Synthesis and structural features of tetranuclear rhodium complexes of amidophosphito- and phosphitocavitands

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Interactions of acetylacetonatodicarbonylrhodium(I) with amidophosphito- and phosphitocavitands were studied. First representatives of tetranuclear cavity complexes of rhodium(I) were obtained. It was established by NMR spectroscopy and X-ray diffraction studies that the chemically identical phosphorhodium centers in these complexes differ in the spatial arrangement, and the system as a whole becomes unsymmetrical.

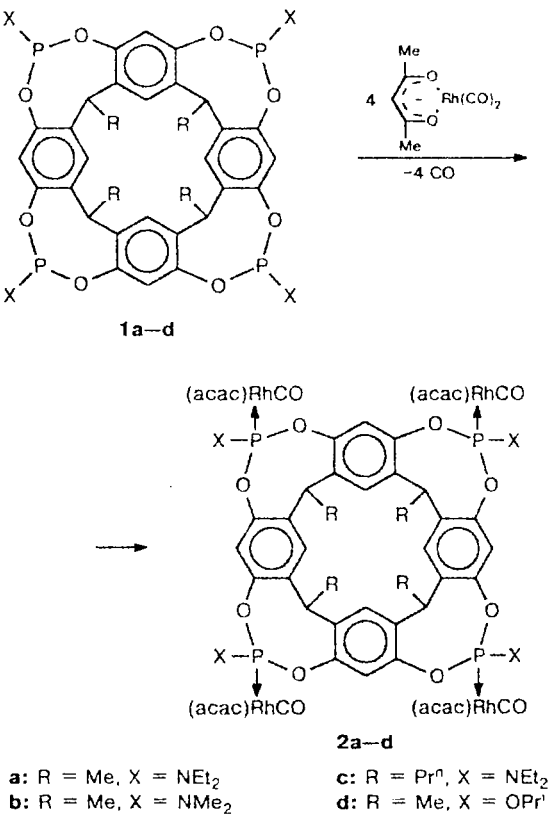
Key words: phosphocavitands; rhodium, complexation; conformation, X-ray structural analysis.

P^{III}-Phosphocavitands containing four reactive phosphorus centers are very promising compounds for constructing cavity molecules with different configurations. These cavitands readily enter into oxidation reactions,[1—4] undergo alkylation with alkyl halides,[4,5] and form complex compounds.[6—8] The major characteristic features of the above-mentioned processes are worthy of note. First, most of these processes occur stereoregularly to form symmetrical stereoisomers in which substituents attached to phosphorus atoms are in axial orientations, *i.e.*, are directed toward the cavity of the cavitand. Second, the molecular skeleton of the macrocycle does not undergo structural changes in the course of the reaction. As part of continuing studies of the properties of P^{III}-phosphocavitands and their characteristic features, in this work we studied complexation of amidophosphito- and phosphitocavitands with acetylacetonatodicarbonylrhodium(I), $(acac)Rh(CO)_2$.

The reactions of P^{III}-phosphocavitands **1a—d** with acetylacetonatodicarbonylrhodium(I) (Scheme 1) were carried out in dioxane or chloroform in the temperature range of 20—100 °C. The course of the reaction was monitored by ^{31}P NMR spectroscopy.

The reaction in dioxane proceeded to completion only upon heating to 100 °C, while this reaction in chloroform proceeded to completion at room temperature. The portionwise addition of $(acac)Rh(CO)_2$ to amidophosphite **1a** demonstrated that two of four P atoms in the cavitand molecule were readily coordinated to rhodium with vigorous CO evolution. The coordination of the third P atom occurred more slowly, and the fourth P atom was difficult to coordinate (Table 1). Apparently, steric hindrances, which are due to the spatial proximity of four P atoms fixed at the rigid skeleton of P^{III}-phosphocavitands, are of prime importance in these processes.

Scheme 1



1a—d

2a—d

a: R = Me, X = NEt_2
b: R = Me, X = NMe_2
c: R = Pr^n, X = NEt_2
d: R = Me, X = OPr^i

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Table 1. Composition of the reaction mixture in the course of the reaction of cavitand **1a** (0.03 mmol) with $(acac)Rh(CO)_2$ in dioxane according to the data of ^{31}P NMR spectroscopy

$n_{(acac)Rh(CO)_2}$ /mmol	T/°C	t /h	Noncoordinated P		Coordinated P		
			δ ^{31}P	I_Σ (%)	δ ^{31}P	$^1J_{PRh}$/Hz	I_Σ (%)
0.00	20		142.7	100			
0.03	20	1	142.1, 144.7, 145.8	75	125.9	270.3	25
0.06	20	1	144.8, 146	50	129.2	267.4	50
0.09	20	2	144.1	25	134.1, 126.5	267.4, 273.2	75
0.12	20	24	144.2	20	134.2, 130.2, 126.6	267.4, 273.9, 273.2	80
0.12	100	3			130.2	273.9	100

Note: n is the total number of millimoles; t is time; I_Σ is the total intensity of the signals.

