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Pt(II) and Pd(II) Complexes with (2-Bromo-1-phenylvinyl)diphenylphosphine and Tris(Z-styryl)phosphine

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Abstract—Methods were developed for selective synthesis of geometric isomers of Pt(II) and Pd(II) complexes with (2-bromo-1-phenylvinyl)diphenylphosphine and tris(Z-styryl)phosphine.

Transformations of unsaturated organophosphorus compounds in the metal coordination sphere [1-3] and catalytic processes involving transition metaphosphine complexes [4-6] are new fields of heteroorganic chemistry. Therefore, synthesis of new complexes containing unsaturated organophosphorus ligands in the coordination sphere is of interest.

We have previously reported on the synthesis of complexes of Pt(II), Pd(II), and Ni(II) with diphenyl-(1-cyclohexenyl)phosphine and diphenyl(1-phenyl-vinyl)phosphine [7]. Proceeding with these studies, we have prepared Pt(II) and Pd(II) complexes with (2-bromo-1-phenylvinyl)diphenylphosphine and tris-(*Z*-styryl)phosphine.

The synthetic methods and X-ray data for noncoordinated (2-bromo-1-phenylvinyl)diphenylphosphine were published in [8]. Tris(Z-styryl)phosphine can be readily prepared by direct phosphorylation of phenylacetylene with elemental phosphorus in the presence of strong bases [9, 10].

The Pt(II) complexes with (2-bromo-1-phenylvinyl)diphenylphosphine were prepared from dichlorobis-(dimethyl sulfoxide)platinum(II) by substitution of sulfoxide in the coordination sphere with the corresponding phosphines.

 $[PtCl_2(Me_2SO)_2] + 2Ph_2PC(Ph)=CHBr$ $\longrightarrow [PtCl_2(Ph_2PC(Ph)=CHBr)_2] + 2Me_2SO.$

The geometry of the bisphosphine complex formed depends on the ratio of the starting reactants. The trends were similar to those in the reaction of dichlorobis(dimethyl sulfoxide)platinum(II) with diphenyl-(1-cyclohexenyl)phosphine [7]. With the starting di-

methyl sulfoxide complex in excess, *trans*-dichlorobis[(2-bromo-1-phenylvinyl)diphenylphosphine]platinum(II) was formed exclusively. If the reaction was carried out with excess phosphine, the *cis* complex was obtained.

The reaction of potassium tetrachloroplatinate(II) with tris(Z-styryl)phosphine taken in a small excess yields exclusively *trans*-dichlorobis[tris(Z-styryl)-phosphine]platinum(II).

 $\begin{array}{rcl} & K_2PtCl_4 + 2(PhCH=CH)_3P \\ \longrightarrow \ trans-\{PtCl_2[(PhCH=CH)_3P]_2\} + 2KCl. \end{array}$

At the same time, it is known [11, 12] that *cis* complexes are usually formed under similar conditions. Such an unusual reaction pathway may be due to the steric hindrance to coordination of the bulky phosphorus ligand.

The structures of the isomeric products obtained are confirmed by the v(Pt–Cl) stretching frequencies and the J_{PtP} coupling constants in the ³¹P NMR spectra, characteristic of Pt(II) *cis*- and *trans*-bisphosphine complexes [13].

An attempt to prepare Pt(II) bisphosphine complexes by the substitution of the labile sulfoxide ligands in the reaction of dichlorobis(dimethyl sulfoxide)platinum with tris(Z-styryl)phosphine leads, according to the ³¹P NMR data, to a complex mixture of products. In the spectrum of this mixture, we tentatively assign a signal at -28.4 ppm with the coupling constant J_{PtP} 3507 Hz to the bisphosphine complex of the *cis* structure.

The reaction of palladium(II) chloride with tris(Z-styryl)phosphine in an acidic medium gives dichlorobis[tris(Z-styryl)phosphino]palladium(II).

$$PdCl_4^{2-} + 2(PhCH=CH)_3P$$

$$\longrightarrow \{PdCl_2[(PhCH=CH)_3P]_2\} + 2Cl^{-}.$$

In the ¹H NMR spectra of *trans*-dichlorobis[tris-(Z-styryl)phosphine]platinum(II) and *trans*-dichlorobis[tris(Z-styryl)phosphine]palladium(II), the effect of the so-called "virtual splitting" of the vinyl proton signals is observed. This effect is due to the additional coupling with the *trans*-located phosphorus atom. A similar effect was noted previously [13] for *trans*-dichlorobis(vinyldiphenylphosphine)palladium and was observed by us in the ¹H NMR spectra of Pd(II) and Pt(II) *trans* complexes with diphenyl(1-cyclohexenyl)phosphine and diphenyl(1-phenylvinyl)phosphine [7].

