Reactions of chiral phosphoramidites with complexes $Pd(COD)Cl_2$ and $Pt(COD)Cl_2$

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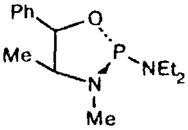
Reactions of phosphoramidites based on (−)-ephedrine and [(1*S*)-*endo*]-(−)-borneol with the complexes $M(COD)Cl_2$ (M is Pd or Pt, and COD is cycloocta-1,5-diene) were studied. The formation of *cis* and *trans* complexes of the general formulas MCl_2L_2 and $M_2Cl_2(\mu\text{-}Cl)_2L_2$ was observed. The structures of the resulting compounds were established by ^{31}P, ^{13}C, and ^{195}Pt NMR and IR spectroscopy and by plasma desorption mass spectrometry.

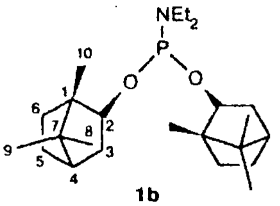
Key words: phosphoramidites, palladium complexes, platinum complexes, coordination, 2-diethylamino-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine, dibornyl diethylphosphoramidite

The structures of the products of the reaction of the $Pt(COD)Cl_2$ complex (COD is cycloocta-1,5-diene) with phosphines in the molar ratio L/M = 1 depend mainly on the spatial structure of the ligand. The coordination of ligands with a small Tolman cone angle[1] results in $PtCl_2L_2$ complexes, and half of the initial complex $Pt(COD)Cl_2$ remains unconsumed. If the cone angle is 165—170°, dimeric complexes $Pt_2Cl_2(\mu\text{-}Cl)_2L_2$ are obtained.[2,3] The most sterically hindered phosphines, such as $P(o\text{-}C_6H_4Me)_3$ (the cone angle is 194°) and $P(C_6H_3\text{-}2,6\text{-}Me_2)_3$ (the cone angle is 212°), do not react with $Pt(COD)Cl_2$ at all even upon prolonged boiling in $CHCl_3$.

In the present work, we studied the coordination of chiral phosphoramidites **1a,b** with the complexes $M(COD)Cl_2$ (M = Pd or Pt) in the molar ratios L/M = 1 and 2.



1a



1b

Results and Discussion

Ligands **1a** and **1b** were synthesized by the reactions of *l*-ephedrine and [(1*S*)-*endo*]-(−)-borneol, respectively, with $P(NEt_2)_3$. Ligand **1a** exists as a mixture of diastereomers, which are manifested in the ^{31}P NMR spectrum as single signals at δ 132.7 and 145.3 with relative intensities of 97.5 and 2.5%, respectively, which is typical of analogous phosphacyclanes based on ephedrine.[4] However, the minor stereoisomer has not been observed previously.[5]

The coordination reactions of compounds **1a,b** were carried out in a solution of $CHCl_3$ at room temperature. The reactions of **1a** with $M(COD)Cl_2$ (M = Pd or Pt) taken in a L/M molar ratio of 1 or 2 afforded a mixture of *cis* and *trans* palladium complexes (**2a**) and only *cis* platinum complex (**3a**) of the general formula MCl_2L_2, respectively. Thus the ^{31}P NMR spectrum of **3a** in $CDCl_3$ has two pseudotriplets at δ 70.7 with $^1J_{P,Pt}$ = 5546 Hz (89%) and at δ 53.5 with $^1J_{P,Pt}$ = 5439 Hz (11%), which correspond to the two stereoisomers of the complex. The observed value of the $^{31}P-^{195}Pt$ spin-spin coupling constant is typical of coordinated phosphoramidites with the *cis* configuration of chloride ligands.[6,7] The coordination of two phosphorus ligands to the platinum atom is evidenced by the ^{195}Pt NMR spectrum, which shows a triplet at δ −3802 with $^1J_{P,Pt}$ = 5535 Hz. The ^{31}P NMR spectrum of complex **2a** in $CDCl_3$ is more complicated because of the presence of a mixture of *trans* and *cis* isomers. The major form is characterized by the following parameters: δ 100.5 and 98.1 for *trans*-$PdCl_2L_2$ (68%) and *cis*-$PdCl_2L_2$ (20%), respectively. The minor form is characterized by the following parameters: δ 91.1 (3%) and 76.0 (9%). The

