)	0.5912(6)	0.1316(7)	0.4716(8)	6.64(10)
C(26)	0.4796(5)	0.1123(6)	0.4528(7)	5.06(9)
C(31)	0.2186(4)	0.2456(5)	0.5225(5)	3.45(8)
C(32)	0.1116(5)	0.2830(5)	0.5207(6)	4.29(9)
C(33)	0.0619(6)	0.3756(5)	0.6501(7)	5.42(9)
C(34)	0.1162(7)	0.4340(6)	0.7825(7)	6.52(10)
C(35)	0.2246(7)	0.4002(7)	0.7827(6)	6.73(10)
C(36)	0.2732(6)	0.3067(6)	0.6540(6)	5.03(9)
C(9)	0.5514(6)	−0.3574(6)	−0.1142(6)	15.1(1)
Cl(1)	0.4222(4)	−0.3630(5)	−0.1764(5)	15.8(1)
Cl(2)[a]	0.5737(6)	−0.1830(5)	0.0311(7)	14.5(1)
Cl(3)[a]	0.5471(8)	−0.4303(7)	−0.0340(8)	22.6(1)
Cl(4)[a]	0.5795(7)	−0.2602(7)	0.0649(6)	15.2(1)
Cl(5)[a]	0.5715(8)	−0.5246(6)	−0.1932(9)	29.4(1)
a) Occupancy factor: 0.5.				
(2) **11**				
Rh(1)	0.41731(5)	0.41375(5)	0.33321(7)	2.00(1)
Cl(1)	0.44086(12)	0.65675(18)	0.33671(16)	3.06(5)
S(1)	0.30704(12)	0.39616(19)	0.20582(13)	2.65(5)
P(1)	0.32626(11)	0.49599(19)	0.43919(14)	2.23(5)
P(2)	0.50764(12)	0.38711(20)	0.22675(14)	2.47(5)
O(1)	0.5527(4)	0.1819(6)	0.5406(5)	4.10(18)
N(1)	0.3361(4)	0.1561(6)	0.2879(5)	2.49(16)
N(2)	0.4430(4)	0.1614(6)	0.4172(5)	2.59(16)
N(3)	0.2369(5)	0.1553(8)	0.1517(5)	4.0(2)
N(4)	0.5176(4)	0.3634(6)	0.4411(4)	2.50(16)
C(1)	0.2891(5)	0.2236(8)	0.2103(6)	2.9(2)
C(2)	0.5109(4)	0.2364(8)	0.4731(5)	2.63(19)
C(3)	0.3964(4)	0.2233(7)	0.3463(5)	2.17(18)
C(4)	0.3174(6)	0.0118(8)	0.3023(6)	3.5(2)
C(5)	0.3407(6)	−0.0228(8)	0.4013(7)	3.6(2)
C(6)	0.4321(6)	0.0186(8)	0.4381(6)	3.4(2)
C(7)	0.1916(7)	0.2255(12)	0.0706(7)	5.1(3)
C(8)	0.1672(12)	0.1291(17)	−0.0076(9)	9.1(6)
C(9)	0.5855(5)	0.4413(8)	0.4961(6)	2.9(2)
C(10)	0.6746(5)	0.3897(10)	0.4968(7)	4.3(3)
C(11)	0.2474(5)	0.3424(7)	0.4613(5)	2.5(2)
C(12)	0.1959(5)	0.2840(9)	0.3856(6)	3.0(2)
C(13)	0.1331(5)	0.1937(9)	0.3957(7)	3.8(3)
C(14)	0.1195(6)	0.1636(10)	0.4823(8)	4.6(3)
C(15)	0.1684(6)	0.2240(12)	0.5576(7)	4.8(3)
C(16)	0.2304(6)	0.3139(10)	0.5472(6)	3.8(3)
C(21)	0.3927(4)	0.5028(9)	0.5508(6)	2.8(2)
C(22)	0.4222(6)	0.6339(9)	0.5714(6)	3.4(2)
C(23)	0.4783(6)	0.6619(11)	0.6524(6)	4.2(3)
C(24)	0.5063(6)	0.5604(12)	0.7121(7)	4.9(3)
C(25)	0.4790(6)	0.4303(11)	0.6916(6)	4.3(3)
C(26)	0.4235(5)	0.4036(9)	0.6133(5)	3.1(2)
C(31)	0.2562(5)	0.6117(7)	0.4138(6)	2.7(2)
C(32)	0.2232(6)	0.6744(9)	0.4822(7)	4.0(3)
C(33)	0.1661(6)	0.7784(10)	0.4604(8)	4.6(3)
C(34)	0.1368(6)	0.8165(9)	0.3719(8)	4.5(3)
C(35)	0.1675(6)	0.7528(9)	0.3008(7)	4.1(3)
C(36)	0.2271(5)	0.6518(8)	0.3221(6)	3.4(2)
C(41)	0.6191(5)	0.4414(9)	0.2575(6)	3.0(2)
C(42)	0.6353(6)	0.5707(10)	0.2919(7)	3.9(3)
C(43)	0.7186(6)	0.6204(11)	0.3074(8)	4.8(3)
C(44)	0.7844(6)	0.5432(13)	0.2901(7)	4.9(3)
C(45)	0.7678(6)	0.4190(13)	0.2548(8)	5.3(4)
C(46)	0.6872(5)	0.3666(11)	0.2379(7)	4.1(3)
C(51)	0.4790(5)	0.4735(9)	0.1177(6)	3.1(2)
C(52)	0.4242(5)	0.5800(9)	0.1032(6)	3.3(2)
C(53)	0.4089(6)	0.6471(10)	0.0197(8)	4.8(3)
C(54)	0.4522(7)	0.6075(12)	−0.0495(7)	4.9(3)
C(55)	0.5073(8)	0.5046(14)	−0.0341(8)	5.7(4)
C(56)	0.5228(6)	0.4368(12)	0.0475(8)	4.9(3)
C(61)	0.5116(5)	0.2103(8)	0.1985(6)	3.2(2)
C(62)	0.4591(6)	0.1548(10)	0.1235(7)	4.3(3)
C(63)	0.4551(7)	0.0176(11)	0.1091(8)	5.3(4)
C(64)	0.5047(8)	−0.0649(11)	0.1714(9)	5.6(4)
C(65)	0.5565(8)	−0.0134(10)	0.2472(8)	5.1(3)
C(66)	0.5606(6)	0.1236(10)	0.2619(6)	4.1(3)
C(1A)	0.8952(15)	−0.0208(47)	0.2509(18)	21.7(19)
Cl(1A)	0.8901(8)	−0.0529(19)	0.3463(8)	32.8(10)
Cl(2A)	0.8169(6)	0.0303(12)	0.1701(7)	21.1(5)
O(2)	0.5741(5)	−0.0139(8)	0.6773(5)	5.2(2)
(3) **12**				
Rh(1)	0.14207(3)	0.82477(5)	0.57815(5)	2.60(2)
S(1)	0.10640(11)	0.75366(19)	0.45132(16)	3.32(7)
Cl(1)	0.07847(11)	0.95767(17)	0.59857(15)	3.32(7)
Cl(2)	0.20396(12)	0.85661(19)	0.69996(17)	4.14(7)
P(1)	0.07249(11)	0.72971(18)	0.64646(16)	2.86(7)
P(2)	0.20310(12)	0.92654(19)	0.50253(16)	3.11(7)
O(1)	0.2000(4)	0.5261(7)	0.3185(6)	7.0(3)