Tetrarhodium complexes **2a—d** were isolated in the pure form in 53—81% yields. The ^{31}P NMR spectra of these compounds measured at 37 °C have a single doublet with the spin-spin coupling constant $^1J_{PRh}$ typical of the planar-square complexes containing phosphite ligands[9] (Table 2). The ^1H NMR spectra of complexes **2a—d** measured at 22 °C have a set of signals for all types of protons (see Table 2). These facts indicate that four phosphocine rings in the molecules of cavitands **2** are chemically and structurally identical. The IR spectra of amide derivativs **2a—c** show two bands corresponding to stretching vibrations of the carbonyl groups at the Rh atoms: at 1980 and 1995 cm^{-1} (**2a**); 1975 and 1988 cm^{-1} (**2b**); and 1975 and 1998 cm^{-1} (**2c**). The exception is phosphite complex **2d**: the IR spectra of a solution of **2d** as well as of solid samples have only one band typical of vibrations of carbonyl groups (at 1987 and 1998 cm^{-1}, respectively). ^{31}P NMR spectral studies of amide and phosphite tetranuclear rhodium complexes (**2a** and **2d**, respectively) at low temperature demonstrated that the structures of the phosphorhodium fragments in these compounds are different. Thus, even at 0 °C the phosphorus nuclei in cavitand **2a** become magnetically nonequivalent (Fig. 1, *b*). The NMR spectrum of compound **2a** recorded at −60 °C has four distinct doublets with close values of chemical shifts and spin-spin coupling constants $^1J_{PRh}$ (Fig. 1, *c*). The ratio of integrated intensities of the doublets is 2 : 1 : 1. When the sample was heated to 20 °C, three doublets merge into one signal again (Fig. 1, *a*). An analogous situation is also observed for complex **2d**. In the ^{31}P NMR spectrum of this compound at −60 °C, three doublets at δ 127.0, 126.0, and 115.5 (spin-spin coupling constants $^1J_{PRh}$ = 291.5, 285.2, and 291.0 Hz, respec-

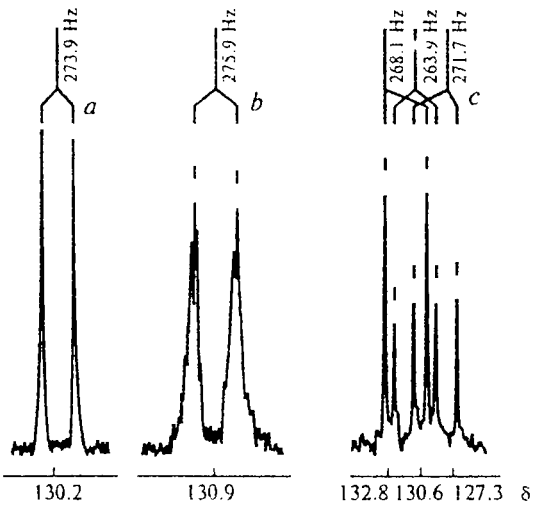


Fig. 1. ^{31}P NMR spectra of complex **2a** recorded at 20 °C (*a*), 0 °C (*b*), and −60 °C (*c*).

Table 2. Parameters of the ^{31}P and ^1H NMR spectra of complex **2** (in $CDCl_3$)

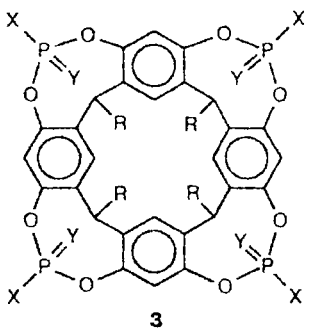
Compound	δ ^{31}P ($^1J_{PRh}$/Hz)	δ ^1H					
		H_m (C, 4 H)	H_o (C, 4 H)	CH (4 H)	R	X	acac
2a	130.2 (d, J = 273.9)	7.24	7.05	4.92 (q)	1.80 (d, 12 H, CH_3)	3.70 (m, 16 H, NCH_2); 1.22 (t, 24 H, CH_3)	5.43 (s, 4 H, CH); 2.03 (s, 12 H, CH_3)
2b	131.1 (d, J = 279.0)	7.28	7.02	4.92 (q)	1.82 (d, 12 H, CH_3)	3.09 (d, 24 H, NCH_3)	5.45 (s, 4 H, CH); 2.01 (s, 12 H, CH_3)
2c	130.1 (d, J = 271.9)	7.28	7.11	4.78 (t)	2.29, 1.42, 1.01 (21 H, CH_2—CH_2—CH_3)	3.70 (m, 16 H, NCH_2); 1.18 (t, 24 H, CH_3)	5.46 (s, 4 H, CH); 2.01 (s, 12 H, CH_3)
2d	121.6 (d, J = 290.6)	7.21	7.05	4.92 (q)	1.79 (d, 12 H, CH_3)	5.49 (m, 4 H, OCH); 1.39 (d, 24 H, CH_3)	5.40 (s, 4 H, CH); 2.03 (s, 12 H, CH_3)

Table 3. Principal bond lengths (d) and bond angles (ω) in the structure of **2d**

Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Rh(1)—P(1)	2.173(2)	C(50)—Rh(1)—P(1)	90.7(2)	O(4)—P(2)—Rh(2)	123.9(1)
Rh(2)—P(2)	2.179(2)	O(13)—Rh(1)—P(1)	87.1(1)	O(5)—P(2)—Rh(2)	112.5(1)
Rh(3)—P(3)	2.166(2)	O(14)—Rh(1)—P(1)	176.2(1)	O(9)—P(3)—O(8)	106.2(2)
Rh(4)—P(4)	2.167(2)	C(56)—Rh(2)—P(2)	92.5(2)	O(9)—P(3)—O(7)	96.5(2)
Rh—(CO)	1.806(6)—1.816(6)	O(16)—Rh(2)—P(2)	87.6(1)	O(8)—P(3)—O(7)	104.8(2)
		O(17)—Rh(2)—P(2)	176.5(1)	O(9)—P(3)—Rh(3)	118.9(2)
Rh—O(acac)	2.013(3)—2.061(4)	C(62)—Rh(3)—P(3)	90.6(2)	O(8)—P(3)—Rh(3)	114.4(2)
		O(19)—Rh(3)—P(3)	87.8(2)	O(7)—P(3)—Rh(3)	113.9(2)
P(1)—O(1)	1.612(3)	O(20)—Rh(3)—P(3)	177.6(2)	O(12)—P(4)—O(10)	98.7(2)
P(1)—O(2)	1.616(4)	C(68)—Rh(4)—P(4)	91.1(2)	O(12)—P(4)—O(11)	98.6(2)
P(2)—O(4)	1.614(4)	O(23)—Rh(4)—P(4)	91.5(1)	O(10)—P(4)—O(11)	104.4(2)
P(2)—O(5)	1.626(4)	O(22)—Rh(4)—P(4)	170.9(1)	O(12)—P(4)—Rh(4)	111.4(2)
P(3)—O(8)	1.590(4)	O(3)—P(1)—O(1)	94.3(2)	O(10)—P(4)—Rh(4)	121.3(2)
P(3)—O(7)	1.607(4)	O(3)—P(1)—O(2)	98.3(2)	O(11)—P(4)—Rh(4)	118.5(1)
P(4)—O(10)	1.617(4)	O(1)—P(1)—O(2)	102.6(2)	C(24)—O(1)—P(1)	119.4(3)
P(4)—O(11)	1.617(4)	O(3)—P(1)—Rh(1)	123.5(2)	C(1)—O(2)—P(1)	130.6(3)
P—O(Pr^i)	1.576(4)—1.583(3)	O(1)—P(1)—Rh(1)	117.6(1)	C(3)—O(4)—P(2)	131.9(3)
		O(2)—P(1)—Rh(1)	116.2(1)	C(8)—O(5)—P(2)	121.7(3)
		O(6)—P(2)—O(4)	94.1(2)	C(10)—O(7)—P(3)	126.1(3)
		O(6)—P(2)—O(5)	98.1(2)	C(15)—O(8)—P(3)	138.4(3)
		O(4)—P(2)—O(5)	105.0(2)	C(17)—O(10)—P(4)	135.1(3)
		O(6)—P(2)—Rh(2)	119.0(2)	C(22)—O(11)—P(4)	124.2(3)
				C(42)—O(12)—P(4)	125.9(4)

tively) are observed. The ratio of integrated intensities is 1 : 2 : 1. Therefore, unlike all reactions studied previously,[1–8] the reactions of P^{III}-phosphocavitands with (acac)$Rh(CO)_2$ lead to a distortion of the structure of the molecular skeleton of the cavitands.

X-ray diffraction study of complex **2d** demonstrated that phosphocavitand **2d** cocrystallizes with one hexane molecule of solvation. The hexane molecules are located in cavities between cavitand molecules (after storage *in vacuo*, the analytical sample did not contain hexane). The geometric parameters of compound **2d** (Table 3) are similar to the corresponding values in phosphocavitands **3** studied previously.[3,4,10,12]



3

R = Me, X = OPr^i, Y = S;[3]
R = Pr, X = NEt_2, Y = НЭП;[4]
R = Bu, X = NMe_2, Y = НЭП;[10]
R = Me, X = NEt_2, Y = S [12]
(LEP is the lone electron pair)

Each P atom is incorporated into the eight-membered PO_2C_5 ring. The Rh atoms are coordinated to the carbonyl and acetylacetonate ligands. The Rh—P distances are in the range of 2.167(2)—2.179(2) Å. The P atoms are characterized by a distorted octahedral coordination. Like molecules studied previously, phosphocavitand **2d** has a "bowl" shape (Figs. 2 and 3) with the hydrophobic methyl substituents at the "bottom" (the C(5), C(12), C(19), and C(26) atoms) and the hydrophilic P(OPr^i)[Rh(CO)(acac)] fragments at the "cover" (the C(2), C(9), C(16), and C(23) atoms). In the crystal of **2d**, the Rh(CO)(acac) groups have a different arrangement, namely, the metal-containing fragment at the P(1) atom is directed toward the center of the "bowl," while the fragments at the P(2), P(3), and P(4) atoms are located outside the cavity of the cavitand (see Fig. 2). The angles between the planes of the Rh(CO)(acac) groups and the plane through the P atoms are 101°, 125.7°, 85.1°, and 76.6° for Rh(1), Rh(2), Rh(3), and Rh(4), respectively.