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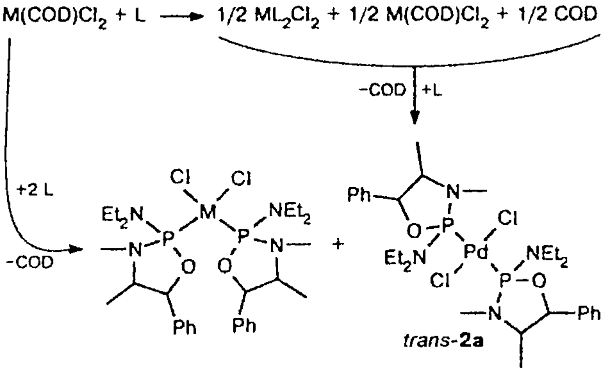
ratio of the *cis* and *trans* isomers of **2a** depends on the polarity of the solvent. The ^{31}P NMR spectrum of a solution of **2a** in DMSO-d_6 has signals at δ 105.5 and 101.8 (for the major form). The portion of the *cis* complex was 35%. The assignment of the signals was made with consideration of the results of the previous study[8] (based on data on a large number of complexes, the authors have demonstrated that *trans* isomers of phosphite complexes of palladium and platinum are characterized by larger downfield chemical shifts than those of *cis* isomers). Note that in the case of complexation of ligand **1a**, the portion of the minor diastereomer was increased both for platinum and palladium.

When the reaction of **1a,b** was carried out with an equimolar amount of $M(COD)Cl_2$, half of the initial complex remained unconsumed. This also follows from the fact that the ^{13}C NMR spectra of the resulting solutions have signals with equal intensities, which correspond to the carbon atoms of $Pd(COD)Cl_2$ (at δ 117.0 and 31.0)[9] or $Pt(COD)Cl_2$ (at δ 100.4 ($^1J_{C,Pt}$ = 152 Hz) and 30.8)[10] and COD (at δ 128.4 and 27.8). Only when an additional molar equivalent of ligand **1a** was added, did the signals of the complexes $Pd(COD)Cl_2$ and $Pt(COD)Cl_2$ completely disappear. Therefore, the characteristic features of complexation of **1a** with $Pd(COD)Cl_2$ and $Pt(COD)Cl_2$ can be represented by Scheme 1.

Scheme 1



L = **1a**, M = Pd (*cis*-**2a**); Pt (**3a**)

The ^{13}C NMR spectral data of complexes **2a** and **3a** in comparison with the data for ligand **1a** are given in Table 1.

The IR spectral studies (the ν(M—Cl) region) of powders of complexes **2a** and **3a** confirmed[11] the *cis* configuration of the chloride ligands in **3a** (ν = 306 and 283 cm^{-1}) and the presence of a mixture of the *trans* and *cis* isomers of **2a** (ν = 360, 304, and 283 cm^{-1}). The data of plasma desorption mass spectrometry are consistent with the suggested structures of compounds **2a** and **3a**. In the mass spectra of both complexes, intense peaks of $[M-Cl]^+$ ions are observed, which is typical[12] of many chloride complexes of palladium and platinum.