Contrary to tris(Z-styryl)phosphine, the reaction with (2-bromo-1-phenylvinyl)diphenylphosphine under the similar conditions is unselective, and the product yield is low. Therefore, to prepare dichlorobis[(2-bromo-1-phenylvinyl)diphenylphosphine]palladium(II), we used the substitution of the nitrile by phosphine in the coordination sphere of dichlorobis-(benzonitrile)palladium(II).

$$[PdCl_2(PhCN)_2] + 2Ph_2PC(Ph)=CHBr$$

$$\longrightarrow [PdCl_2(Ph_2PC(Ph)=CHBr)_2] + 2PhCN.$$

The phosphorus chemical shifts, coupling constants J_{PtP} , and v(Pt-Cl) and v(Pd-Cl) stretching frequencies are listed in the table.

EXPERIMENTAL

The IR spectra were recorded on FSM-1201 (400–4000 cm⁻¹) and Hitachi FIS-3 (200–400 cm⁻¹) spectrometers. The ¹H and ³¹P NMR spectra were measured on a Bruker AC-200 spectrometer (working frequences 200.132 and 81.026 MHz, respectively) in CDCl₃. The chemical shifts were measured against TMS (¹H) and 85% H₃PO₄ (³¹P).

(2-Bromo-1-phenylvinyl)diphenylphosphine [8]. IR spectrum (KBr), v, cm⁻¹: 465 (0.315), 502 (0.125), 532 (0.377), 577 (0.301), 668 (0.314), 677 (0.288), 698 (0.035), 739 (0.077), 748 (0.158), 778 (0.148), 854 (0.552), 913 (0.100), 997 (0.407), 1028 (0.321), 1067 (0.279), 1094 (0.302), 1156 (0.390), 1304 (0.382), 1329 (0.393), 1404 (0.294), 1432 (0.091), 1445 (0.302), 1478 (0.194), 1489 (0.211), 1568 (0.313), 1588 (0.345), 1595 (0.362), 3000 (0.219), 3027 (0.200), 3067 (0.183). ¹H NMR spectrum, δ, ppm: 6.02 d (1H, CH=, ${}^{3}J_{\rm HP}$ 11.4 Hz), 7.27–7.64 m (15H, Ph). $\delta_{\rm P}$ –5.29 ppm.

Tris(Z-styryl)phosphine [9, 10]. IR spectrum, v,

Spectral characteristics of the transition metal complexes with α,β -unsaturated phosphines and free ligands

Compound	δ _p , ppm	J _{PtP} , Hz	ν, cm ⁻¹
Ph ₂ PC(Ph)=CHBr	-5.29	_	_
Z, \overline{Z}, Z -(PhCH=CH) ₃ P	-59.0	_	_
<i>trans</i> -{PtCl ₂ [Ph ₂ PC(Ph)=CHBr] ₂ }	29.0	2684	344
cis -{PtCl ₂ [Ph ₂ PC(Ph)=CHBr] ₂ }	21.1	3708	305,
			327
<i>trans</i> -{PdCl ₂ [Ph ₂ PC(Ph)=CHBr] ₂ }	27.7	_	359
<i>trans</i> -{ $PtCl_2[(PhCH=CH)_3P]_2$ }	-32.5	2401	344
trans-{ $PdCl_2[(PhCH=CH)_3P]_2$ }	-25.8	_	358

cm⁻¹: 523 (0.358), 532 (0.360), 592 (0.877), 610 (0.577), 640 (0.640), 695 (0.222), 719 (0.337), 745 (0.275), 779 (0.213), 843 (0.438), 916 (0.511), 975 (0.619), 999 (0.750), 1028 (0.521), 1074 (0.550), 1159 (0.392), 1178 (0.393), 1225 (0.715), 1300 (0.819), 1319 (0.745), 1333 (0.759), 1358 (0.794), 1445 (0.295), 1492 (0.255), 1572 (0.368), 1594 (0.296), 2929 (0.915), 2986 (0.551), 3023 (0.446), 3057 (0.429). ¹H NMR spectrum, δ , ppm: 6.35 d (1H, CH=, ${}^{3}J_{\rm HH}$ 13 Hz), 7.18 d.d (1H, CH=, ${}^{3}J_{\rm HH}$ 13, ${}^{3}J_{\rm HP}$ 24 Hz), 7.31 m, 7.59 m (5H, Ph). $\delta_{\rm P}$ –59.0 ppm.

cis-Dichlorobis[(2-bromo-1-phenylvinyl)diphenylphosphine]platinum(II). (2-Bromo-1-phenylvinyl)diphenylphosphine, 226 mg, was dissoved in 10 ml of chloroform, and 50.0 mg of dichlorobis(dimethyl sulfoxide)platinum was added. The reaction mixture was refluxed for 1 h. The starting complex dissolved. After the reaction completion, the mixture was filtered. The product was precipitated from the filtrate with hexane. The precipitate was washed with ethanol and diethyl ether and dried. Yield 41.7 mg (35%), mp 184°C. IR spectrum (KBr), v, cm⁻¹: 465 (0.794), 486 (0.829), 507 (0.728), 523 (0.803), 542 (0.716), 585 (0.731), 691 (0.585), 714 (0.651), 745(0.734), 774 (0.804), 821 (0.922), 841 (0.943), 929 (0.910), 945 0.864), 1000 (0.877), 1028 (0.839), 1073 (0.865), 1096 (0.660), 1157 (0.898), 1188 (0.899),1406 (0.895), 1435 (0.680), 1483 (0.833), 1572 (0.893), 1593 (0.897), 1648 (0.904), 1889 (0.941), 2853 (0.869), 2924 (0.869), 3053 (0.822). ¹H NMR spectrum, δ , ppm: 6.75–7.40 m (Ph, =CHBr). Found, %: C 47.9; H 3.1; Cl 7.1; Pt 19.5. C₄₀H₃₂Br₂Cl₂P₂Pt. Calculated, %: C 48.0; H 3.2; Cl 7.1; Pt 19.5.