Table 2. (Continued)

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
N(1)	0.1896(3)	0.7080(6)	0.5512(5)	3.4(2)	C(45)	0.1493(5)	0.4678(8)	0.7000(7)	4.7(4)
N(2)	0.1872(4)	0.6018(6)	0.4374(6)	4.3(3)	C(46)	0.1324(5)	0.5652(7)	0.7035(7)	3.9(3)
N(3)	0.1066(4)	0.5810(7)	0.3397(6)	4.8(3)	C(51)	0.1677(4)	0.9802(7)	0.4085(6)	3.1(3)
C(1)	0.1662(4)	0.6782(7)	0.4817(6)	3.6(3)	C(52)	0.2017(5)	1.0185(8)	0.3480(7)	4.2(3)
C(2)	0.1655(5)	0.5690(8)	0.3605(7)	5.0(4)	C(53)	0.1750(5)	1.0636(8)	0.2818(7)	4.9(4)
C(3)	0.2417(4)	0.6619(8)	0.5960(7)	4.5(3)	C(54)	0.1131(5)	1.0742(8)	0.2718(7)	5.0(4)
C(4)	0.2515(6)	0.5657(9)	0.5588(9)	6.7(5)	C(55)	0.0790(5)	1.0358(8)	0.3306(6)	4.0(3)
C(5)	0.2462(6)	0.5640(9)	0.4716(9)	6.8(5)	C(56)	0.1050(4)	0.9888(7)	0.3977(6)	3.0(3)
C(11)	0.0757(5)	0.5688(9)	0.2597(7)	5.3(4)	C(61)	0.2379(4)	1.0330(7)	0.5530(6)	3.4(3)
C(12)	0.1019(6)	0.5381(13)	0.1893(9)	9.2(6)	C(62)	0.2129(5)	1.0776(7)	0.6175(6)	3.6(3)
C(13)	0.0682(7)	0.5316(14)	0.1181(8)	9.4(6)	C(63)	0.2384(5)	1.1640(8)	0.6468(7)	4.9(4)
C(14)	0.0093(7)	0.5545(10)	0.1118(8)	6.7(5)	C(64)	0.2857(6)	1.2020(8)	0.6146(8)	5.7(4)
C(15)	−0.0169(6)	0.5801(10)	0.1793(8)	6.2(4)	C(65)	0.3104(5)	1.1589(9)	0.5500(8)	5.7(4)
C(16)	0.0148(5)	0.5865(8)	0.2532(7)	5.1(4)	C(66)	0.2869(5)	1.0747(8)	0.5182(7)	4.9(4)
C(21)	−0.0061(4)	0.7351(7)	0.6019(6)	3.2(3)	C(71)	0.2679(4)	0.8619(7)	0.4687(7)	3.6(3)
C(22)	−0.0252(4)	0.7939(7)	0.5382(6)	3.3(3)	C(72)	0.3186(5)	0.8517(8)	0.5220(8)	5.1(4)
C(23)	−0.0850(4)	0.7992(7)	0.5096(6)	3.5(3)	C(73)	0.3684(5)	0.8021(9)	0.4980(9)	6.3(5)
C(24)	−0.1266(4)	0.7548(7)	0.5469(7)	4.0(3)	C(74)	0.3686(5)	0.7660(10)	0.4205(10)	7.1(5)
C(25)	−0.1089(4)	0.6855(8)	0.6110(7)	4.2(3)	C(75)	0.3175(6)	0.7747(9)	0.3679(8)	6.3(5)
C(26)	−0.0492(4)	0.6786(8)	0.6392(7)	4.1(3)	C(76)	0.2665(5)	0.8231(8)	0.3904(7)	4.8(3)
C(31)	0.0642(4)	0.7536(8)	0.7565(6)	3.4(3)					
C(32)	0.0437(5)	0.6834(8)	0.8082(6)	4.2(3)	Cl(81)	0.1334(2)	0.8054(4)	0.2311(4)	12.4(2)
C(33)	0.0308(5)	0.7059(9)	0.8867(7)	4.8(4)	Cl(82)	0.2346(3)	0.7776(6)	0.1435(4)	15.9(3)
C(34)	0.0405(6)	0.7945(9)	0.9166(7)	5.5(4)	Cl(83)	0.1388(2)	0.8984(5)	0.0776(3)	14.1(3)
C(35)	0.0615(6)	0.8660(9)	0.8685(7)	5.6(4)	C(80)	0.1799(9)	0.8528(11)	0.1629(9)	9.7(7)
C(36)	0.0742(5)	0.8441(7)	0.7870(6)	4.1(3)	Cl(91)	−0.0152(3)	0.8764(5)	0.1471(4)	14.5(3)
C(41)	0.0913(4)	0.6028(7)	0.6449(6)	2.9(3)	Cl(92)	−0.1232(2)	0.8313(9)	0.2116(4)	23.4(5)
C(42)	0.0686(4)	0.5446(7)	0.5815(6)	3.5(3)	Cl(93)	−0.0182(3)	0.8184(4)	0.3135(3)	11.0(2)
C(43)	0.0846(5)	0.4488(7)	0.5787(7)	4.2(3)	C(90)	−0.0557(7)	0.8782(11)	0.2337(10)	8.4(6)
C(44)	0.1252(5)	0.4130(8)	0.6357(8)	5.2(4)					