The reactions of ligand **1b** with the complexes $M(COD)Cl_2$ taken in a molar ratio L/M = 2 proceeded analogously to the reactions of **1a** to give compounds of the general formula MCl_2L_2. Complex **2b** exists as a mixture of *trans* and *cis* isomers in a ratio of 9 : 1 (δ_P 99.7 and 98.1, respectively; $CDCl_3$). The portion of the *trans* complex is larger in the case of **2b** than in the case of **2a**, which is, apparently, associated with greater steric hindrances in ligand **1b**. In a benzene solution, the concentration of the *cis* complex decreased virtually to zero, and only the *trans* isomer was observed (δ_P 101.7 (C_6D_6); ν(Pd—Cl) 356 cm^{-1} (C_6H_6)). Platinum complex **3b** is the *cis* isomer, as follows from the data of ^{31}P and ^{195}Pt NMR spectroscopy in $CDCl_3$: a pseudotriplet at δ_P 70.1 ($^1J_{P,Pt}$ = 5607 Hz) and a triplet at δ_{Pt} −4114 ($^1J_{Pt,P}$ = 5598 Hz), respectively. The results of far-IR spectroscopic studies of powders of **2b** and **3b** confirm the *trans* configuration of the chloride ligands in $PdCl_2L_2$ and their *cis* arrangement in $PtCl_2L_2$ (ν(Pd—Cl) 354 cm^{-1}, and ν(Pt—Cl) 314 and 291 cm^{-1}). The mass spectrum of complex **3b**, as in the cases of **2a** and **3a**, has an intense peak of an $[M-Cl]^+$ ion.

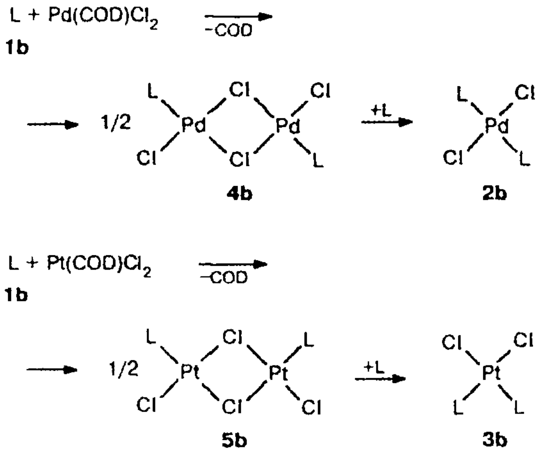
The reaction of ligand **1b** with an equimolar amount of $M(COD)Cl_2$ gave products other than complexes **2b** and **3b** (Scheme 2).

Thus after addition of ligand **1b** to $Pd(COD)Cl_2$ in $CDCl_3$, the ^{31}P NMR spectrum of the solution shows a singlet at δ 68.6, and the long-wavelength region of the IR spectrum has three absorption bands at ν(Pd—Cl) 356, 298, and 256 cm^{-1} (the ratio of intensities was 10 : 4 : 8), which unambiguously indicates that the resulting complex (**4b**) containing the bridging chloride ligands has the binuclear structure.[13—16] The ^{13}C NMR

Table 1. Data of ^{13}C NMR spectroscopy for compounds **1a**, **2a**, and **3a**

Compound	Solvent	δ_C ($^2J_{C,P}$/Hz)						
		POCH	PNCH	$PNCH_3$	$CH\underline{C}H_3$	NCH_2	$CH_2\underline{C}H_3$	Ph
1a	$CDCl_3$	81.9 (*J* = 10.2)	59.3	29.1 (*J* = 21.1)	13.5	38.1 (*J* = 5.7)	15.1	125.6; 126.8; 127.8; 139.5
2a	DMSO-d_6	79.9	60.1	33.9	13.5	38.9	13.2	125.1; 127.3; 127.9; 137.0
3a	$CDCl_3$	80.5	61.9	34.1	14.4	39.4	13.7	125.4; 127.4; 128.1; 137.0

Scheme 2



spectral data for complexes **2b** and **4b** are given in Table 2. Note that in **2b** and **4b** the signals for the carbon atoms of the OCH and NCH_2 groups adjacent to the phosphorus atom undergo downfield coordination shifts, while the resonance signals for the other atoms remain virtually unchanged compared to the ligand.[17] Thus, the structure of complex **4b** is described by the formula *trans*-$Pd_2Cl_2(\mu\text{-}Cl)_2L_2$.

