The First Example of Coordination of a Tricyclic Hydrophosphorane to Platinum(II). X-ray Crystal Structure of an Unusual Platinated Phosphorane

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The reaction of (4*S*,9*S*)-4,9-diethyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo[6.3.0.0$^{1.5}$]-undecane (**1**) with [Pt(COD)Cl_2] (COD = cycloocta-1,5-diene) at 0 °C gave [(1,2:5,6-η)-1,5-cyclooctadiene][(4*S*,9*S*)-4,9-diethyl-5*H*-5,8-diaza-2,11-dioxa-1λ^5-phosphatricyclo[6.3.0.0$^{1.5}$]-undecyl-1]chloroplatinum chloride (**2**). If the reaction was performed in the presence of $AgBF_4$, the corresponding BF_4^- salt (**4**) was isolated. Complex **2** was converted to *cis*-dichloro{(4*S*,9*S*)-4,9-diethyl-2,11-dioxa-5,8-diaza-1-phosphabicyclo[6.3.0]undecane-*P*,*N*}platinum (**3**). Variable-temperature ^{31}P NMR studies of complexes **2** and **4** have been carried out in the range from −93 to 50 °C. The structure of compound **4** has been determined by X-ray crystallography. Complex **4** has a slightly distorted trigonal-bipyramidal geometry around the phosphorus, with the platinum fragment in the equatorial position. The P−N_{ax} bond distance is 2.002(5) Å. The Pt atom exhibits a nearly square-planar coordination geometry.

Introduction

In our recent review on the coordination chemistry of hydrophosphorane (HP) compounds we concluded that complexation of tricyclic HPs has been virtually unexplored.[1] Indeed, the first representatives of this group of compounds, called "triquinphosphoranes", were synthesized only in 1990.[2] The authors of that pioneering article[2] also reported the synthesis of a borane adduct in which the boron atom is bonded to the apical nitrogen atom. More recently, a number of new "triquinphosphoranes" including chiral compounds based on ephedrine, as well as their complexes with BH_3, were synthesized.[3a,b] In the following years, there has been a steady interest in coordination chemistry of "triquinphosphoranes". The authors of a pioneering communication[2] reported the results of detailed studies[4a] (including X-ray diffraction) of the adducts of tricyclic HPs with borane and the synthesis of some complexes of these compounds with zirconium, tungsten,[4b] and molybdenum.[4c]

In 1995, we synthesized[5a] the new chiral tricyclic HP **1** and obtained its complex with Pd(II), which was studied in detail more recently.[5b] It is noteworthy that P-monodentate phosphoranide coordination, typical of palladium complexes, was not observed earlier. For instance, complexation of ligand **1** with BF_3 or $ZnCl_2$ involved[5c] N-monodentate coordination without changing the HP structure, while the reaction of **1** with [Rh(CO)$_2$Cl]$_2$ resulted in a chelate complex with P,N-bidentate coordination of the "open" structure of HP **1**.[5d] In a preliminary communication[6] we have briefly outlined the results of our studies of the reaction of compound **1** and [Pt(COD)Cl_2] (COD = 1,5-cyclooctadiene). The aim of the present work was to carry out detailed spectral and structural investigations of both the primary reaction product and products of its further transformations.

Results and Discussion

Complexation of the tricyclic HP **1** with [Pt(COD)Cl_2] was performed in CH_2Cl_2 solution at 0 °C following Scheme 1.

The direct coordination of the phosphoranide center to the Pt atom was confirmed by a ^{31}P NMR study of

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Table 1. ^{13}C NMR Spectral Parameters of Compounds 1−3[a]

	C atom						
compd	HC=CH	H_2CCH_2	$POCH_2$	PNCH	$PNCH_2$	CH_2	CH_3
1			64.0 62.5	56.6 ($^2J_{C,P}$ = 7.8) 52.8 ($^2J_{C,P}$ = 15.2)	42.5 ($^2J_{C,P}$ = 6.2) 38.1 ($^2J_{C,P}$ = 15.1)	26.2 ($^3J_{C,P}$ = 8.2) 23.7 ($^3J_{C,P}$ 4.8)	8.9 8.7
2	123.3 ($^2J_{C,P}$ = 19.8) 119.8 ($^2J_{C,P}$ = 21.6, $^1J_{C,Pt} \approx 40$) 92.3 ($^1J_{C,Pt}$ = 184.9) 89.6 ($^1J_{C,Pt}$ = 192.1)	34.8 ($^3J_{C,P}$ = 5.4) 30.1 29.7 25.4	69.7 ($^2J_{C,P}$ = 9.0) 65.5 ($^2J_{C,P}$ = 5.1)	57.3 ($^2J_{C,P}$ = 12.6) 55.8($^2J_{C,P}$ = 3.6)	39.7 ($^2J_{C,P}$ = 5.4) 36.1 ($^2J_{C,P}$ = 7.2)	24.6 ($^3J_{C,P}$ = 5.4) 21.1	10.7 8.7
3			74.2 ($^2J_{C,P}$ = 5.4) 71.0	63.7 60.2	52.9 41.7 ($^2J_{C,P}$ = 7.3)	23.9 23.0	10.1 9.8

[a] Spectra taken in $CDCl_3$. δ values are in ppm and J values in Hz.