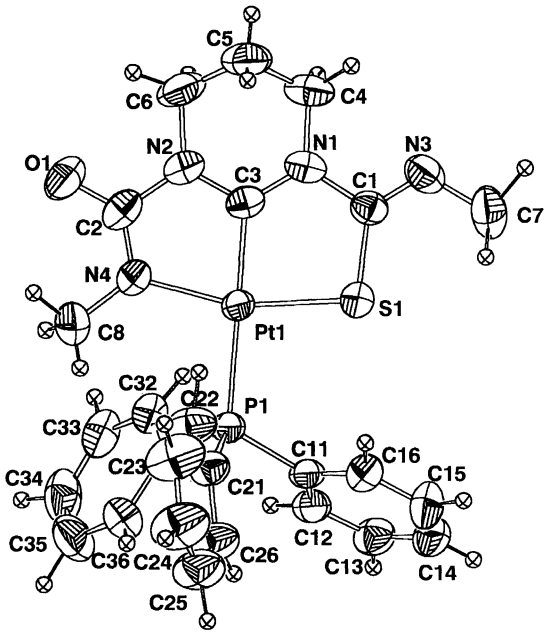


Fig. 1. ORTEP drawing of **10** with the atom-numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å.

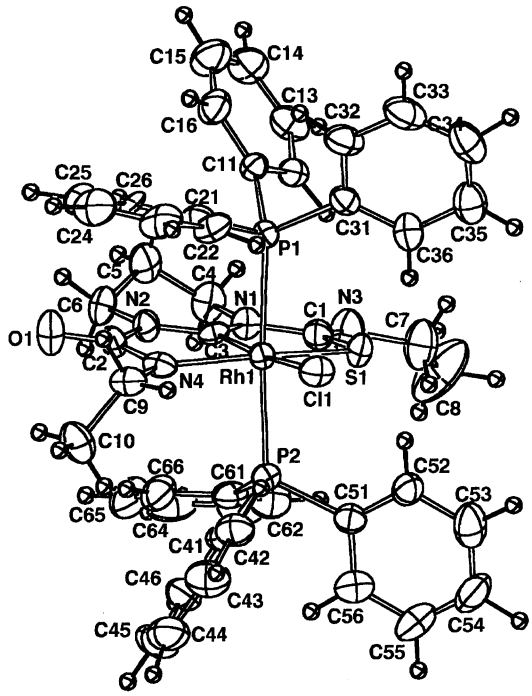


Fig. 2. ORTEP drawing of **11** with the atom-numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å.

Table 3. Selected Bond Lengths (l) and Bond Angles (θ) of Non-H Atoms of **10** and **11**