The reaction of **1b** with the platinum complex proceeded analogously. The ^{31}P NMR spectrum of a solution of **5b** in $CDCl_3$ that was obtained after addition of **1b** to $Pt(COD)Cl_2$ has a pseudotriplet at δ 51.6 ($^1J_{P,Pt}$ = 4830 Hz). The doublet signal in the ^{195}Pt NMR spectrum (δ –3730, $^1J_{P,Pt}$ = 4830 Hz) is indicative of the coordination of one phosphorus atom to the platinum atom. Based on the published data,[3] the formula *cis*-$Pt_2Cl_2(\mu\text{-}Cl)_2L_2$ may be assigned to complex **5b**. The ^{13}C NMR spectrum of the reaction solution in which signals for the free cycloocta-1,5-diene are observed indicates that the cyclooctadiene ligand is displaced in the complexation with the phosphorus ligand. The ^{13}C NMR spectra of complexes **5b** and **4b** are virtually identical (see Table 2). We failed to isolate individual compounds **4b** and **5b** from solutions because they underwent isomerization and disproportionation. In particular, the ^{31}P NMR spectrum of a solution of the resulting powder in $CDCl_3$ has resonance signals at δ 32.6 ($^1J_{P,Pt}$ = 5851 Hz) and 92.7 ($^1J_{P,Pt}$ = 3704 Hz) in addition to the above-mentioned signal for compound **5b**. When the values of the spin-spin coupling constants and the chemical shifts are taken into account, the above-mentioned resonance signals correspond to the *trans*-$Pt_2Cl_2(\mu\text{-}Cl)_2L_2$ and *trans*-$PtCl_2L_2$ complexes, respectively. These signals also appeared upon storage (or more rapidly upon heating) of a solution of **5b** formed *in situ*. The formation of these complicated mixtures of complexes is not surprising. Analogous processes that occurred in the reactions of some phosphines with $Pt(COD)Cl_2$ have been reported previously.[3]

Therefore, the character of the products of the reactions of cyclooctadiene complexes of palladium and platinum with phosphoramidites taken in equimolar ratios depends substantially on steric factors. The coordination of bulky ligands afforded labile dimeric complexes containing chloride bridges, which are, apparently, intermediates in reactions carried out in the molar ratio L/M = 2. It was noted that the steric factor of the ligand favors the *trans* orientation of the chloride ligands in $PdCl_2L_2$. The dependence on the nature of the metal atom is also evident: *trans*-$PdCl_2L_2$ and *cis*-$PtCl_2L_2$ were predominantly formed. The ratio of the *cis* and *trans* isomers of $PdCl_2L_2$ is also affected by the polarity of the solvent, namely, the portion of the *cis* isomer increases in more polar solvents.

Experimental

The IR spectra were recorded on a Specord M-80 instrument as Nujol mulls between CsI plates and as solutions in $CHCl_3$ and C_6H_6 in polyethylene cells. The ^{31}P NMR spectra were recorded on Bruker MSL-300 and Bruker AC-200 instruments operating at 121.4 and 81.0 MHz, respectively, relative to a 85% H_3PO_4 solution in D_2O as the external standard. The ^{13}C NMR spectra were obtained on the same instruments operating at 75.5 and 50.3 MHz, respectively, relative to Me_4Si. The ^{195}Pt NMR spectra were recorded on a Bruker MSL-300 instrument (64.5 MHz) relative to a 1 *M* H_2PtCl_6 solution in D_2O. The plasma desorption mass spectra were measured on a MSVKh time-of-flight mass spectrometer with ionization by nuclear fragments of californium-252.

Table 2. Data of ^{13}C NMR spectroscopy for compounds **2b**, **4b**, and **5b** ($CDCl_3$)

Compound	δ_C ($^2J_{C,P}$/Hz)											
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	CH_2	CH_3
2b	50.1	82.7; 81.9	37.9; 37.2	45.2	28.2	26.7	47.5	18.9; 18.8	19.9	13.9; 13.8	40.4	14.9
4b	50.1	86.6 (J = 5.5); 85.0 (J = 9.7)	37.4; 37.3	45.0	28.1	26.7; 26.6	47.5; 47.4	19.0; 18.8	19.8	13.9; 13.7	42.2 (J = 8.3)	14.9
5b	49.7	85.6	36.8	44.7	27.9	26.2	47.3	18.5	19.5	13.6	41.2	14.5

All reactions were carried out under an atmosphere of dry argon. The solvents were dehydrated according to known procedures[18] and stored over 3 Å and 4 Å molecular sieves in the dark. Ligands **1a,b** and $P(NEt_2)_3$ were distilled immediately before use. The initial complexes $Pd(COD)Cl_2$ and $Pt(COD)Cl_2$ were prepared according to known procedures[19,20] and dried immediately before the synthesis (at 50 °C and 0.8 Torr for 1 h).

