Platinum and rhodium complexes with isoleucinol-based bi- and tricyclic hydrophosphoranes

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The complex formation of bi- and tricyclic hydrophosphorane derivatives of isoleucinol with $[Pt(COD)Cl_2]$, $[Rh(CO)_2Cl]_2$, and $[Rh(THF)_2(COD)]^+BF_4^-$ (COD is cycloocta-1,5-diene) was investigated. In all cases, bicyclic hydrospirophosphorane selectively forms the metal chelates $[M(\eta^2\text{-P}\cap\text{N})(X)Cl]$ (M = Pt, X = Cl; M = Rh, X = CO) and $[Rh(\eta^2\text{-P}\cap\text{N})(COD)]^+BF_4^-$. («∩» denotes the residue of the hydrospirophosphorane ligand, which does not contain the P and N atoms). In addition, tricyclic hydrophosphorane (L) generates the phosphoranide complexes $[Pt(\eta^1\text{-L})(COD)Cl]^+Y^-$ (Y = Cl or BF_4). The structures of the new compounds were established by IR spectroscopy, ^{31}P, ^{13}C, ^1H, ^2H, ^{11}B, ^{19}F, and ^{195}Pt NMR spectroscopy, and plasma-desorption and electrospray ionization mass spectrometry. The possible mechanism of coordination of hydrophosphoranes is discussed.

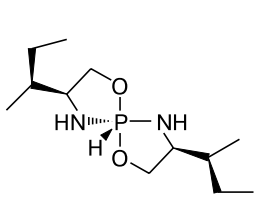
Key words: hydrophosphoranes, platinum complexes, rhodium complexes, hydrospirophosphoranes, tricyclic hydrophosphoranes.

Of hydrophosphorane (HP) ligands (L) studied in coordination chemistry, hydrospirophosphoranes (HSP) and tricyclic hydrophosphoranes (TCP) are the least known.[1] The reactions of oxahydrospirophosphoranes with $[Rh(CO)_2Cl]_2$ and $[M(COD)Cl_2]$ (M = Pd or Pt; COD is cycloocta-1,5-diene) afforded metal chelate derivatives of their open forms, *viz.*, $[M(\eta^2\text{-P}\cap\text{N})(X)Cl]$* (M = Pt or Pd, X = Cl; M = Rh, X = CO).[2—4] By contrast, the open forms of tetraoxahydrospirophosphoranes act as *P*-monodentate ligands.[4,5] The coordination behavior of TCP is more diversified. Their complexes in which the ligands retain the hydrophosphorane structure (with BH_3, BF_3, $ZnCl_2$) were prepared.[6—8] Besides, complexes of TCP characterized by *P*-monodentate phosphoranide coordination (with Pd^{II})[9] and complexes with *P*-monodentate open forms (with W^0, Mo^0)[10,11] were synthesized. Compounds in which the open forms of TCP act as *P*,*N*-bidentate chelating ligands, *viz.*, $[M(\eta^2\text{-P}\cap\text{N})(X)Cl]$ (M = Pt, X = Cl; M = Rh, X = CO), were also prepared.[4,12]

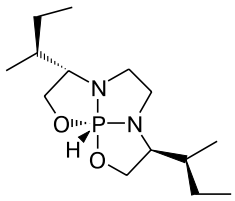
Nevertheless, such examples are few in number. The elucidation of the characteristic features of complex formation involving the above-mentioned groups of hydrophosphoranes calls for further investigations, including the synthesis of a large series of homologous structures. The present study was aimed at preparing new platinum(II) and rhodium(I) complexes with isoleucinol-based HSP and TCP and examining their characteristics.

Results and Discussion

The complex-formation reactions were carried out with the use of HSP **1** and TCP **2**.



1



2

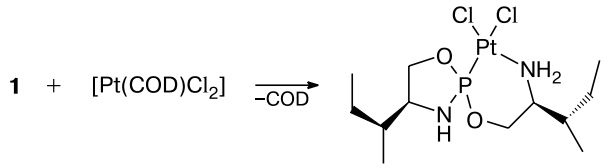
The reaction of HSP **1** with $[Pt(COD)Cl_2]$ gave rise to chelate mononuclear complex **3** with the *cis* arrangement of the P and N atoms in the coordination sphere of the metal atom (Scheme 1).

The proposed structure of this complex is supported by the characteristic[3] parameters of the ^{31}P NMR and

* Hereinafter, the symbol «∩» denotes the residue of the hydrophosphorane ligand, which does not contain the P and N atoms.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 110—115, January, 2003.