	10		**11**
Lengths	l/Å	Lengths	l/Å
Pt(1)–S(1)	2.281(1)	Rh(1)–S(1)	2.335(2)
Pt(1)–P(1)	2.318(2)	Rh(1)–P(1)	2.395(2)
		Rh(1)–P(2)	2.350(2)
		Rh(1)–Cl(1)	2.446(2)
Pt(1)–N(4)	2.064(5)	Rh(1)–N(4)	2.100(6)
Pt(1)–C(3)	1.961(8)	Rh(1)–C(3)	1.940(7)
S(1)–C(1)	1.761(8)	S(1)–C(1)	1.744(8)
O(1)–C(2)	1.244(9)	O(1)–C(2)	1.221(9)
N(1)–C(1)	1.446(10)	N(1)–C(1)	1.419(10)
N(1)–C(3)	1.327(5)	N(1)–C(3)	1.346(9)
N(1)–C(4)	1.450(11)	N(1)–C(4)	1.490(10)
N(2)–C(2)	1.419(6)	N(2)–C(2)	1.443(9)
N(2)–C(3)	1.346(9)	N(2)–C(3)	1.321(9)
N(2)–C(6)	1.483(12)	N(2)–C(6)	1.472(10)
N(3)–C(1)	1.238(6)	N(3)–C(1)	1.281(10)
N(3)–C(7)	1.433(11)	N(3)–C(7)	1.460(13)
N(4)–C(2)	1.312(11)	N(4)–C(2)	1.361(10)
N(4)–C(8)	1.457(7)	N(4)–C(9)	1.453(9)
C(4)–C(5)	1.474(13)	C(4)–C(5)	1.488(13)
C(5)–C(6)	1.507(7)	C(5)–C(6)	1.517(12)
		C(7)–C(8)	1.500(18)
		C(9)–C(10)	1.512(12)
Angles	θ/°	Angles	θ/°
		Cl(1)–Rh(1)–S(1)	100.4(1)
		Cl(1)–Rh(1)–P(1)	83.2(1)
		Cl(1)–Rh(1)–P(2)	90.8(1)
		Cl(1)–Rh(1)–N(4)	97.3(2)
		Cl(1)–Rh(1)–C(3)	172.7(2)
S(1)–Pt(1)–P(1)	96.7(1)	S(1)–Rh(1)–P(1)	95.1(1)
		S(1)–Rh(1)–P(2)	84.9(1)
S(1)–Pt(1)–N(4)	162.7(2)	S(1)–Rh(1)–N(4)	161.7(2)
S(1)–Pt(1)–C(3)	83.8(2)	S(1)–Rh(1)–C(3)	83.7(2)
		P(1)–Rh(1)–P(2)	173.9(1)
P(1)–Pt(1)–N(4)	100.6(2)	P(1)–Rh(1)–N(4)	91.2(2)
P(1)–Pt(1)–C(3)	177.7(2)	P(1)–Rh(1)–C(3)	90.5(2)
		P(2)–Rh(1)–N(4)	90.5(2)
		P(2)–Rh(1)–C(3)	95.6(2)
N(4)–Pt(1)–C(3)	79.0(3)	N(4)–Rh(1)–C(3)	79.1(3)
Pt(1)–S(1)–C(1)	99.5(2)	Rh(1)–S(1)–C(1)	98.4(3)
C(1)–N(1)–C(3)	117.5(6)	C(1)–N(1)–C(3)	119.5(7)
C(1)–N(1)–C(4)	119.7(6)	C(1)–N(1)–C(4)	118.8(7)
C(3)–N(1)–C(4)	122.8(6)	C(3)–N(1)–C(4)	121.7(7)
C(2)–N(2)–C(3)	116.5(6)	C(2)–N(2)–C(3)	117.8(7)
C(2)–N(2)–C(6)	122.0(6)	C(2)–N(2)–C(6)	118.9(7)
C(3)–N(2)–C(6)	121.4(6)	C(3)–N(2)–C(6)	123.2(7)
C(1)–N(3)–C(7)	118.4(7)	C(1)–N(3)–C(7)	117.6(8)
Pt(1)–N(4)–C(2)	114.5(5)	Rh(1)–N(4)–C(2)	112.9(5)
Pt(1)–N(4)–C(8)	128.6(5)	Rh(1)–N(4)–C(9)	133.0(5)
C(2)–N(4)–C(8)	116.9(6)	C(2)–N(4)–C(9)	113.5(6)
S(1)–C(1)–N(1)	115.3(5)	S(1)–C(1)–N(1)	115.6(6)
S(1)–C(1)–N(3)	128.0(6)	S(1)–C(1)–N(3)	125.9(7)
N(1)–C(1)–N(3)	116.6(6)	N(1)–C(1)–N(3)	118.5(8)
O(1)–C(2)–N(2)	117.1(7)	O(1)–C(2)–N(2)	118.5(7)
O(1)–C(2)–N(4)	128.6(7)	O(1)–C(2)–N(4)	129.2(8)
N(2)–C(2)–N(4)	114.3(6)	N(2)–C(2)–N(4)	112.3(7)
Pt(1)–C(3)–N(1)	123.8(5)	Rh(1)–C(3)–N(1)	122.4(6)
Pt(1)–C(3)–N(2)	115.5(5)	Rh(1)–C(3)–N(2)	117.0(6)
N(1)–C(3)–N(2)	120.7(6)	N(1)–C(3)–N(2)	120.6(7)
N(1)–C(4)–C(5)	111.0(7)	N(1)–C(4)–C(5)	110.2(8)
C(4)–C(5)–C(6)	110.5(7)	C(4)–C(5)–C(6)	109.7(8)
N(2)–C(6)–C(5)	109.9(7)	N(2)–C(6)–C(5)	109.3(7)
		N(3)–C(7)–C(8)	110.4(11)
		N(4)–C(9)–C(10)	115.1(7)

the pentalene plane is 0.198 (6) Å.

The crystal structures of **10** and **11** are shown in Figs. 3 and 4, respectively. In the crystal structure of **10**, disordered $CHCl_3$ molecules are loosely surrounded by PPh_3 groups. In the crystals of **11**, a water molecule forms a H-bonding with the O(1) atom of the carbonyl group with distances of O(1)···O(2) and O(1)···H(2A) of 2.788(10) and 1.95(11) Å, respectively, while the CH_2Cl_2 molecules are embedded in the PPh_3 groups. The origin of the water molecule is unknown.