It should be noted that in spite of the possibility of the existence of the local symmetry C_{4v},[12] this symmetry is not actually observed in most of phosphocavitands studied by us.[3,4,10] Apparently, this is mainly due to the effect of molecules of solvation. However, in the case of molecule **2d** the major distortions are due to the steric repulsion between the metal-containing Rh(CO)(acac) fragments as a result of which the "cover" of the molecule is distorted and becomes virtually "rectangular" (the P(1)...P(2), P(2)...P(3), P(3)...P(4), and P(4)...P(1) distances between the adjacent P atoms in molecule **2d** are 7.036, 6.622, 7.447, and 6.420 Å, respectively). The eight-membered phosphorus-containing rings in molecule **2d** adopt different conformations. Thus, the rings involving the P(1), P(2), and P(4) atoms, as in the

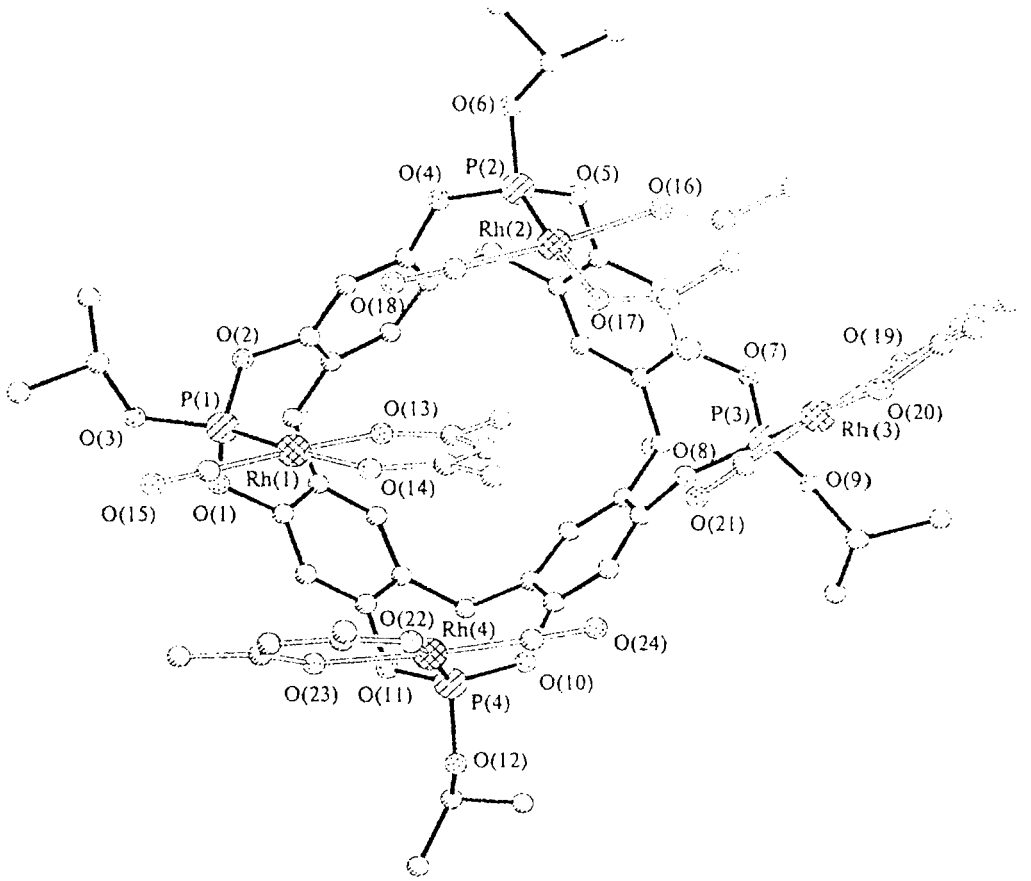


Fig. 2. Mutual arrangement of the acac ligands with respect to the "cover" of phosphocavitand **2d**.

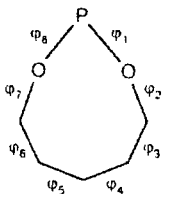
structures of phosphocavitands **3** studied by us previously,[3,4,10,12] adopt a chair-boat conformation (**A**) (Fig. 4), while the ring containing the P(3) atom adopts a boat conformation (**B**). The Rh atoms and the Me groups are in equatorial positions, and the OPr^i group is in the axial position. The endocyclic torsion angles that characterize the above-described conformations are given in Table 4 (their notations are shown in Scheme 2). The C(5)...C(19) and C(12)...C(26) distances (the "bottom" of the phosphocavitand) are 5.309 and 5.261 Å, respectively. The C(2)...C(16) and C(9)...C(23) distances (the "cover") are 7.338 and 8.683 Å, respectively. The intermolecular distances in the crystal structure of **2d** correspond to normal van der Waals contacts.