Scheme 1

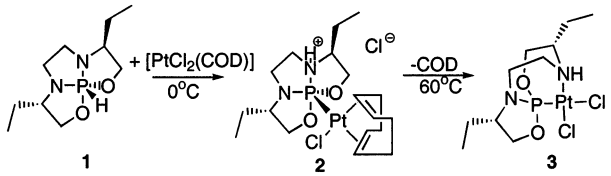
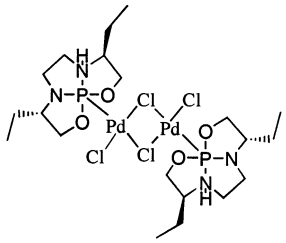


Chart 1



complex **2** in $CDCl_3$ at 0 °C, according to which δ_P −12.8 and $^1J_{P,Pt}$ = 5105.2 Hz. The pseudotriplet in the ^{31}P NMR spectrum corresponds to a doublet with δ_{Pt} −3640 and $^1J_{Pt,P}$ = 5115 Hz in the ^{195}Pt NMR spectrum. As was shown by ^{13}C NMR spectroscopy (see Table 1), the 1,5-cyclooctadiene ligand is a part of complex **2**. Noteworthy is the asymmetric arrangement of this ligand, which is manifested in the fact that each carbon atom exhibits its own signal. This seems to be due to the influence of the bulky organophosphorus ligand, which causes a distortion of the geometry of the metal complex. The presence of the $^2J_{C,P}$ coupling constant, showed by recording the ^{13}C NMR spectra on two spectrometers operating at different frequencies, is evidence of the trans orientation of the phosphoranide ligand and two (out of the four) C atoms of the 1,5-cyclooctadiene molecule. The very small value of the $^1J_{C,Pt}$ coupling constant for one of the olefin atoms of 1,5-cyclooctadiene is the result of the very strong trans influence of the pentacoordinated phosphorus atom. The observed carbon−platinum coupling constants of the C atoms in trans positions with respect to the P atom are approximately one-fifth of the coupling constants of those C atoms which are in trans positions relative to Cl atoms. If the $^2J_{C,P}$ coupling constant were equal to zero, a pseudotriplet with a 1:4:1 intensity ratio and nonzero $^1J_{C,Pt}$ coupling constant would be observed in the spectrum. For complex **2**, the pseudotriplet is split into a multiplet with a 1:5:5:1 intensity ratio since $^2J_{C,P} \approx {}^1/_2{}^1J_{C,Pt}$. The satellite lines are of very low intensity and merge with the line broadening at the base of the central doublet due to small values of the coupling constants. Unfortunately, this effect is observed either when recording the NMR spectra on instruments with different operating frequencies or when extending the signal accumulation time. Therefore, no $^1J_{C,Pt}$ value is presented for one of the olefin atoms; we can only say that the magnitude of this constant is about 40 Hz. In turn, the $^1J_{P,Pt}$ coupling constant is smaller than the expected value, which reflects the strong trans influence of the olefin ligand. An increase in the $^1J_{C,Pt}$ constants of carbon atoms in trans positions with respect to the Cl atom, compared to the starting [Pt(COD)Cl_2] ($^1J_{C,Pt}$ = 152 Hz[7]), should also be pointed out.

The IR spectrum of a solution of complex **2** recorded at 0 °C exhibits only one ν(Pt−Cl) absorption band at 320 cm^{-1} in the far-IR region. This is consistent with displacement of the chloride ligand from the first coordination sphere. In the near-IR region we observed a strongly broadened ν(NH) absorption band with a maximum at 3200 cm^{-1}. Complex **2** carefully isolated from solution (see the Experimental Section) is an unstable powder on long-term storage (longer than 2 or 3 weeks) at 20−25 °C, and it should be stored at 0 °C. The IR spectrum of the powder of **2** is virtually identical with that of its solution. The mass spectrum of complex **2** obtained using the plasma desorption technique exhibits a peak of the [Pt(COD)ClL]$^+$ molecular ion with m/z = 571 and 100% relative intensity, which confirms the cationic nature of the complex. Altogether, the bidentate coordination of the 1,5-cyclooctadiene ligand revealed by the ^{13}C NMR study (one trans position is unambiguously occupied by the P atom), the monodentate coordination of the phosphoranide ligand established by ^{31}P and ^{195}Pt NMR spectroscopy, and the coordination of one Cl$^-$ anion shown using IR spectroscopy exclude any alternative structure of complex **2**. Thus, in contrast to the reaction with [Pd(COD)Cl_2],[5b] compound **1** unexpectedly reacts with [Pt(COD)Cl_2] with the replacement of chlorine (see Chart 1).