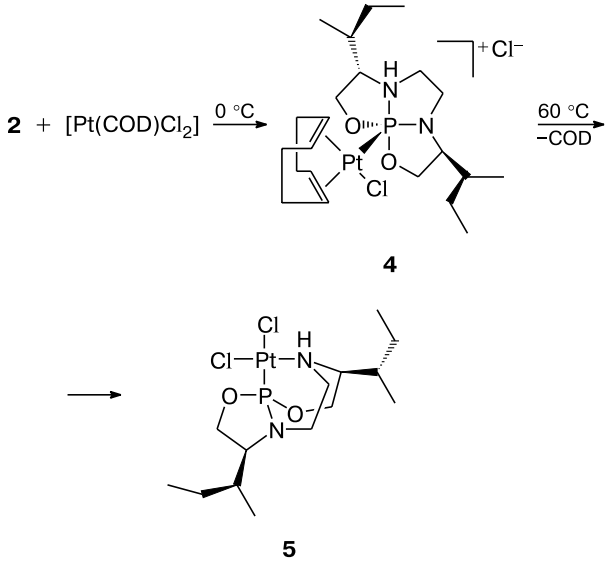
Scheme 1



3

COD is cycloocta-1,5-diene

Scheme 2



4

5

IR spectra of a solution of **3** in $CHCl_3$ (δ_P 65.31, $^1J_{P,Pt}$ = 5673.3 Hz (45%) and δ_P 64.5, $^1J_{P,Pt}$ = 5651.3 Hz (55%); ν(N—H) = 3288 cm^{-1}, ν(NH_2) = 3182 and 3102 cm^{-1}, ν(Pt—Cl) = 342 and 286 cm^{-1}). It should be noted that the presence of doublets in the ^{31}P NMR spectrum of complex **3** is associated with its occurrence as two epimers with respect to the P* stereocenter, whereas two vibrational frequencies ν(Pt—Cl) reflect the different *trans* effects of the phosphorus and nitrogen donor centers. The ^{13}C NMR spectroscopic data are also in good agreement with the structure of complex **3** (see the Experimental section).

By contrast, the reaction of TCP **2** with [Pt(COD)Cl_2] is a very complex process. At 0 °C, this reaction afforded platinated phosphorane **4** (Scheme 2).

This is evidenced by the ^{31}P and ^{195}Pt NMR spectroscopic data for complex **4** in $CDCl_3$ at 0 °C (δ_P –10.9, $^1J_{P,Pt}$ = 5087 Hz; δ_{Pt} –3618, $^1J_{Pt,P}$ = 5100 Hz). The retention of the cycloocta-1,5-diene ligand in the coordination sphere of the platinum atom follows from the ^{13}C NMR spectroscopic data (Table 1).

The IR spectrum of complex **4** has a broadened absorption band ν(NH) = 3260 cm^{-1} ($CHCl_3$) as well as the only absorption band ν(Pt—Cl) = 314 cm^{-1} (Nujol mulls). The latter fact confirms that one of the chloro ligands is displaced to the outer coordination sphere.

Complex **4** is prone to reorganization at a temperature higher than 0 °C or upon prolonged storage. The dynamic ^{31}P NMR measurements of the reaction solution in $CDCl_3$ showed that the high-field pseudotriplet (δ_P 83.1, $^1J_{P,Pt}$ = 5515 Hz) corresponding to chelate complex **5** grew in intesity as the signal of compound **4** weakened. Complex **5** can be prepared by the reaction of ligand **2** with [Pt(COD)Cl_2] in refluxing $CHCl_3$ for 1 h.

The ^{195}Pt NMR spectrum of a solution of complex **5** in $CDCl_3$ has a doublet (δ_{Pt} –3672, $^1J_{Pt,P}$ = 5529 Hz). The ^{13}C NMR spectroscopic data (see Table 1) agree well with the structure proposed for this compound. Noteworthy is the pronounced downfield coordination shift of the