Table 4. Endocyclic torsion angles (φ) in the phosphorus-containing eight-membered rings in the structure of **2d**

Angle	P(1)	P(2)	P(3)	P(4)
φ_1*	82.5	73.0	16.8	72.1
φ_2	−90.5	−78.1	−79.4	−90.3
φ_3	6.2	6.6	8.6	5.5
φ_4	89.9	84.0	92.8	93.5
φ_5	−81.5	−94.3	−69.3	−79.8
φ_6	−9.1	−1.6	11.4	−14.8
φ_7	84.6	87.1	−49.1	82.2
φ_8	86.4	−79.5	75.0	65.6

* For notations of the torsion angles, see Scheme 2.

Scheme 2



Therefore, the insertion of four bulky groups into the molecule of P^{III}-phosphocavitand leads to a loss of its symmetry and results in the formation of the structure with different conformations of four phosphocine rings.

Experimental

The ^1H NMR spectra were recorded on a Bruker WM-200 spectrometer with Me_4Si as the internal standard. The ^{31}P NMR spectra (32.4 MHz, 85% H_3PO_4 solution as the external standard) were recorded on a Bruker WP-80 spectrometer. The IR spectra were obtained on Specord 75-IR (solutions in

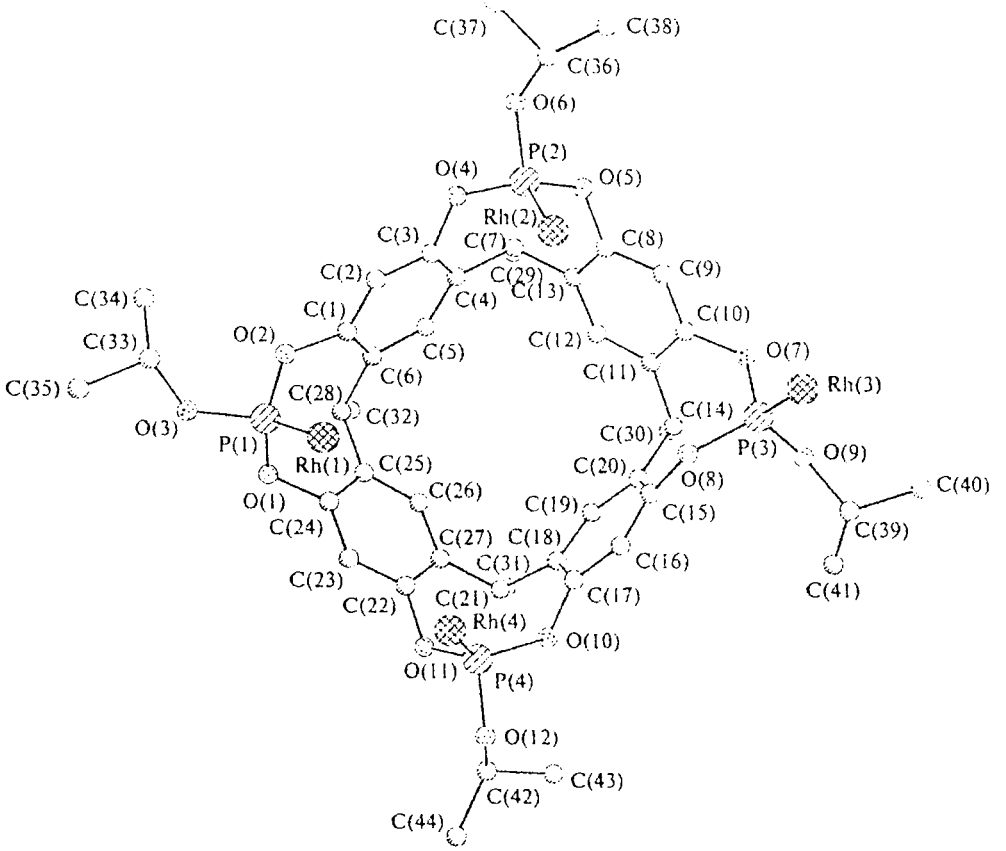


Fig. 3. Overall view of molecule **2d** and the atomic numbering scheme for the skeleton (the acac ligands are omitted for clarity).

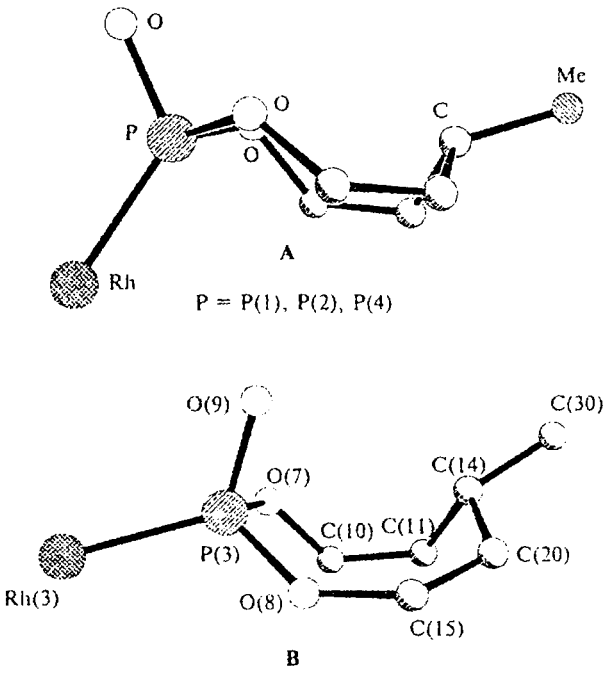


Fig. 4. Conformations of the eight-membered phosphorus-containing rings in the structure of **2d**.