Such processes are known for bulky phosphines; however, they occur in a polar solvent (methanol).[8] Previously,[9] in studies of the reaction of [Pd(COD)Cl_2] and [Pt(COD)Cl_2] with aminophosphoramidite we found that the chelate cycle with participation of 1,5-cyclooctadiene is more stable in the platinum complex compared to the palladium complex.

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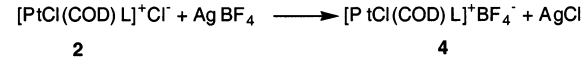
Gradual heating of the reaction solution to 20 °C (faster on reflux in $CHCl_3$) leads to the opening of the phosphorane structure and to the formation of complex **3** (Scheme 1). Disappearance of the signals of complex **2** in the ^{31}P NMR spectrum of the reaction solution recorded in $CDCl_3$ is accompanied by an increase in the intensity of the low-field pseudotriplet with the parameters δ_P 83.2 and $^1J_{P,Pt} = 5562.5$ Hz. The fact that the P atom is coordinated to the metal atom was also confirmed by ^{195}Pt NMR spectroscopy (a doublet with the parameters δ_{Pt} −3678 and $^1J_{Pt,P} = 5551$ Hz). The magnitude of the $^1J_{P,Pt}$ coupling constant is typical of a phosphoramidite P atom bonded to the $PtCl_2$ fragment with cis configuration of the Cl atoms.[9,10] A small, regularly observed[9,10a,b] difference between the $^1J_{P,Pt}$ and $^1J_{Pt,P}$ coupling constants is due to somewhat inaccurate determination of the position of the maximum of the spectral line in the ^{195}Pt NMR spectrum. In comparison to the half-width of the spectral line (40−50 Hz) and to the magnitudes of coupling constants (greater than 5000 Hz) in the ^{195}Pt NMR spectrum, and especially to the magnitudes of coupling constants in the ^{31}P NMR spectrum, the difference of the order of 10−15 Hz between the coupling constants in the ^{195}Pt NMR spectrum can be considered insignificant. It is appropriate to note that despite the possibility of very accurate determination of the coupling constants in the ^1H and ^{31}P NMR spectra, the difference between the $^1J_{H,P}$ and $^1J_{P,H}$ constants usually spans the range from 3 to 7 Hz and can sometimes be as large as 27 Hz.[4a]

The proposed structure of complex **3** is also consistent with the results of a ^{13}C NMR study (Table 1). Noteworthy are substantial changes in the chemical shift of one of the carbon atoms of the NCH_2 groups compared to both the metalated phosphorane **2** and the starting triquinphosphorane **1** due to the coordination of the secondary amino group to the Pt atom. Indeed, P-monodentate coordination of the open structure of compound **1** in the complex $[W(CO)_5L]$ led to a small difference between the chemical shifts of the carbon atoms of two $PNCH_2$ groups (2.5 ppm for the tungsten complex and 11.2 ppm for the platinum complex).[4b]

Diastereoselectivity of the opening of the phosphorane structure deserves particular consideration. On one hand, we cannot rule out the possibility of merging the signals of the two diastereomers by chance. On the other hand, the presence of the one and only narrow pseudotriplet in the ^{31}P NMR spectrum of **3** at temperatures between 20 and 50 °C and the observation of only one set of signals for the carbon atoms in the ^{13}C NMR spectrum substantiates our conclusion about a 100% diastereoselectivity of the transformation of metalated phosphorane **2** into complex **3**. A 100% diastereoselectivity of the opening of the structure of a chiral HP was also demonstrated, taking the reaction of a close analogue of ligand **1** with $Mo(CO)_6$ as an example.[4c] One can assume that the initial coordination of **1** also is a diastereoselective process, since the ^{31}P and ^{13}C NMR spectra of **2** exhibit no signals of the second stereoisomer. At the same time we cannot exclude the possibility of pseudorotation according to Berry with the formation of phosphorus epimers. Pseudorotation in ligand **1** is known to occur rapidly on the time scale of NMR spectroscopy,[4a] thus resulting in the appearance of a singlet in the ^{31}P NMR spectrum. This issue will be considered in more detail below.