Table 1. ^{13}C NMR spectra of complexes **4—6** in $CDCl_3$

Complex	δ_C (*J*/Hz)							
	—HC=CH—	—CH_2—CH_2—	$POCH_2$	PNCH	$PNCH_2$	CH	CH_2	Me
4	87.78 ($^1J_{C,Pt}$ = 183.0); 91.42 ($^1J_{C,Pt}$ = 180.7); 119.62 ($^2J_{C,P}$ = 22.0); 122.56 ($^2J_{C,P}$ = 19.5, $^1J_{C,Pt}$ = 41)	25.29; 27.67; 30.67; 34.19 ($^3J_{C,P}$ = 4.8)	60.56; 67.59 ($^2J_{C,P}$ = 9.8)	56.00; 59.51 ($^2J_{C,P}$ = 12.2)	37.15 ($^2J_{C,P}$ = 7.3); 39.29 ($^2J_{C,P}$ = 7.3)	33.00, 34.36	25.63, 27.32	10.49, 11.75, 12.19, 14.90
5	—	—	69.90 ($^2J_{C,P}$ = 3.7); 70.25 ($^2J_{C,P}$ = 5.1)	61.84 ($^2J_{C,P}$ = 4.7); 65.71 ($^2J_{C,P}$ = 2.9)	40.61 ($^2J_{C,P}$ = 6.3); 53.34	33.75, 36.12	25.85, 26.01	10.77, 11.38, 11.61, 13.87
6	90.32; 93.22; 121.32 ($^2J_{C,P}$ = 20.6); 122.55 ($^2J_{C,P}$ = 19.7)	25.68; 28.05; 30.43; 33.42 ($^3J_{C,P}$ = 3.5)	61.05 ($^2J_{C,P}$ = 5.3); 66.01 ($^2J_{C,P}$ = 11)	55.62 ($^2J_{C,P}$ = 2.3); 59.31 ($^2J_{C,P}$ = 11.1)	37.58 ($^2J_{C,P}$ = 7.6); 38.94 ($^2J_{C,P}$ = 8.4)	33.25; 33.84 ($^3J_{C,P}$ = 3.0)	25.49, 26.39	10.74, 11.42, 11.85, 13.05

signal for one of the C atoms of the NCH_2CH_2N fragment compared to the signals in the spectra of both metallated phosphorane **4** and the starting TCP **2**, which is indicative of the coordination of the secondary amino group to the platinum atom. The signals of other C atoms remain virtually unchanged.

The IR spectrum of complex **5** has vibrational frequencies ν(NH) = 3202 cm^{-1} (KBr) belonging to the coordinated secondary amino group and ν(Pt—Cl) = 338 and 292 cm^{-1} (Nujol mulls), ν(Pt—Cl) = 350 and 294 cm^{-1} ($CHCl_3$) belonging to the *cis*-arranged chloro ligands. The plasma-desorption (PD) mass spectrum shows characteristic peaks of fragmentation ions at m/z (I_{rel} (%)) 519 $[M - Cl]^+$ (62), 483 $[PtL]^+$ (100).

As mentioned above, complex **4** is unstable at ~20 °C and is prone to reorganization. Nevertheless, we succeeded in stabilizing platinated phosphorane by replacing the nucleophilic Cl^- anion with the coordination-neutral BF_4^- anion (Scheme 3).

Scheme 3

$$[PtCl(COD)L]^+Cl^- + AgBF_4 \longrightarrow \underset{\mathbf{4}}{} \longrightarrow [PtCl(COD)L]^+BF_4^- + AgCl$$
$$\mathbf{6}$$

L is TCP **2**

The ^{31}P NMR spectrum of a solution of complex **6** has a pseudotriplet at δ_P −6.4 ($^1J_{P,Pt}$ = 5145 Hz). The presence of the BF_4^- anion in this complex was confirmed by the ^{11}B and ^{19}F NMR spectroscopic data (see the Experimental section). As would be expected, the ^{13}C NMR spectroscopic characteristics of complex **4** are similar to those of complex **6** (see Table 1). The ^2H NMR spectrum of a solution of compound **6**, which was synthesized from deuterated HP **2**, in $CHCl_3$ has a broadened singlet for the deuteron of the secondary amino group (δ_D 3.94).

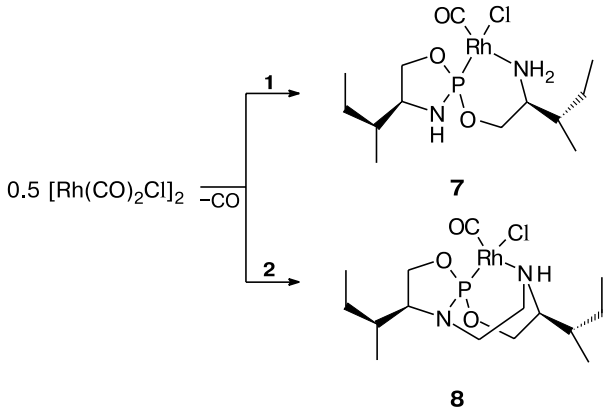
The IR spectrum of complex **6**, like the spectrum of complex **4**, has absorption bands ν(NH) = 3248 cm^{-1} (Nujol mulls) and ν(Pt—Cl) = 320 cm^{-1} (Nujol mulls).

The PD mass spectrum of compound **6** has a signal of the complex cation at m/z (I_{rel} (%)) 627 $[M - BF_4]^+$ (100).

Unlike $[Pt(COD)Cl_2]$, the starting rhodium complex $[Rh(CO)_2Cl]_2$ reacted with both hydrophosphorane ligands **1** and **2** in a similar way. These reactions afforded mononuclear chlorocarbonyl chelate compounds **7** and **8**, respectively (Scheme 4).