CH_2Cl_2) and Nicolet Magna 750 (KBr pellets) instruments. All reactions were carried out in dry solvents under argon. P^{III}-Phosphocavitands were synthesized according to procedures reported previously,[4,10] and (acac)$Rh(CO)_2$ was prepared according to a known procedure.[11]

Complexes 2a,b. A solution of the corresponding amidophosphocavitand **1** (0.155 mmol) and (acac)$Rh(CO)_2$ (0.62 mmol) in chloroform (4 mL) was kept at 20 °C for 16 h. Complex **2** was precipitated from the reaction mixture with hexane, while unconsumed (acac)$Rh(CO)_2$ remained in the solution. The precipitate of compound **2** was filtered off, washed with hexane, and dried *in vacuo*.

1,21,23,25-Tetramethyl-5,9,13,17-tetrakis(diethylamido)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^3]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]benzobis[1,3,2λ^3]dioxaphosphocino-5,9,13,17-tetrakis(acetylacetonatocarbonylrhodium) (2a). The yield was 81%, decomp. temp. 248—251 °C. Found (%): C, 45.98; H, 5.10; P, 6.19; Rh, 21.71. $C_{72}H_{92}N_4O_{20}P_4Rh_4$. Calculated (%): C, 46.27; H, 4.96; P, 6.63; Rh, 22.02. IR (solution in CH_2Cl_2), ν/cm^{-1}: 2965, 2925, 2830, 1995, 1980, 1585, 1519, 1480, 1390, 1370, 1275, 1200, 1165, 1140, 1088, 1019, 997, 940, 880, 850, 750, 610; (KBr pellets), ν/cm^{-1}: 2973, 2930, 2877, 2003, 1987, 1584, 1522, 1485, 1394, 1379, 1282, 1272, 1207, 1174, 1151, 1095, 1024, 1001, 945, 889, 856, 788, 740, 696, 681, 516, 441.

1,21,23,25-Tetramethyl-5,9,13,17-tetrakis(dimethylamido)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^3]dioxaphosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]benzobis[1,3,2λ^3]dioxaphosphocino-5,9,13,17-tetrakis(acetylaceto-

Table 5. Coordinates of nonhydrogen atoms ($\times 10^4$) and their equivalent isotropic temperature factors ($U_{eq} \times 10^3$) in the structure of **2d**