Scheme 2



The cis orientation of the chloride ligands was confirmed by observation of two ν(Pt−Cl) absorption bands at 338 and 280 cm^{-1} in the far-IR region of the spectrum of the powder of complex **3**. A broadened ν(NH) absorption band at 3190 cm^{-1} in the near-IR region is characteristic of a coordinated secondary amino group. Plasma desorption mass spectrometric examination of compound **3** revealed the mononuclear nature of the complex (m/z (I, %)): 463 (48), $[PtClL]^+$; 427 (100), $[PtL]^+$. Intense peaks for the $[M - Cl]^+$ ions are typical of many chloride complexes of palladium and platinum.[9,10b,11] Sedimentation analysis of complex **3** (in DMF) confirmed its mononuclear nature, namely M_z = 524 (M_{calcd} = 498). Evaluation of the species size from its diffusion coefficients showed that a solvated molecule of compound **3** can be inscribed in a sphere of diameter 11.1 Å, which is in good agreement with the results of AM1 calculations of the equilibrium geometry of this molecule (10.8 Å). Earlier,[10a] we found that the results of particle size determination for metal complexes by sedimentation analysis and using the results obtained from AM1 calculations and by X-ray diffraction analysis are also in good agreement. Reaction of ligand **1** with $[Pt(COD)Cl_2]$ at room temperature immediately resulted in a mixture of complexes **2** and **3**.

Unfortunately, numerous attempts at growing single crystals of complexes **2** and **3** suitable for an X-ray diffraction study failed. Undoubtedly, a possible reason is the instability of compound **2** at temperatures above 10 °C. To obtain a more stable and crystalline platinated phosphorane, we carried out an ion exchange reaction according to Scheme 2.

The ^{31}P NMR spectrum of the solution of complex **4** in $CDCl_3$ recorded at 0 °C exhibits a pseudotriplet with the parameters δ_P −12.1 and $^1J_{P,Pt} = 5093$ Hz. In contrast to complex **2**, the stability of complex **4** allowed us to collect spectral data at higher temperatures. Heating of the solution of compound **4** led to an insignificant change in the chemical shift and to a slight increase in the $^1J_{P,Pt}$ value. In particular, δ_P −11.8 and $^1J_{P,Pt}$ = 5113 Hz at 25 °C (cf. δ_P −11.2 and $^1J_{P,Pt}$ = 5141 Hz at 50 °C). The fact that the BF_4^- anion is a part of complex **4** was confirmed by ^{11}B and ^{19}F NMR spectroscopy (see the Experimental Section). In contrast to complexes **2** and **3**, the IR spectra of both the solution and powder forms of complex **4** exhibit a narrow, clearly seen ν(NH) absorption band at 3216 and 3212 cm^{-1}, respectively. Close values of the ν(NH) frequencies in the IR spectra of compounds **2**−**4** should not be surprising, since all the compounds contain a tetracoordinated

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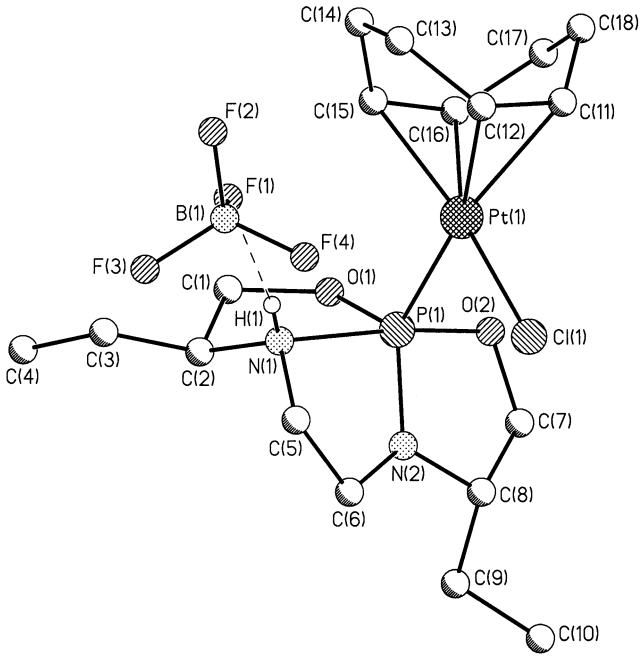


Figure 1. X-ray structure of complex **4** and numbering scheme. All hydrogen atoms linked to carbon atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4

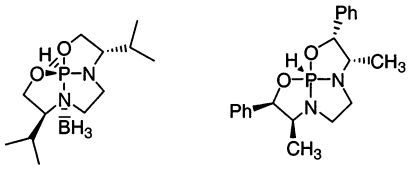
Pt(1)−C(11)	2.327(5)	P(1)−N(2)	1.659(5)
Pt(1)−C(12)	2.318(5)	O(1)−C(1)	1.445(6)
Pt(1)−C(15)	2.191(5)	O(2)−C(7)	1.394(8)
Pt(1)−C(16)	2.158(5)	N(1)−C(2)	1.483(6)
Pt(1)−P(1)	2.2994(15)	N(1)−C(5)	1.466(7)
Pt(1)−Cl(1)	2.3070(15)	N(2)−C(6)	1.423(6)
P(1)−O(1)	1.597(4)	N(2)−C(8)	1.421(7)
P(1)−O(2)	1.647(4)	C(11)−C(12)	1.394(8)
P(1)−N(1)	2.002(5)	C(15)−C(16)	1.412(7)
P(1)−Pt(1)−Cl(1)	89.33(6)	O(1)−P(1)−Pt(1)	116.57(15)
O(1)−P(1)−O(2)	92.8(2)	O(1)−P(1)−N(1)	85.88(19)
O(1)−P(1)−N(2)	118.1(2)	O(2)−P(1)−Pt(1)	93.29(14)
O(2)−P(1)−N(1)	173.6(2)	O(2)−P(1)−N(2)	91.8(2)
N(1)−P(1)−Pt(1)	92.90(16)	N(2)−P(1)−Pt(1)	124.7(2)
N(2)−P(1)−N(1)	83.3(2)	C(2)−N(1)−P(1)	106.8(3)
C(5)−N(1)−P(1)	105.9(4)	C(5)−N(1)−C(2)	116.6(5)
C(6)−N(2)−P(1)	122.2(4)	C(6)−N(2)−C(8)	120.3(5)
C(8)−N(2)−P(1)	115.6(4)		