Ligand 1a. A mixture of *l*-ephedrine (3.305 g, 0.02 mol) and $P(NEt_2)_3$ (4.947 g, 0.02 mol) was heated to 120 °C under argon with continuous stirring and kept at this temperature for 1 h. The reaction mixture was evacuated (2 Torr) at 100 °C for 30 min and then at 60 °C and 1 Torr for 30 min to completely remove $HNEt_2$. The product obtained was distilled. B.p. 120—125 °C (0.8 Torr). The yield was 64%. The data of ^1H NMR spectroscopy and elemental analysis agree with the published data on the synthesis of **1a** based on ephedrine hydrochloride.[5] The ^{31}P NMR spectra were discussed above. The parameters of the ^{13}C NMR spectrum are given in Table 1.

Synthesis of ligand 1b and its spectral characteristics were reported previously.[17]

Complexes of palladium and platinum. Complexes **2a** and **3a** were prepared according to the following general procedure. A solution of ligand **1a** (0.533 g, 0.002 mol) in $CHCl_3$ (10 mL) was added dropwise to a solution of the cyclooctadiene complex of the corresponding metal (0.001 mol; 0.285 g of $Pd(COD)Cl_2$ or 0.374 g cf $Pt(COD)Cl_2$) in $CHCl_3$ (10 mL). The resulting solution was stirred for 1 h and concentrated to ~2 mL *in vacuo*. The complex was precipitated with a hexane—ether mixture (2 : 1, v/v). The precipitate that formed was thoroughly washed three times with ether to completely remove cycloocta-1,5-diene, separated by centrifugation, and dried in air and *in vacuo* (1 Torr).

Bis(2-diethylamino-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine)palladium dichloride (2a), m.p. 97—98 °C. The yield was 89.2%. Yellow powder. Found (%): C, 47.64; H, 6.45; Cl, 10.19. $C_{28}H_{46}Cl_2N_4O_2P_2Pd$. Calculated (%): C, 47.37; H, 6.53; Cl, 9.99. MS, *m/z* (I_{rel} (%)): 674 $[M-Cl]^+$ (63), 639 $[M-2\ Cl]^+$ (16), 408 $[PdLCl]^+$ (20), 373 $[PdL]^+$ (25), 267 $[L]^+$ (53).

Bis(2-diethylamino-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine)-*cis*-platinum dichloride (3a), m.p. 214—216 °C (decomp.). The yield was 91.7%. White powder. Found (%): C, 41.90; H, 6.03; Cl, 8.65. $C_{28}H_{46}Cl_2N_4O_2P_2Pt$. Calculated (%): C, 42.11; H, 5.81; Cl, 8.88. MS, *m/z* (I_{rel} (%)): 799 $[M]^+$ (9), 763 $[M-Cl]^+$ (75), 728 $[M-2\ Cl]^+$ (39), 267 $[L]^+$ (21).

Complexes **2b** and **3b** are soluble in organic solvents, and therefore, they could be prepared according to the following general procedure. A solution of ligand **1b** (0.409 g, 1 mmol) in $CHCl_3$ (10 mL) was added dropwise to a solution of the cyclooctadiene complex of the corresponding metal (0.5 mmol; 0.143 g of $Pd(COD)Cl_2$ or 0.187 g of $Pt(COD)Cl_2$) in $CHCl_3$ (10 mL). The resulting solution was stirred for 1 h, concentrated to dryness *in vacuo*, and dried at 60 °C and 0.8 Torr for 2 h. The complexes were obtained in quantitative yields.