This is evidenced by the parameters of the ^{31}P NMR and IR spectra of solutions of the complexes in $CHCl_3$ (**7**: δ_P 137.72, $^1J_{P,Rh}$ = 241.3 Hz (38%); δ_P 132.86, $^1J_{P,Rh}$ = 244.1 Hz (62%); ν(NH) = 3275 cm^{-1}, ν(NH_2) = 3195, 3120 cm^{-1}, ν(CO) = 2008 cm^{-1}, ν(Rh—Cl) = 288 cm^{-1};

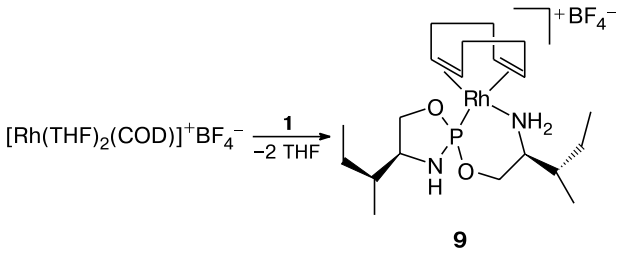
Scheme 4



8: δ_P 162.66, $^1J_{P,Rh}$ = 236.4 Hz, ν(NH) = 3230 cm^{-1}, ν(CO) = 2000 cm^{-1}, ν(Rh—Cl) = 282 cm^{-1}). It should also be noted that the ^{13}C NMR spectroscopic characteristics of platinum(II) chelate complex **5** are similar to those of rhodium(I) chelate complex **8** (see the Experimental section).

By contrast, HP **1** and **2** show different coordination behavior in the reactions with the cationic rhodium(I) complex $[Rh(THF)_2(COD)]^+BF_4^-$ as the starting compound. Thus, HSP **1** reacted with this complex to give mononuclear metal chelate **9** (Scheme 5).

Scheme 5

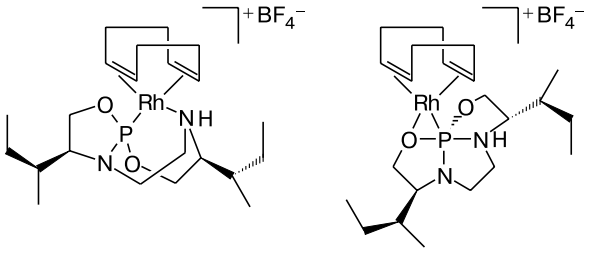


The ^{31}P NMR spectrum of a reaction solution in a $CHCl_3$—THF mixture has doublets (δ_P 131.37, $^1J_{P,Rh}$ = 231.5 Hz (40%); δ_P 126.17, $^1J_{P,Rh}$ = 236.5 Hz (60%)) of both epimers of compound **9**. The IR spectrum of this solution shows vibrational frequencies ν(NH) = 3564 cm^{-1}, ν(NH_2) = 3191 and 3130 cm^{-1} of the endocyclic secondary and coordinated primary amino groups. The electrospray ionization (ESI) mass spectrum of chelate **9** has peaks of the complex cation and its fragmentation products at m/z (I_{rel} (%)) 473 $[M - BF_4]^+$ (16), 263 $[L + H]^+$ (100).

It should be noted that much care must be taken to perform the synthesis and isolation of complexes **7—9** under inert conditions to prevent their destruction. Apparently, this is associated with the hygroscopicity and

hydrolytic instability of these complexes. Thus, the mass spectrum of complex **9** has the above-mentioned peaks along with a pronounced (I_{rel} = 96%) $[M - BF_4 + H_2O]^+$ signal at m/z 471 belonging to monohydrate of the complex cation.

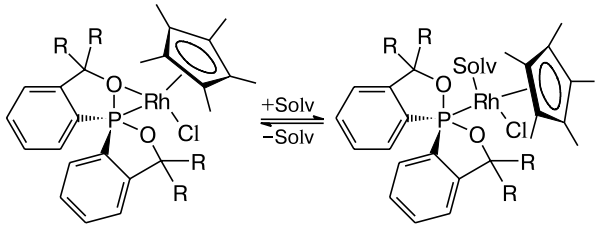
The reaction of TCP **2** with $[Rh(THF)_2(COD)]^+BF_4^-$ (molar ratio Rh : L = 1) proceeded nonselectively. The ^{31}P NMR spectrum of the reaction solution in a $CHCl_3$—THF mixture has a doublet (δ_P 153.81, $^1J_{P,Rh}$ = 219.4 Hz) assigned to cationic complex **10a** formed by the open form of HP **2** and a very broad signal with the maximum at δ_P −16.92. It can be assumed that the latter signal corresponds to structural isomer **10b** with the *P,O*-bidentate phosphoranide ligand. Conceivably, such a broadening of the signal is associated with the exchange processes of the cleavage and formation of the Rh—O bond,[9] including those proceeding in the course of competitive coordination with THF molecules. We failed to achieve an essential narrowing of this signal even by decreasing the temperature of the solution to 220 K. It should be emphasized that the reaction solution contained no compounds, which incorporate two phosphorus-containing ligands in the coordination sphere of the rhodium atom (^{31}P NMR spectrum remained unchanged upon the addition of the second equivalent of phosphorane **2** to the reaction mixture, and an excess of the ligand was unconsumed).