nitrogen atom. The mass spectrum of complex **4** is virtually identical with that of complex **2**.

We carried out an X-ray diffraction study of the platinum phosphorane complex **4**. The results obtained are presented in Figure 1 and listed in Table 2. Our analysis of the structures available in the CSD showed that compound **4** is not only the first platinated tricyclic phosphorane but also the first complex of the type [Pt(COD)ClL] (where L is an organophosphorus ligand) which was studied by X-ray diffraction analysis.

An intriguing feature of the crystal of complex **4** is that the phosphorane structure remains unchanged. despite the hydrogen migration from the phosphorus to the nitrogen atom. The pentacoordinated phosphorus atom is characterized by a nearly ideal trigonal-bipyramidal (TBP) environment with the N(1) (NH group) and O(2) atoms in apical positions. The P atom in the phosphorane TBP has an *R* configuration. Theoretically, one can assume that the *R* configuration of **4** is retained for complex **2** and, if the cleavage of the apical P−NH bond is taken into account, unambiguously establishes the configuration of the P atom in compound **3**. However, this assignment seems to be doubtful. Indeed, replacement of the counterion can result in complete domination of one phosphorus epimer due to the formation of stronger hydrogen bonds in the single crystal and/or in solution. By the use of the dihedral angle method,[12] it was estimated that the structure is displaced by only 5.6% along the Berry coordinate from the ideal TBP (0%) toward the ideal SP (100%). Insignificant structural distortion is reflected in the slight variation of the bond angles in the equatorial plane (from 116.1(2) to 124.7(2)°), of the axial−equatorial angles (from 83.8(2) to 93.29(14)°), and finally of the N(1)-P(1)O(1) angle, which is equal to 173.6(2)°.

Chart 2



5 **6**

The P(1) atom deviated from the Pt(1)−O(1)−N(2) plane toward the O(2) atom by 0.083(3) Å. The five-membered rings adopted slightly distorted envelope conformations characterized by deviations of the C(2) and C(7) atoms for corresponding OPNCC rings and of the N(1) atom for the NPNCC ring.

While the Pt(1) atom is characterized by the expected planar configuration, the exchange of one of the Cl atoms by the phosphorane ligand caused some distortions of Pt(1) reflected in a significant deviation (0.19 Å) of the Cl(1) atom from the plane of Pt(1), P(1), and the midpoints of the C(15)−C(16) and C(11)−C(12) bonds (rms deviation 0.0008 Å).

Analysis of the molecular geometry of complex **4** revealed that it is similar to the recently investigated structure of the triquinphosphorane−borane complex **5**[4a] (Chart 2). The most interesting feature of the geometries of compounds **4** and **5** is the remarkable elongation of the axial N(1)−P(1) bond up to 2.002(5) and 1.932(2) Å, respectively, compared to the similar tricyclic phosphorane **6** with an unsubstituted axial nitrogen (1.772(2) Å).[3b]

In complex **4**, not only is the N(1)−P(1) distance greater than the sum of corresponding covalent radii but it also is one of the longest known bond lengths. The above-mentioned elongation leads to corresponding shortening of the axial P(1)−O(2) bond to 1.647(4) Å (cf. 1.693(2) Å in **6**). It is noteworthy that further elongation of the bond up to 3.57(2) Å (in fact, disruption of this bond) recently found in the thriquinphosphorane complex with $Mo(CO_5)$[4c] does not affect the $P-O_{ax}$ bond lengths (1.644(3) Å), thereby indicating that the contribution of the N_{ax} lone electron pair to the three-center bonding in the axial OPN fragment in complex **4** is negligible. We believe that another compound of molybdenum with the tetracyclic phosphorane cyclenPH[13] can be considered as an intermediate case between the

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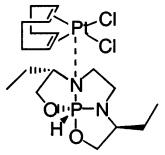
extremely long P−N_{ax} bond in the platinated phosphorane **4** and breakdown of this bond in the molybdenum complex with triquinphosphorane. In this case, the distance between the phosphorus atom and nitrogen atom in the NH fragment is 2.356(23) Å, which is more than ∼0.4 Å longer than the lengths of the axial P−N bonds in other derivatives of cyclenPH. On the other hand, this value is smaller than the sum of the van der Waals radii. It is noteworthy that both NMR and IR spectroscopy cannot detect the P−NH bond.[13]