Atom	*x*	*y*	*z*	U_{eq}/Å^2	Atom	*x*	*y*	*z*	U_{eq}/Å^2
Rh(1)	6019(1)	2408(1)	7667(1)	36(1)	C(24)	5231(3)	1242(3)	9442(3)	33(1)
Rh(2)	3823(1)	6378(1)	6411(1)	39(1)	C(25)	4682(3)	1708(3)	9833(2)	32(1)
Rh(3)	133(1)	6313(1)	5516(1)	53(1)	C(26)	3726(4)	1689(3)	9858(2)	33(1)
Rh(4)	3828(1)	1157(1)	7076(1)	41(1)	C(27)	3302(3)	1223(3)	9528(2)	32(1)
P(1)	6600(1)	1994(1)	8795(1)	35(1)	C(28)	5137(4)	2242(3)	10182(3)	34(1)
P(2)	4023(1)	6685(1)	7375(1)	37(1)	C(29)	3033(4)	5505(4)	9935(3)	48(1)
P(3)	57(1)	5586(1)	6688(1)	40(1)	C(30)	110(4)	4423(4)	9329(3)	45(1)
P(4)	2983(1)	701(1)	8002(1)	37(1)	C(31)	1850(4)	1108(4)	10275(3)	45(1)
O(1)	6221(2)	1193(2)	9437(2)	35(1)	C(32)	4788(4)	2151(4)	10929(3)	42(1)
O(2)	6453(2)	2809(2)	9099(2)	38(1)	C(33)	8447(4)	1987(4)	8739(3)	50(1)
O(3)	7696(2)	1529(2)	9076(2)	45(1)	C(34)	8661(5)	2555(5)	9146(4)	70(2)
O(4)	4736(3)	5986(2)	8099(2)	39(1)	C(35)	9299(5)	1225(5)	8771(5)	74(2)
O(5)	3014(3)	6998(2)	7687(2)	40(1)	C(36)	4369(6)	8321(5)	6590(4)	74(2)
O(6)	4440(3)	7551(2)	7283(2)	47(1)	C(37)	5300(10)	8569(9)	6499(7)	158(6)
O(7)	189(3)	6173(2)	7164(2)	44(1)	C(38)	3571(11)	9100(6)	6617(6)	155(6)
O(8)	843(3)	4629(2)	7064(2)	43(1)	C(39)	−1567(5)	5102(5)	6562(3)	59(2)
O(9)	−928(3)	5380(3)	6971(2)	50(1)	C(40)	−2404(6)	5890(6)	6190(5)	98(3)
O(10)	1970(3)	1356(2)	8046(2)	39(1)	C(41)	−1825(6)	4268(5)	7119(4)	73(2)
O(11)	3513(2)	271(2)	8827(2)	37(1)	C(42)	2223(5)	−791(4)	8680(4)	58(2)
O(12)	2615(3)	−169(2)	8040(2)	47(1)	C(43)	1195(6)	−426(6)	8645(6)	95(3)
O(13)	4796(2)	3060(2)	7932(2)	39(1)	C(44)	2490(5)	−1723(4)	8650(5)	75(2)
O(14)	5422(3)	2881(3)	6602(2)	45(1)	C(45)	4034(4)	3543(3)	7498(3)	37(1)
O(15)	7809(3)	1350(4)	7345(3)	76(1)	C(46)	3909(4)	3729(4)	6756(3)	41(1)
O(16)	2658(3)	7493(3)	6060(2)	50(1)	C(47)	4578(4)	3408(4)	6351(3)	44(1)
O(17)	3553(3)	6146(3)	5484(2)	52(1)	C(48)	3248(4)	3962(4)	7858(3)	47(1)
O(18)	5643(3)	4926(3)	6795(2)	58(1)	C(49)	4334(5)	3706(5)	5538(3)	59(2)
O(19)	−864(4)	7412(3)	5562(3)	79(1)	C(50)	7114(4)	1756(4)	7480(3)	49(1)
O(20)	166(4)	7052(4)	4405(2)	84(2)	C(51)	2117(5)	7798(4)	5454(3)	56(2)
O(21)	1579(5)	4696(5)	5493(3)	95(2)	C(52)	2200(5)	7424(5)	4930(3)	60(2)
O(22)	4566(3)	1437(3)	6147(2)	54(1)	C(53)	2890(5)	6637(5)	4972(3)	57(2)
O(23)	5047(3)	250(3)	7686(2)	46(1)	C(54)	1317(6)	8626(5)	5357(5)	86(2)
O(24)	2179(4)	2600(4)	6120(3)	73(1)	C(55)	2824(6)	6291(5)	4366(4)	71(2)
C(1)	5635(3)	3478(3)	9080(3)	34(1)	C(56)	4933(4)	5466(4)	6673(3)	43(1)
C(2)	5522(4)	4384(3)	8559(3)	34(1)	C(57)	−1204(7)	8199(5)	5028(5)	95(3)
C(3)	4778(4)	5063(3)	8593(3)	34(1)	C(58)	−904(9)	8464(7)	4329(6)	108(4)
C(4)	4143(4)	4884(3)	9134(3)	34(1)	C(59)	−261(8)	7904(8)	4048(4)	99(4)
C(5)	4283(3)	3965(3)	9640(3)	32(1)	C(60)	−1995(11)	8838(7)	5224(7)	166(6)
C(6)	5017(3)	3245(3)	9629(2)	32(1)	C(61)	−61(8)	8289(8)	3241(4)	135(5)
C(7)	3318(4)	5657(3)	9162(3)	37(1)	C(62)	1024(5)	5320(6)	5504(3)	66(2)
C(8)	2375(4)	6426(3)	7907(3)	36(1)	C(63)	5450(5)	1108(4)	6122(3)	54(2)
C(9)	1621(4)	6553(3)	7419(3)	40(1)	C(64)	6094(5)	508(4)	6728(3)	53(1)
C(10)	985(4)	5994(3)	7646(3)	38(1)	C(65)	5874(5)	129(4)	7454(3)	50(1)
C(11)	1087(4)	5296(3)	8348(3)	34(1)	C(66)	5784(6)	1410(6)	5360(4)	75(2)
C(12)	1843(4)	5209(3)	8830(3)	36(1)	C(67)	6682(5)	−502(5)	8036(4)	71(2)
C(13)	2491(4)	5764(3)	8632(3)	34(1)	C(68)	2791(5)	2022(5)	6513(3)	52(1)
C(14)	419(4)	4637(3)	8558(3)	37(1)	C(1s)*	7056(20)	−3613(23)	8113(14)	133(9)
C(15)	989(4)	3795(3)	7710(3)	36(1)	C(2s)	7769(17)	−3449(23)	8447(18)	339(26)
C(16)	1350(4)	3012(3)	7582(3)	38(1)	C(3s)	7912(32)	−2749(32)	7709(23)	164(18)
C(17)	1694(4)	2172(3)	8177(3)	35(1)	C(4s)	8533(29)	−2590(31)	7957(33)	139(15)
C(18)	1707(3)	2114(3)	8901(3)	32(1)	C(5s)	9123(30)	−1757(34)	7358(38)	183(26)
C(19)	1267(3)	2918(3)	8997(3)	33(1)	C(6s)	9640(23)	−1567(21)	7622(20)	252(12)
C(20)	880(3)	3772(3)	8416(3)	33(1)	C(7s)	9991(31)	−864(38)	6950(31)	184(15)
C(21)	2243(4)	1233(3)	9538(3)	36(1)	C(8s)	8593(70)	−2845(39)	8458(35)	428(99)
C(22)	3887(4)	786(3)	9142(2)	32(1)	C(9s)	9155(50)	−620(43)	6844(31)	269(31)
C(23)	4847(3)	782(3)	9099(3)	33(1)	C(10s)	8834(25)	−2216(36)	7748(31)	157(21)

* The C(1s)—C(10s) atoms belong to the disordered hexane molecule of solvation.

natocarbonylrhodium) (2b). The yield was 67.5%, decomp. temp. 245—247 °C. Found (%): C, 43.24; H, 4.49; P, 7.00; Rh, 22.99. $C_{84}H_{76}N_4O_{20}P_4Rh_4$. Calculated (%): C, 43.76; H, 4.36; P, 7.05; Rh, 23.43. IR (CH_2Cl_2), ν/cm^{-1}: 2969, 2925, 2800, 1988, 1974, 1570, 1510, 1470, 1379, 1270, 1260, 1160, 1139, 1080, 965, 872, 846, 605.