10a **10b**

It should be noted that the rhodium phosphoranide complex with the three-membered P—O—Rh ring, which was described and characterized by X-ray diffraction analysis,[13] showed the behavior similar to that of complex **10b** in solutions (Scheme 6).

Scheme 6

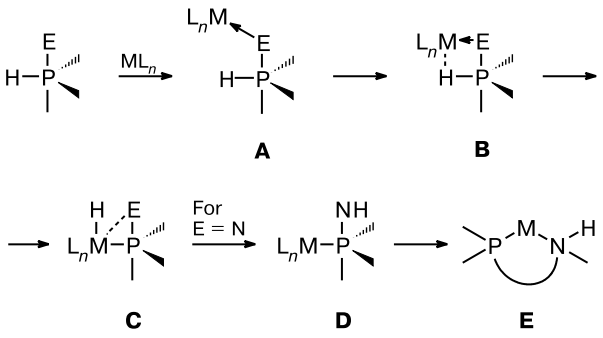


R = CF_3

Unfortunately, in spite of all precautions, the ^{31}P NMR spectrum of the $[Rh(THF)_2(COD)]^+BF_4^-$—HP **2** system has signals of compounds **10a,b** along with signals of their destruction products (δ_P 24.84, 7.0, and 3.12). Refluxing of the reaction solution even over a short period led to a substantial increase in the intensities of the latter signals, while the ratio between isomers **10a** and **10b** changed only slightly. These facts did not allow us to separate complexes **10a** and **10b** and prepare these compound in pure form. The ESI mass spectrum has peaks at m/z (I_{rel} (%)) 517 $[M - BF_4 + H_2O]^+$ (16), 391 $[RhL]^+$ (7), 289 $[L + H]^+$ (100). The PD mass spectrum shows peaks at m/z 637 $[M - BF_4 + H_2O + CHCl_3]^+$ (49), 619 $[M - BF_4 + CHCl_3]^+$ (33), 288 $[L]^+$ (100).

To summarize, it should be noted that HSP **1** always selectively forms metal chelate derivatives of its open form, whereas TCP **2** is also able to be involved in the phosphoranide coordination. Of particular interest is platinated phosphorane **4**. Earlier,[1,3,9] we have proposed the mechanism of complex formation of HP without the involvement of their P^{III} tautomers (Scheme 7). According to this mechanism, the first step gives rise to complexes **A** coordinated at the apical donor atoms followed by the formation of agostic (**B**)[14,15] and metal hydride (**C**) intermediates. Further reductive elimination affords metallated phosphoranes **D**, which are able to undergo reorganization giving rise to metal chelates **E**.

Scheme 7

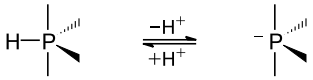


In essence, metal-complex catalysis of the cleavage of the hydrophosphorane structure takes place. In this respect, complex **4** can be considered as a rather stable intermediate through which metal chelate **5** is formed. In the case of TCP, these intermediates are stabilized by the macrocyclic effect.[1,9]

An alternative mechanism of the formation of compound **4** is based on the equilibrium[16] shown in Scheme 8.

However, deprotonation of TCP **2** with BuLi did not give a phosphoranide lithium salt. The ^{31}P NMR spectrum of the reaction solution has only signals of lithium derivatives of the open *P,N* and *P,O* forms (δ_P 172.5, 163.8, 97.2, and 96.0). In our opinion, this is direct evi-

Scheme 8



dence for the involvement of platinum in the proton transfer from the P atom upon the formation of complex **4**.

Experimental

The IR spectra were recorded on Specord M-80 and Nicolet instruments in $CHCl_3$, Nujol mulls, polyethylene cells, between CsI plates, and in KBr pellets. The ^{31}P, ^{13}C, ^{11}B, ^{1}H, and ^{2}H NMR spectra were measured on a Bruker AMX-400 instrument (162.0, 100.6, 128.4, 400.13, and 61.4 MHz, respectively) relative to Me_4Si (^{1}H and ^{13}C), $CDCl_3$ (^{2}H), 85% H_3PO_4 in D_2O (^{31}P), and $BF_3 \cdot Et_2O$ (^{11}B). The assignments of the signals in the ^{13}C NMR spectra were made with the use of the DEPT technique. The ^{19}F NMR spectra were recorded on a Bruker WP-200-SY instrument (188.3 MHz) with respect to CF_3COOH. The ^{195}Pt NMR spectra were measured on a Bruker AC-200 instrument (43.0 MHz) relative to a 1 *M* H_2PtCl_6 solution in D_2O. The mass spectra (EI, 70 eV) were measured on a Varian MAT-311 instrument. The PD mass spectra were obtained on an MSVKh instrument with the use of ^{252}Cf fission fragments. The ESI mass spectra were measured on a Micromass Bio II-ZS mass spectrometer.