In contrast to the axial plane, the equatorial bond lengths are virtually unaffected both by the N_{ax} substitutent and by replacement of the hydrogen atom at the P atom by a Pt atom. In particular, the P(1)−O(1) bond (1.597(4) Å) is only slightly shorter than the corresponding bonds in complexes **5** and **6** (1.607(2) and 1.615(2) Å, respectively). The same situation is also observed for the P(1)−N(2) bond (1.659(2) Å), which is slightly longer than in compound **5** (1.640(2) Å) but is nearly equal to the corresponding value in complex **6**. It is noteworthy that despite the similarity of the P−N_{eq} bond lengths in complex **4** and in compounds **5** and **6**, the corresponding nitrogen atom is characterized by different degrees of planarity. In compound **5**, the N_{eq} atom is virtually planar with a sum of the bond angles around it being 359.9(2)°, while the corresponding sum for complex **4** is only 329.3(3)°, thus indicating significant pyramidalization of the N_{eq} atom. These differences in the N_{eq} configuration and in the P−N_{eq} bond lengths in complexes **4** and **5** are in line with possible hyperconjugation between the phosphorus center and N_{eq}.[14]

Analysis of the crystal packing in compound **4** revealed that the cation and anion form a contact pair by means of H-bonding. In the crystal, the BF_4^- anion is involved in the B(1)−F(1)···H(1)−N(1) hydrogen bond of moderate strength (H(1)···F(1) = 1.88 Å, N(1)···F(1) = 2.877(7) Å, B(1)−F(1)−H(1) = 170°). Evidently, such a specific interaction slightly reduces the positive charge on the N(1) center and thus can be a reason for the stabilization of the phosphorane structure in the solid.

As can be seen from the above discussion, the influence of the [Pt(COD)Cl] fragment on the phosphorane geometry is not as strong as could be expected. In contrast, the trans influence of the phosphorane on the 1,5-cyclooctadiene ligand is more pronounced, reflected in the significant inequivalence of the Pt-η^2(C=C) bond lengths. The Pt(1)−C(11) and Pt(1)−C(12) bonds (2.327(5) and 2.318(5) Å, respectively), which are in positions trans to the phosphorus ligand, are considerably elongated compared to the Pt(1)−C(15) and Pt(1)−C(16) bonds (2.191(5) and 2.158(5) Å, respectively). It is noteworthy that, according to an analysis of the structures available in the CSD, the above-mentioned Pt−C bonds in complex **4** are the longest known for the Pt−η^4-COD complex with nonmetal ligands. For comparison, the corresponding values for the [Pt(COD)Cl_2] complex are ca. 2.172 Å.[15] Thus, the asymmetry of the cyclooctadiene ligand and strong trans influence of phosphoranide revealed for complex **2** by ^{13}C NMR spectroscopy were confirmed by the X-ray study of complex **4**. Earlier analysis of the published data also suggested a strong trans influence of the phosphoranide phosphorus atom.[1] The Pt−P bond is rather long (2.2994(15) Å). Nevertheless, this value is typical of platinated phosphoranes with monodentate coordination of the phosphoranide ligand.[16] The Pt−Cl bond length, 2.3070(15) Å, differs only slightly from the corresponding value in the starting complex [Pt(COD)Cl_2].[15]

Chart 3



We have repeatedly discussed the coordination mechanism of HPs.[5b,d,17] It should be remembered that the first stage of the mechanism we have proposed involves the formation of an adduct in which the metal atom is bonded to the apical nitrogen (oxygen) center. To confirm the proposed HP coordination scheme, we monitored the course of complexation of compound **1** in CD_2Cl_2 by dynamic ^{31}P NMR spectroscopy. Mention may be made that coordination of HP **1** to [Pt(COD)Cl_2] occurs at temperatures much lower than in the case of hydrospirophosphoranes.[5d,17] We failed to determine the lower temperature bound of detectable complexation. Reaction of ligand **1** with [Pt(COD)Cl_2] results in the primary adduct (δ_P −35.7 and $^1J_{P,H}$ = 742.2 Hz) already at −93 °C (the freezing point of CH_2Cl_2 is −94.9 °C). The ^{31}P NMR spectrum of the solution of **1** recorded under the same conditions exhibits a doublet with δ_P −36.1 and $^1J_{P,H}$ = 714.5 Hz. Having analyzed a great body of information, we showed[1] that both the low-field shift of δ_P and an increase in the $^1J_{P,H}$ coupling constant are a result of coordination of the apical nitrogen atom. The ease of adduct formation is an obvious consequence of the presence of such an atom in the structure of ligand **1**. Since both the change in the chemical shift and the increase in the phosphorus−hydrogen coupling constant are small, the structure of the primary product of complexation of ligand **1** with [Pt(COD)Cl_2] can be described as shown in Chart 3.