Structure of 12. The molecular structure of Rh complex **12**, obtained from the bis-carbonyl derivative of tetraazathiapentalene **9**, is depicted in Fig. 5. Selected bond distances and angles are listed in Table 4. The hypervalent sulfur atom of **9** has not been replaced by the metal, but coordinates with Rh directly. The Rh atom is coordinated by the bidentate ligand of S and N atoms and two Cl atoms equatorially, and is also coordinated by two PPh_3 groups axially, as a consequence of the elimination of one of the phenylamide groups. Thus, no carbene complex could be obtained from the tetraazathiapentalene with bis-carbonyl groups. The length of the Rh(1)–S(1) bond is 2.376(3) Å, which is longer than the corresponding bonds of Rh–carbene complexes, **4a**, **4c**, and **11**. The length of the Rh(1)–N(1) bond is 2.018(8) Å, which is shorter than the corresponding bonds of the Rh–carbene complexes. The S(1)–C(1) bond (1.745(10) Å) is significantly longer than those of the tetraazathiapentalenes (1.705—1.717 Å). A four-membered ring consisting of Rh(1), S(1), C(1), and N(1) is plannar with the maximum deviation of 0.011(8) Å of C(1), although the shape of the ring is far from rectangular square. The angles of S(1)–Rh(1)–N(1) and Rh(1)–S(1)–C(1) are 67.4(2) and 79.1(4)°, respectively. Such small bond angles have been observed for the Rh–S–C–N four-membered ring of chloro-(*N*,*N*-dimeth-

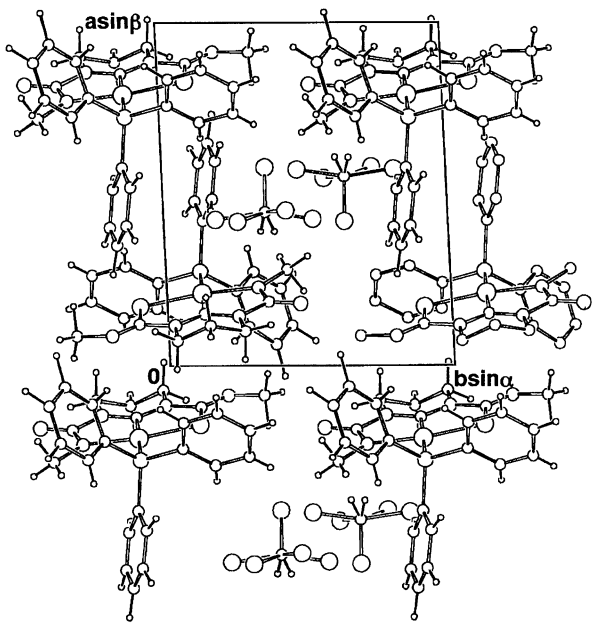


Fig. 3. Projection of the crystal structure of **10** viewed along the c axis.

Table 4. Selected Bond Lengths (l), Bond Angles (θ), and Torsion Angles (τ) of **12**

Lengths	l/Å	Lengths	l/Å
Rh(1)–S(1)	2.376(3)	N(1)–C(3)	1.474(13)
Rh(1)–Cl(1)	2.382(3)	N(2)–C(1)	1.394(13)
Rh(1)–Cl(2)	2.372(3)	N(2)–C(2)	1.387(15)
Rh(1)–P(1)	2.390(3)	N(2)–C(5)	1.487(16)
Rh(1)–P(2)	2.384(3)	N(3)–C(2)	1.345(15)
Rh(1)–N(1)	2.018(8)	N(3)–C(11)	1.437(14)
S(1)–C(1)	1.745(10)	C(3)–C(4)	1.501(17)
O(1)–C(2)	1.228(15)	C(4)–C(5)	1.418(21)
N(1)–C(1)	1.281(13)		
Angles	θ/°	**Angles**	θ/°
S(1)–Rh(1)–Cl(1)	106.7(1)	Rh(1)–N(1)–C(1)	105.8(7)
S(1)–Rh(1)–Cl(2)	160.3(1)	Rh(1)–N(1)–C(3)	131.0(7)
S(1)–Rh(1)–P(1)	89.2(1)	C(1)–N(1)–C(3)	123.2(9)
S(1)–Rh(1)–P(2)	88.1(1)	C(1)–N(2)–C(2)	127.9(10)
S(1)–Rh(1)–N(1)	67.4(2)	C(1)–N(2)–C(5)	113.8(10)
Cl(1)–Rh(1)–Cl(2)	92.9(1)	C(2)–N(2)–C(5)	117.2(10)
Cl(1)–Rh(1)–P(1)	87.3(1)	C(2)–N(3)–C(11)	127.2(10)
Cl(1)–Rh(1)–P(2)	88.7(1)	S(1)–C(1)–N(1)	107.6(8)
Cl(1)–Rh(1)–N(1)	174.0(2)	S(1)–C(1)–N(2)	126.9(8)
Cl(2)–Rh(1)–P(1)	94.1(1)	N(1)–C(1)–N(2)	125.4(10)
Cl(2)–Rh(1)–P(2)	90.1(1)	O(1)–C(2)–N(2)	118.5(11)
Cl(2)–Rh(1)–N(1)	93.0(2)	O(1)–C(2)–N(3)	124.4(11)
P(1)–Rh(1)–P(2)	174.3(1)	N(2)–C(2)–N(3)	116.9(10)
P(1)–Rh(1)–N(1)	91.3(2)	N(1)–C(3)–C(4)	109.2(10)
P(2)–Rh(1)–N(1)	92.3(2)	C(3)–C(4)–C(5)	114.7(12)
Rh(1)–S(1)–C(1)	79.1(4)	N(2)–C(5)–C(4)	111.8(12)
Torsion angles	τ/°	**Torsion angles**	τ/°
Rh(1)–S(1)–C(1)–N(1)	0.9(5)	C(1)–N(2)–C(2)–O(1)	154.2(7)
Rh(1)–S(1)–C(1)–N(2)	−176.4(5)	C(1)–N(2)–C(2)–N(3)	−30.3(13)
S(1)–C(1)–N(2)–C(2)	−0.1(12)	O(1)–C(2)–N(3)–C(11)	−16.5(14)