All reactions were carried out under dry argon with the use of anhydrous solvents. (3*S*,8*S*,1′*S*)-3,8-Di(1′-methylpropyl)-1,6-dioxa-4,9-diaza-5λ^5-phosphaspiro[4.4]nonane (**1**) and (4*S*,9*S*,1′*S*)-4,9-di(1′-methylpropyl)-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (**2**) were prepared according to procedures described earlier.[9,17] The starting $[Rh(CO)_2Cl]_2$, $[Rh(THF)_2(COD)]^+BF_4^-$, and $[Pt(COD)Cl_2]$ complexes were synthesized according to known procedures.[18—20]

(3*S*,8*S*,1′*S*)-3,8-Di(1′-methylpropyl)-1,6-dioxa-4,9-diaza-5λ^5-phosphaspiro[4.4]nonane (1). A white paraffin-like compound, b.p. 98—100 °C (0.8 Torr), m.p. 46—48 °C. Found (%): C, 55.11; H, 9.98; N, 10.33. $C_{12}H_{27}N_2O_2P$. Calculated (%): C, 54.94; H, 10.37; N, 10.68. ^{31}P NMR ($CDCl_3$), δ: −54.32 ($J_{P,H}$ = 740.9 Hz) (59%); −53.79 ($J_{P,H}$ = 735.0 Hz) (41%). ^{13}C NMR ($CDCl_3$), δ: major epimer: 62.69 (CH_2O); 54.15 (CHN, $^{2}J_{C,P}$ = 10.5 Hz); 39.22 (CH, $^{3}J_{C,P}$ = 6.6 Hz); 25.39 (CH_2); 13.88 and 10.88 (Me); minor epimer: 62.50 (CH_2O); 54.22 (CHN, $^{2}J_{C,P}$ = 10.8 Hz); 38.91 (CH, $^{3}J_{C,P}$ = 4.0 Hz); 25.43 (CH_2); 14.28 and 10.92 (Me). MS, *m*/*z* (I_{rel} (%)): 262 $[M]^+$ (5), 205 $[M - Bu]^+$ (59).

(4*S*,9*S*,1′*S*)-4,9-Di(1′-methylpropyl)-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undecane (2). A colorless oil, b.p. 118—120 °C (0.8 Torr), n_D^{20} = 1.4941. Found (%): C, 58.56; H, 9.87; N, 10.03. $C_{14}H_{29}N_2O_2P$. Calculated (%): C, 58.31; H, 10.14; N, 9.71. ^{31}P NMR ($CDCl_3$), δ: −34.39 (d, $^{1}J_{P,H}$ = 711.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 59.79, 59.20 (CH_2O); 59.59 (CHN, $^{2}J_{C,P}$ = 10.5 Hz); 55.27 (CHN, $^{2}J_{C,P}$ = 14.5 Hz); 43.62, 38.54 (CH_2N); 36.65, 34.30 (CH, $^{3}J_{C,P}$ = 5.8 Hz); 25.75, 25.12 (CH_2); 12.69, 12.46, 11.71, 11.52 (Me). ^{1}H NMR (C_6D_6), δ: 7.16 (d, 1 H, PH, $^{1}J_{H,P}$ = 705.7 Hz); 3.85 (ddd, 1 H, CH_2O, $^{3}J_{H,P}$ = 16.0 Hz, ^{2}J = 8.9 Hz, ^{3}J = 7.0 Hz); 3.76 (ddd, 1 H, CH_2O, $^{3}J_{H,P}$ = 13.0 Hz, ^{2}J = 8.9 Hz, ^{3}J = 7.1 Hz); 3.67 (ddd, 1 H, CH_2O, $^{3}J_{H,P}$ = 12.8 Hz, ^{2}J = 8.9 Hz, ^{3}J = 6.1 Hz); 3.60 (ddd, 1 H, CH_2O, $^{3}J_{H,P}$ = 11.3 Hz, ^{2}J = 8.9 Hz, ^{3}J = 6.9 Hz); 3.05 (m, 1 H, CH_2N); 2.91 (m, 1 H, CHN); 2.80 (m, 1 H, CHN); 2.79 (m, 1 H, CH_2N); 2.66 (m, 2 H, CH_2N); 1.55 (m, 2 H, CH); 1.35 (m, 2 H, CH_2); 1.05 (m, 2 H, CH_2); 0.92 (t, 3 H, Me, ^{3}J = 7.1 Hz); 0.91 (t, 3 H, Me, ^{3}J = 7.1 Hz); 0.88 (d, 3 H, Me, ^{3}J = 6.8 Hz); 0.86 (t, 3 H, Me, ^{3}J = 6.8 Hz). IR (KBr), ν/cm^{-1}: 2348 (ν(P—H)). MS, *m*/*z* (I_{rel} (%)): 288 $[M]^+$ (12), 258 $[M - 2\ Me]^+$ (7), 231 $[M - Bu]^+$ (100).