Heating of the solution to −65 °C leads to the appearance of a pseudotriplet with δ_P −14.6 and $^1J_{P,Pt}$ = 5049 Hz corresponding to complex **2**. The low formation rate of the resulting complex should also be pointed out. Indeed, completion of the reaction takes a rather long time, even at −40 °C. Further heating is accompanied by an insignificant change in δ_P and by an increase in the $^1J_{P,Pt}$ value for the resultant complex **2**. Though unambiguous determination of the structure of this intermediate requires additional studies, the results obtained are consistent with the HP coordination scheme proposed earlier. Taking into account the instability of complex **2** and the abnormally long P−N_{ax} bond in complex **4**, one can suggest that these compounds are also stable intermediates of the coordination mechanism we proposed earlier.

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Experimental Section

All reactions were carried out under a dry argon atmosphere in freshly dried and distilled solvents. Infrared spectra were recorded on a Specord M80 spectrophotometer using the samples prepared as KBr pellets, Nujol mulls between CsI plates, and $CHCl_3$ solutions between KBr plates and in polyethylene cells. The ^{11}B and ^{19}F NMR spectra were recorded on Bruker AMX-400 and Bruker AC-200 instruments at 128.38 and 188.3 MHz, respectively. The ^{11}B and ^{19}F chemical shifts were referenced to external $BF_3 \cdot Et_2O$ and $CFCl_3$, respectively. The ^{31}P NMR spectra were recorded on Bruker MSL-300, Bruker AC-200, and Bruker AMX-400 instruments operating at 121.4, 81.0, and 162.0 MHz, respectively, relative to 85% H_3PO_4 solution in D_2O as the external standard. The ^{13}C NMR spectra were recorded on Bruker MSL-300 and Bruker AC-200 spectrometers operating at 75.5 and 50.3 MHz, respectively, relative to tetramethylsilane. Complete assignment of signals in the ^{13}C NMR spectra was achieved using the DEPT technique. The ^{195}Pt NMR spectra were recorded on Bruker MSL-300 and Bruker AC-200 spectrometers operating at 64.5 and 43.0 MHz, respectively, relative to 1 M H_2PtCl_6 solution in D_2O. Mass spectra were recorded on a MSVKh TOF spectrometer with ionization by californium-252 fission fragments (plasma desorption technique). Sedimentation analyses were performed on a MOM-3180 analytical ultracentrifuge following the known procedures.[18] Elemental analyses were performed at the Laboratory of Microanalysis (A. N. Nesmeyanov Institute of Organoelement Compounds, Moscow). Optical rotation was measured on a Perkin-Elmer 141 polarimeter.

Preparation of Platinum Complexes. $[Pt(COD)Cl_2]$[19] and (4*S*,9*S*)-4,9-diethyl-2,11-dioxa-5,8-diaza-1λ^5-phosphatricyclo-[6.3.0.0$^{1.5}$]undecane[5b] were synthesized by following the known procedures.

[(1,2:5,6-η)-1,5-Cyclooctadiene][(4*S*,9*S*)-4,9-diethyl-5*H*-5,8-diaza-2,11-dioxa-1λ^5-phosphatricyclo[6.3.0.0$^{1.5}$]undecyl-1]chloroplatinum Chloride (2). To a solution of $[Pt(COD)Cl_2]$ (0.374 g, 0.001 mol) in CH_2Cl_2 (15 mL) was carefully added ligand **1** (0.232 g, 0.001 mol) dissolved in CH_2Cl_2 (15 mL) dropwise with stirring for ~30 min at 0 °C. The solution was stirred for an additional 30 min at the same temperature, concentrated to ~0.5 mL, and precipitated with a hexane/ether (1/1 by volume) mixture cooled to 0 °C. The resin thus obtained was washed with cooled ether and dried in air and then in vacuo (1 mmHg). Yield: 0.582 g, 96%. Light yellow powder. Mp: 122−124 °C dec. $[\alpha]^{20}_D = +16$ ($c = 0.8$, $CHCl_3$). Anal. Calcd for $C_{18}H_{33}N_2O_2PPtCl_2$: C, 35.65; H, 5.48; N, 4.62; Cl, 11.69. Found: C, 35.39; H, 5.31; N, 4.80; Cl, 11.84. MS (PD; *m*/*z* (*I*, %)): 571 (100), [Pt(COD)ClL]$^+$; 535.5 (32), [Pt(COD)L]$^+$; 427 (54), [PtL]$^+$; 232 (36), [L]$^+$.