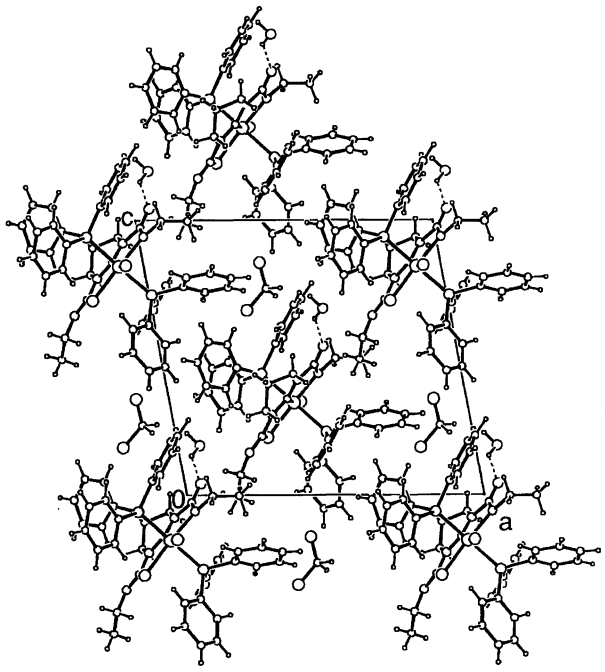


Fig. 4. Projection of the crystal structure of **11** viewed along the b axis.

ylthiocarboximido)(*N*,*N*-dimethyl-*N*′-phenylthioureido)triphenylphosphine–rhodium(III) (S–Rh–N: 60.3, Rh–S–C: 80.9°).[12] The angles of Cl(1)–Rh(1)–S(1), Cl(1)–Rh(1)–Cl(2), and Cl(2)–Rh(1)–N(1) are 106.7(1), 92.9(1), and 93.0(2)°, respectively. Rh and its four coordinating atoms make a plane with the maximum deviation of 0.057(8) Å of N(1). The phenylamide group rotated around the N(2)–C(2) bond with the torsion angle of 30(1)° of C(1)–N(2)–C(2)–N(3), so that the length of the Rh(1)···N(3) contact (3.028(18) Å) is longer than the hypervalent S–N bond (1.9 Å). The length of S(1)···H(3N) is 2.43(10) Å. The lengths of the C–N bonds are different from those of the starting tetraazathiapentalene.

The crystal structure is shown in Fig. 6. The packing of the molecules is a van der Waals' type.

Formation Mechanism. From these results, we conclude that at least one thiocarbonyl group seems to be necessary for the formation of new carbene complexes. No complexes with N–M–N and O–M–S types could be obtained. In order to investigate the difference in the reactivities between the thiocarbonyl and carbonyl groups, we calculated the frontier orbital electron densities for these three thiapentalenes (**1**, **8**, and **9**) using the program PM3.[13] The electron densities of HOMO and LUMO of selected atoms of the starting tetraazathiapentalenes are given in Table 5 and Fig. 7. In this figure the size of the circles is proportional to the densities. As for the densities of HOMO, the differences between the carbonyl

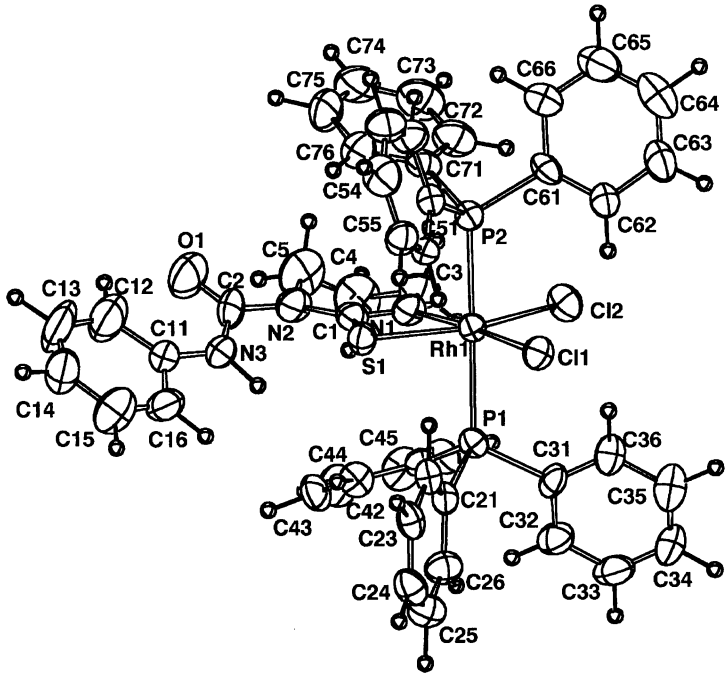


Fig. 5. ORTEP drawing of **12** with the atom-numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å.