***cis*-Dichloro[(2′*S*,4*S*)-2-(2′-amino-2′-*sec*-butylethoxy)-4-*sec*-butyl-1,3,2-oxazaphospholidine-*P*,*N*]platinum (3).** Complex **3** was synthesized according to a known procedure.[3] The yield was 0.466 g (88%), a white powder, m.p. 125—127 °C (decomp.). Found (%): C, 27.95; H, 6.12; N, 4.85. $C_{12}H_{27}Cl_2N_2O_2PPt$. Calculated (%): C, 27.28; H, 5.15; N, 5.30. ^{13}C NMR ($CDCl_3$), δ: 10.34, 10.74, 10.85, 11.13, 13.85, 13.98, 14.05, 14.30 (Me); 25.05, 25.57, 25.73, 26.29 (CH_2); 35.65 (CH); 37.00 (CH, ^{3}J = 7.6 Hz); 37.23 (CH); 38.92 (CH, ^{3}J = 3.4 Hz); 54.89, 55.97 (CHNH); 57.34, 60.15 ($CHNH_2$); 66.43, 67.19 ($POCH_2$ of metallocycle); 71.10 ($POCH_2$ of phosphocycle, ^{2}J = 4.2 Hz); 73.57 ($POCH_2$ of phosphocycle).

{[1,2:5,6-η-(1,5-Cyclooctadiene)],[(4*S*,9*S*,1′*S*)-4,9-di(1′-methylpropyl)-2,11-dioxa-5*H*-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undec-1-yl]chloroplatinum} chloride (4). A solution of ligand **2** (0.288 g, 0.001 mol) in CH_2Cl_2 (15 mL) was added carefully dropwise with stirring to a solution of $[Pt(COD)Cl_2]$ (0.374 g, 0.001 mol) in the same solvent (15 mL) for 30 min at 0 °C. The resulting solution was stirred at this temperature for 30 min, concentrated *in vacuo* to ~0.5 mL at the same temperature, and precipitated with a hexane—Et_2O mixture (1 : 1, v/v) cooled to 0 °C. The resulting resin was washed with cold Et_2O and dried in air and *in vacuo* (1 Torr). The yield was 0.609 g (92%), a yellowish powder, m.p. 109—111 °C (decomp.). Found (%): C, 40.21; H, 5.87; Cl, 10.94; N, 4.05. $C_{22}H_{41}Cl_2N_2O_2PPt$. Calculated (%): C, 39.88; H, 6.24; Cl, 10.70; N, 4.23.

***cis*-Dichloro{(4*S*,9*S*,1′*S*)-4,9-di(1′-methylpropyl)-2,11-dioxa-5,8-diaza-1-phosphabicyclo[6.3.0]undecane-*P*,*N*}platinum (5).** A solution of ligand **2** (0.288 g, 0.001 mol) in $CHCl_3$ (15 mL) was added carefully dropwise with stirring to a solution of $[Pt(COD)Cl_2]$ (0.374 g, 0.001 mol) in the same solvent (15 mL) at 20 °C for 30 min. The resulting solution was refluxed for 1 h. The product was isolated by concentrating the solution to ~2 mL and precipitating the complex with a hexane—Et_2O mixture (3 : 1, v/v). The residues was thoroughly washed three times with Et_2O to completely remove COD, separated by centrifugation, and dried in air and *in vacuo* (1 Torr). The yield was 0.493 g (89%), a white powder, m.p. 120—121 °C (decomp.). Found (%): C, 30.63; H, 4.92; Cl, 13.13; N, 4.84. $C_{14}H_{29}Cl_2N_2O_2PPt$. Calculated (%): C, 30.33; H, 5.27; Cl, 12.79; N, 5.05. MS (PD), *m*/*z* (I_{rel} (%)): 519 $[M - Cl]^+$ (62), 483 $[PtL]^+$ (100).