1,21,23,25-Tetrapropyl-5,9,13,17-tetrakis(diethylamido)-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^5]dioxa-

phosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]benzobis-[1,3,2λ^5]dioxaphosphocino-5,9,13,17-tetrakis(acetylacetonato-carbonylrhodium) (2c). A solution of cavitand **1c** (0.053 g, 0.05 mmol) and (acac)Rh(CO)$_2$ (0.052 g, 0.203 mmol) in chloroform (2 mL) was kept at 20 °C for 48 h. The chloroform was distilled off. The residue was dissolved in diethyl ether (2 mL). Unconsumed (acac)Rh(CO)$_2$ was frozen out in the temperature range from −7 to −10 °C and filtered off. Diethyl ether was distilled off. Complex **2c** was dried *in vacuo*. The yield was 0.056 g (57%), decomp. temp. 220—223 °C. Found (%): C, 48.08; H, 5.72; P, 5.84; Rh, 20.41. $C_{80}H_{108}N_4O_{20}P_4Rh_4$. Calculated (%): C, 48.50; H, 5.50; P, 6.25; Rh, 20.78. IR (CH_2Cl_2), ν/cm^{-1}: 2998, 2955, 2929, 2868, 2080, 1995, 1978, 1715, 1570, 1516, 1475, 1372, 1278, 1200, 1161, 1140, 1089, 1061, 1010, 921, 880, 778, 762, 620, 592, 505.

1,21,23,25-Tetramethyl-5,9,13,17-tetraisopropoxy-2,20:3,19-dimetheno-1*H*,21*H*,23*H*,25*H*-bis[1,3,2λ^3]dioxa-phosphocino[5,4-*i*:5′,4′-*i*′]benzo[1,2-*d*:5,4-*d*′]benzo-bis[1,3,2λ^3]dioxaphosphocino-5,9,13,17-tetrakis(acetylaceto-natocarbonylrhodium) (2d). A solution of cavitand **1d** (0.0599 g, 0.0669 mmol) and (acac)Rh(CO)$_2$ (0.069 g, 0.267 mmol) in chloroform (2 mL) was kept at 20 °C for 18 h. The major portion of the chloroform was distilled off. Cold hexane (1 mL) was added to the residue. The precipitate of complex **2d** was filtered off, washed with cold hexane, and dried *in vacuo*. The yield was 0.0656 g (54%), m.p. 230 °C. Found (%): C, 44.61; H, 4.85; P, 6.34; Rh, 22.41. $C_{68}H_{80}O_{24}P_4Rh_4$. Calculated (%): C, 44.95; H, 4.44; P, 6.82; Rh, 22.65. IR (solution in CH_2Cl_2), ν/cm^{-1}: 2973, 1987, 1570, 1515, 1479, 1380, 1250, 1150, 1090, 975, 880, 853, 710, 699, 620; (KBr pellets), ν/cm^{-1}: 2975, 1988, 1632, 1583, 1523, 1487, 1386, 1284, 1156, 1096, 994, 891, 862, 771, 687, 617, 514.

X-ray diffraction study of complex 2d. Crystals of **2d** are triclinic, at −80 °C a = 14.361(6) Å, b = 16.074(6) Å, c = 19.760(7) Å, α = 67.09(2)°, β = 89.75(3)°, γ = 77.03(3)°, V = 4077(3) Å^3, M = 1903.01, space group $P\bar{1}$, Z = 2, d_{calc} = 1.550 g cm^{-3}, $F(000)$ = 1940, μ = 1.550 mm^{-1}. X-ray diffraction study of compound **2d** was carried out on an automated four-circle Syntex P2$_1$ diffractometer (Mo-Kα radiation, graphite monochromator, θ/2θ scanning technique, 2θ < 50°) at −80 °C. Of a total of 14195 measured reflections, 13573 independent reflections were used in calculations and the refinement.

The structure was solved by direct methods and refined by the full-matrix least-squares method in the anisotropic-isotropic approximation based on F^2. The positions of the hydrogen atoms were located from difference electron density syntheses and refined using the riding model. The final values of the R factors were as follows: wR_2 = 0.1540, GOF = 1.043 based on all reflections (R_1 = 0.0478 based on 10792 reflections with $I > 2\sigma(I)$, R was calculated with the use of F). All calculations were carried out on an IBM PC/AT computer using the SHELXTL PLUS program package (Version 5). The atomic coordinates and their thermal parameters are given in Table 5.

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