Bis(dibornyl diethylphosphoramidite)palladium dichloride (2b), m.p. 139—141 °C. Pale-yellow, powder. Found (%): C, 58.15; H, 9.12; Cl, 6.96. $C_{48}H_{88}Cl_2N_2O_4P_2Pd$. Calculated (%): C, 57.86; H, 8.90; Cl, 7.12.

Bis(dibornyl diethylphosphoramidite)-*cis*-platinum dichloride (3b), m.p. 93—95 °C. White powder. Found (%): C, 52.97; H, 7.89; Cl, 6.77. $C_{48}H_{88}Cl_2N_2O_4P_2Pt$. Calculated (%): C, 53.13; H, 8.17; Cl, 6.53. MS, *m/z* (I_{rel} (%)): 1084 $[M]^+$ (8), 1049 $[M-Cl]^+$ (31), 1013 $[M-2\ Cl]^+$ (15).

Complexes **4b** and **5b** were investigated without isolation. The specimens suitable for NMR studies were prepared as follows. A solution of the corresponding ligand (0.2 mmol) in $CDCl_3$ (1.5 mL) was slowly added dropwise to a solution of the corresponding cyclooctadiene complex (0.2 mmol; 57.1 mg of $Pd(COD)Cl_2$ or 74.8 mg of $Pt(COD)Cl_2$) in $CDCl_3$ (1.5 mL) with intense stirring. Then the solutions of the complexes were transferred into NMR tubes, and the spectra were recorded. Then an additional amount of the ligand (0.2 mmol) was added with stirring, and the NMR spectra were recorded again.

References

1. C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.
2. G. K. Anderson, H. C. Clark, and J. A. Davies, *Inorg. Chem.*, 1981, **20**, 3607.
3. I. M. Al-Najjar, *Inorg. Chim. Acta.*, 1987, **128**, 93.
4. D. Bernard and R. Burgada, *Phosphorus*, 1974, **3**, 187.
5. E. E. Nifant'ev, E. N. Rasadkina, and I. D. Rozhdestvenskaya, *Koord. Khim.*, 1979, **5**, 1846 [*Sov. J. Coord. Chem.*, 1979, **5** (Engl. Transl.)].
6. V. S. Reddy, K. V. Katti, and C. L. Barnes, *Inorg. Chem.*, 1995, **34**, 5483.
7. S. D. Pastor and A. Togni, *Inorg. Chim. Acta*, 1989, **159**, 3.
8. N. Ahmad, E. W. Ainscough, T. A. James, and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 1973, 1148.
9. M. F. Rettig, R. M. Wing, and G. R. Wiger, *J. Am. Chem. Soc.*, 1981, **103**, 2980.
10. M. H. Rakowsky, J. C. Woolcock, L. L. Wright, D. B. Green, M. F. Rettig, and R. M. Wing, *Organometallics*, 1987, **6**, 1211.
11. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1986.
12. A. Albinati, F. Lianza, H. Berger, P. S. Pregosin, H. Rüegger, and R. W. Kunz, *Inorg. Chem.*, 1993, **32**, 478.
13. R. G. Goodfellow, P. L. Goggin, and L. M. Venanzi, *J. Chem. Soc., A*, 1967, 1897.
14. R. G. Goodfellow, J. G. Evans, P. L. Goggin, and D. A. Duddell, *J. Chem. Soc., A*, 1968, 1604.
15. D. M. Adams and P. J. Chandler, *J. Chem. Soc., A*, 1969, 588.
16. D. A. Duddell, P. L. Goggin, R. G. Goodfellow, M. G. Norton, and J. G. Smith, *J. Chem. Soc., A*, 1970, 545.
17. K. N. Gavrilov, I. S. Mikhel, K. A. Lysenko, M. Yu. Antipin, G. I. Timofeeva, A. I. Polosukhin, and A. V. Korostylev, *Zh. Neorg. Khim.*, 1997, **42**, 593 [*Russ. J. Inorg. Chem.*, 1997, **42**, 520 (Engl. Transl.)].
18. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 1988.
19. D. Drew and J. R. Doyle, *Inorg. Synth.*, 1972, **13**, 52.
20. H. C. Clark and L. E. Manzer, *J. Organomet. Chem.*, 1973, **59**, 411.

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