{[1,2:5,6-η-(1,5-Cyclooctadiene)],[(4*S*,9*S*,1′*S*)-4,9-di(1′-methylpropyl)-2,11-dioxa-5*H*-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0^{1,5}]undec-1-yl]chloroplatinum} tetrafluoroborate (6). A cold solution of $AgBF_4$ (0.195 g, 0.001 mol) in THF (15 mL) was added to a solution of compound **4** formed *in situ* in THF (0.001 mol) at 0 °C. The reaction mixture was stirred for 10 min, filtered, concentrated to ~1 mL, precipitated with a hexane—Et_2O mixture (3 : 1, v/v), and dried in air and *in vacuo* (1 Torr). The yield was 0.606 g (85%), a white powder, m.p.

136—138 °C (decomp.). Found (%): C, 36.77; H, 5.90; Cl, 4.75; N, 3.61. $C_{22}H_{41}BClF_4N_2O_2PPt$. Calculated (%): C, 37.01; H, 5.79; Cl, 4.97; N, 3.92. MS (PD), m/z (I_{rel} (%)): 626 $[M - BF_4]^+$ (100). ^{19}F NMR ($CDCl_3$), δ: −152.52 (s, 80%); −152.46 (s, 20%). ^{11}B NMR ($CDCl_3$), δ: −1.27 (s).

Complexes **7** and **8** were synthesized according to a procedure published earlier.[4]

[(2´*S*,4*S*)-2-(2´-Amino-2´-*sec*-butylethoxy)-4-*sec*-butyl-1,3,2-oxazaphospholidine-*P*,*N*]chlorocarbonylrhodium (7). The yield was 0.360 g (84%), an orange powder, m.p. 131—132 °C (decomp.). Found (%): C, 36.75; H, 6.02; N, 6.77. $C_{13}H_{27}ClN_2O_3PRh$. Calculated (%): C, 36.42; H, 6.35; N, 6.53.

{(4*S*,9*S*)-4,9-Di(*sec*-butyl)-2,11-dioxa-5,8-diaza-1-phosphabicyclo[6.3.0]undecane-*P*,*N*}chlorocarbonylrhodium (8). The yield was 0.409 g, (90%), an orange powder, m.p. 138—140 °C (decomp.). Found (%): C, 39.49; H, 6.67; N, 5.97. $C_{15}H_{29}ClN_2O_3PRh$. Calculated (%): C, 39.62; H, 6.43; N, 6.16. ^{13}C NMR ($CDCl_3$), δ: 10.61, 11.77, 12.00, 14.45 (Me); 25.67, 26.21 (CH_2); 33.78 (CH, $^3J_{C,P}$ = 2.6 Hz); 36.45 (CH); 43.26 (CH_2N, $^3J_{C,P}$ = 11.7 Hz); 51.48 (CH_2N, $^3J_{C,P}$ = 3.1 Hz); 61.95, 66.37 (CHN); 68.17, 68.77 ($POCH_2$); 187.54 (CO, $^1J_{C,Rh}$ = 78.8 Hz, $^2J_{C,P}$ = 18.1 Hz).

{[1,2:5,6-η-(1,5-Cyclooctadiene)],[(2´*S*,4*S*)-2-(2´-amino-2´-*sec*-butylethoxy)-4-*sec*-butyl-1,3,2-oxazaphospholidine-*P*,*N*]rhodium} tetrafluoroborate (9). A solution of ligand **1** (0.262 g, 0.001 mol) in $CHCl_3$ (15 mL) was added carefully dropwise with stirring to a solution of $[Rh(THF)_2(COD)]^+BF_4^-$ (0.442 g, 0.001 mol) in THF (15 mL) at 20 °C for ~30 min. The resulting solution was stirred for 20 min. The complex was isolated by concentrating the solution to ~2 mL and precipitating with a hexane—Et_2O mixture (3 : 1, v/v). The residue was washed three times with hexane, separated by centrifugation, and dried in air and *in vacuo* (1 Torr). The yield was 0.487 g (87%), an orange powder, m.p. 144—145 °C (decomp.). Found (%): C, 43.11; H, 6.84; N, 5.28. $C_{20}H_{39}BF_4N_2O_2PRh$. Calculated (%): C, 42.88; H, 7.02; N, 5.00.

For NMR experiments, complexes **10a,b** were prepared according to the following procedure. A solution of ligand **2** (0.087 g, $3 \cdot 10^{-4}$ mol) in $CDCl_3$ (1.5 mL) was slowly added dropwise to a solution of $[Rh(THF)_2(COD)]^+BF_4^-$ (0.133 g, $3 \cdot 10^{-4}$ mol) in THF (1.5 mL). Then the reaction mixture (1 mL) was placed in an NMR tube or an IR cell and analyzed.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos. 00-15-99341 and 00-15-97427) and Haldor Topsøe A/S.

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Received July 10, 2002;
in revised form October 10, 2002