***cis*-Dichloro{(4*S*,9*S*)-4,9-diethyl-2,11-dioxa-5,8-diaza-1-phosphabicyclo[6.3.0]-undecane-*P*,*N*}platinum (3).** Complex **3** was prepared by two different procedures, I and II. (I) A solution of complex **2** (0.606 g) in $CHCl_3$ (20 mL) was refluxed for 2 h and concentrated to ~2 mL; the complex precipitated on addition of a hexane/ether (3/1 by volume) mixture. The precipitate was thoroughly washed three times with ether to completely remove 1,5-cyclooctadiene, separated by centrifugation, and dried in air and then in vacuo (1 mmHg). Yield: 0.473 g, 95%. (II) To a solution of $[Pt(COD)Cl_2]$ (0.374 g, 0.001 mol) in $CHCl_3$ (15 mL) was carefully added ligand **1** (0.232 g, 0.001 mol) dissolved in $CHCl_3$ (15 mL) dropwise with stirring for ~30 min at 20 °C. The solution obtained was refluxed for 2 h. The product was isolated by following procedure I. Yield: 0.474 g, 95%. White air-stable powder. Mp: 186−188 °C dec. $[\alpha]^{20}_D = +62.47$ ($c = 0.9$, $CHCl_3$). Anal. Calcd for $C_{10}H_{21}N_2O_2PPtCl_2$: C, 24.11; H, 4.25; N, 5.62; Cl, 14.23. Found: C, 24.32; H, 4.03; N, 5.77; Cl, 14.35. MS (PD; *m*/*z* (*I*, %)): 463 (48), [PtClL]$^+$; 427 (100), [PtL]$^+$; 232 (81), [L]$^+$.

[(1,2:5,6-η)-1,5-cyclooctadiene][(4*S*,9*S*)-4,9-diethyl-5*H*-5,8-diaza-2,11-dioxa-1λ^5-phosphatricyclo[6.3.0.0$^{1.5}$]undecyl-1]chloroplatinum Tetrafluoroborate (4). To compound **2** (0.001 mol) synthesized in situ in CH_2Cl_2 at 0 °C was added a cooled solution of $AgBF_4$ (0.195 g, 0.001 mol) in THF (15 mL). The solution was stirred for 10 min, filtered, concentrated to ~1 mL, and precipitated with a hexane/ether (3/1 by volume) mixture. The precipitate was dried in air and in vacuo (1 mmHg). Yield: 0.570 g, 87%. White air-stable powder. Mp: 151−153 °C dec. $[\alpha]^{20}_D = +9.27$ ($c = 0.75$, $CHCl_3$). Anal. Calcd for $C_{18}H_{33}N_2O_2PPtClBF_4$: C, 32.87; H, 5.06; N, 4.26; Cl, 5.39. Found: C, 33.11; H, 5.35; N, 3.98; Cl, 5.67. MS (PD; *m*/*z* (*I*, %)): 571 (100), [Pt(COD)ClL]$^+$; 535.5 (35), [Pt(COD)L]$^+$; 427 (52), [PtL]$^+$; 232 (34), [L]$^+$. ^{19}F NMR (δ, $CDCl_3$): −152.52 (s, 80%), −152.46 (s, 20%). ^{11}B NMR (δ, $CDCl_3$): −1.27 (s). IR (cm^{-1}, Nujol): ν(PtCl) 318.

X-ray Diffraction Study of Compound 4. Crystals suitable for an X-ray diffraction study were obtained by slow evaporation from a dichloromethane solution. Crystallographic data for compound **4**: at 295 K, the crystals of $C_{18}H_{33}BClF_4N_2O_2PPt$ are orthorhombic, the space group is $P2_12_12_1$, $a = 8.4428(9)$ Å, $b = 9.3054(10)$ Å, $c = 29.927(3)$ Å, $V = 2351.2(4)$ Å^3, $Z = 4$, $M_r = 657.78$, $d_{calcd} = 1.858$ g cm^{-3}, μ(Mo Kα) = 61.98 cm^{-1}, and $F(000) = 1288$. The intensities of 23 998 reflections were measured with a Smart 1000 CCD diffractometer at 295 K (λ(Mo Kα) = 0.710 73 Å, ω scans with 0.3° step in ω and 10 s per frame exposure, $2\theta < 60°$). A total of 6714 independent reflections ($R_{int} = 0.0590$) were used in further refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F^2 in the anisotropic−isotropic approximation. The hydrogen atom linked to the nitrogen atom was located from the Fourier synthesis and refined in the isotropic approximation. Positions of the rest of the hydrogen atoms were calculated geometrically and refined in the "riding" model approximation. Refinement of the absolute structure led to a Flack parameter value of −0.006(6) in the case of the *S*,*S* configuration of the C(2) and C(8) atoms. The refinement converged to wR2 = 0.0519 and GOF = 0.959 for all independent reflections (R1 = 0.0356 was calculated against *F* for 3907 observed reflections with $I > 2\sigma(I)$). The number of refined parameters was 275. All calculations were performed using the SHELXTL 5.1 program package.

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Supporting Information Available: X-ray crystallographic data in CIF format for complex **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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