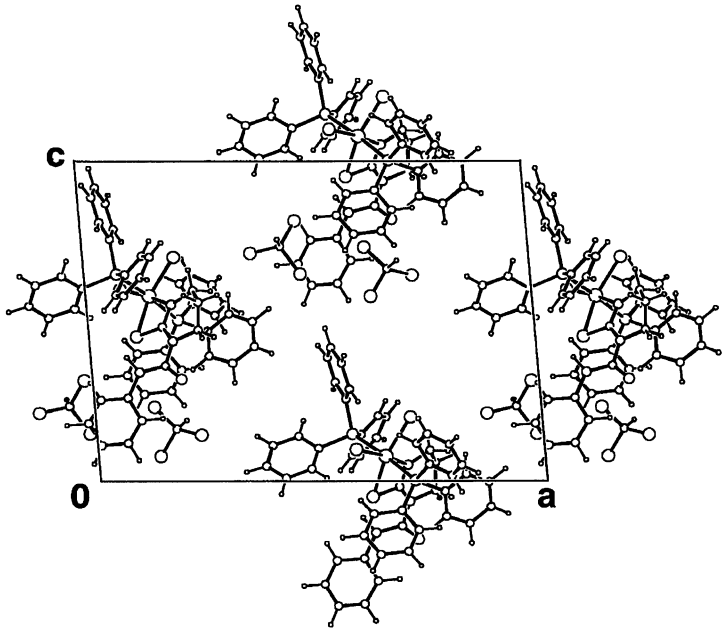


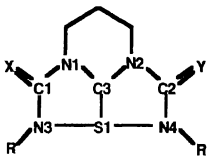
Fig. 6. Projection of the crystal structure of **12** viewed along the *b* axis within the range y=0.5—1.0.

and thiocarbonyl groups are clearly shown. Large densities of HOMO are shown at the S atoms of the thiocarbonyl groups. However, frontier electrons are not distributed on the O atoms of the carbonyl groups. In the case of the bis-carbonyl compound, the HOMO electron densities are mainly distributed on the hypervalent S atom. For all compounds, large LUMO densities are found at the central C atom of the pentalene framework. This means that these C atoms are easily attacked by the nucleophiles.

From these calculations, we presume that the formation mechanism of the metal–carbene complex is as shown in Scheme 2. (A) In the solutions one PPh_3 group is removed from the metal reagent, such as $Pt(PPh_3)_4$, $Pd(PPh_3)_4$, and $RhCl(PPh_3)_3$. These reagents then become active nucleophiles and attack the central carbon atom of the pentalene ring. (B) Weak hypervalent S–N bonds are easily cleaved and a tricyclic SCM is formed. (C) A strongly nucleophilic sulfur atom of the thiocarbonyl group coordinates the metal. (D) The central C–S bond of the three-membered ring is cleaved and removed as $S{=}PPh_3$. In fact, $S{=}PPh_3$ was obtained as a by-product during the reaction. (E) An S or N atom of the thioamide group (the amide group in the case of mono-

Table 5. Frontier Electron Density of Tetraazathiapentalenes

	1 X=S, Y=S		**8** X=O, Y=S		**9** X=O, Y=O	
	$fr^{(E)}$	$fr^{(N)}$	$fr^{(E)}$	$fr^{(N)}$	$fr^{(E)}$	$fr^{(N)}$
X	0.555	0.044	0.039	0.013	0.126	0.018
Y	0.563	0.044	1.055	0.049	0.136	0.018
S(1)	0.260	0.254	0.256	0.242	0.365	0.227
C(3)	0.015	0.837	0.019	0.899	0.053	0.980
N(1)	0.037	0.210	0.015	0.257	0.049	0.270
N(2)	0.038	0.205	0.070	0.211	0.045	0.269
C(1)	0.001	0.062	0.010	0.015	0.026	0.022
C(2)	0.001	0.061	0.001	0.076	0.029	0.021
N(3)	0.248	0.123	0.104	0.058	0.312	0.054
N(4)	0.246	0.124	0.395	0.139	0.352	0.054



carbonyl derivative **8**) of the other side coordinates the metal to form a symmetrical S–M–S complex or an asymmetric N–M–S complex.

In this reaction scheme, the role of the central hypervalent sulfur atom seems to form a three-membered ring, and is removed as $S{=}PPh_3$. One of the S atoms of the thiocarbonyl groups works as a nucleophile. Then, if there would be any other strong nucleophilic ligand, it may coordinate the metal. This means that a starting material would not be necessarily an N–S–N hypervalent system, and that a ligand S atom would not be necessarily a thiocarbonyl group, since the thioamide group could easily rotate around the C–N bond. From these points of view, a similar carbene complex should be obtained from a trithiapentalene derivative, as shown in Scheme 3. In fact, we recently obtained metal complexes **15** from a diselenathiapentalene **14**. The details concerning these structures will be presented elsewhere.

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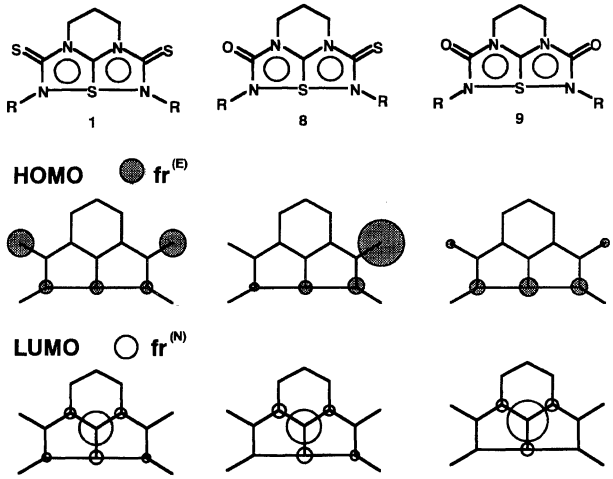
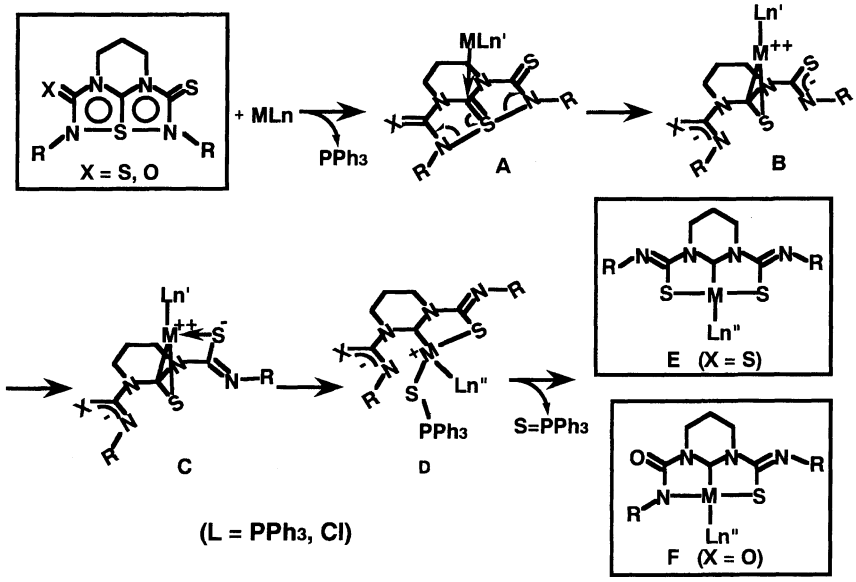
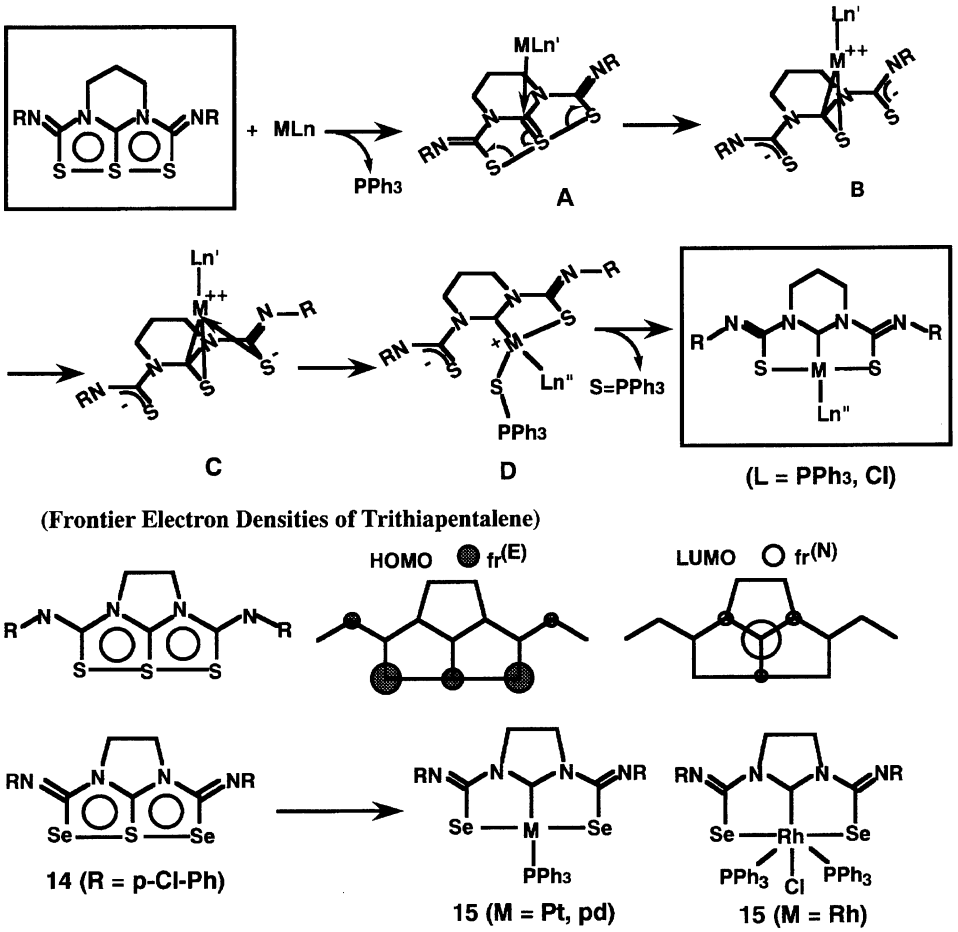


Fig. 7. Schematic drawings of frontier electron densities of tetraazathiapentalenes calculated by PM3 method.



Scheme 2.



Scheme 3.

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