trans-Dichlorobis[(2-bromo-1-phenylvinyl)diphenylphosphine]platinum(II) was prepared similarly from 53.3 mg of (2-bromo-1-phenylvinyl)diphenylphosphine and 34.1 mg of dichlorobis(dimethyl sulfoxide)platinum(II). Yield 25.3 mg (31%), mp

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191°C. IR spectrum (KBr), v, cm⁻¹: 460 (0.220), 590 (0.310), 610 (0.300), 685 (0.500), 740 (0.670), 762 (0.714), 898 (0.700), 930 (0.655), 995 (0.608), 1025 (0.582), 1095 (0.479), 1425 (0.332), 1470 (0.330), 1605 (0.132), 1625 (0.160). ¹H NMR spectrum, δ , ppm: 6.95–7.85 m (Ph, CHBr). Found, %: C 47.8; H 3.1, Cl 7.2, Pt 19.4. C₄₀H₃₂Br₂Cl₂P₂Pt. Calculated,%: C 48.0; H 3.2; Cl 7.1; Pt 19.5.

trans-Dichlorobis[(2-bromo-1-phenylvinyl)diphenylphosphine]palladium(II). A solution of 395 mg of (2-bromo-1-phenylvinyl)diphenylphosphine in 5 ml of methylene chloride was added in small portions under argon to a solution of 193 mg of dichlorobis(benzonitrile)palladium(II) in 5 ml of methylene chloride. The mixture was left overnight. The solvent was partially distilled off, and the residue was poured into 30 ml of hexane. The precipitate thus formed was filtered off, washed with diethyl ether, and dried. Yield 176 mg (38%), mp 182°C. IR spectrum (KBr), v, cm⁻¹: 461 (0.816), 502 (0.693), 533 (0.874), 558 (0.801), 592 (0.832), 691 (0.585), 745 (0.765), 766 (0.862), 809 (0.931), 816 (0.927), 901 (0.892), 935 (0.880), 999 (0.894), 1028 (0.882), 1071 (0.887), 1093 (0.806), 1154 (0.935), 1186 (0.911), 1276 (0.898), 1310 (0.910), 1434 (0.677), 1480 (0.847), 1487 (0.846), 1561 (0.844), 1578 (0.830),3051 (0.889). ¹H NMR spectrum, δ, ppm: 6.90-7.75 m (Ph, CHBr=). Found, %: C 52.6; H 3.6; Cl 7.7; Pd 11.7. C₄₀H₃₂Br₂Cl₂P₂Pd. Calculated, %: C 52.7; H 3.5; Cl 7.8; Pd 11.7.

trans-Dichlorobis[tris(Z-styryl)phosphine]platinum(II). A solution of 183 mg of tris(Z-styryl)phosphine in 5 ml of ethanol was added dropwise with stirring under argon over a period of 1 h to a saturated solution of 99.2 mg of potassium tetrachloroplatinate(IV). The precipitate thus formed was filtered off, washed with ethanol and diethyl ether, and dried. Yield 101 mg (45%), mp 171°C. IR spectrum (KBr), v, cm⁻¹: 529 (0.678), 598 (0.861), 615 (0.888), 655 (0.849), 692 (0.648), 702 (0.688), 741 (0.778), 777 (0.609), 852 (0.901), 917 (0.905), 1027 (0.912), 1073 (0.905), 1156 (0.928), 1179 (0.933),1229 (0.949), 1320 (0.949), 1364 (0.952), 1399 (0.944), 1444 (0.829), 1491 (0.814), 1572 (0.831), 1593 (0.798), 2925 (0.906), 2996 (0.884), 3023 (0.844), 3051 (0.846), 3438 (0.708). ¹H NMR spectrum, δ, ppm: 6.29 m (1H, CH=), 6.86 m (1H, CH=), 7.19-7.43 m (5H, Ph). Found, %: C 60.9; H 4.4; Cl 7.5; Pt 20.6. C₄₈H₄₂Cl₂P₂Pt. Calculated, %: C 60.9; H 4.5; Cl 7.5; Pt 20.6.

trans-Dichlorobis[tris(Z-styryl)phosphine]palladium(II). A solution of 0.420 g of palladium chloride in 11 ml of concentrated hydrochloric acid and 11 ml of water was added dropwise with stirring under argon to a boiling solution of 1.632 g of tris(Zstyryl)phosphine in 20 ml of ethanol. The precipitate of the complex thus formed was filtered off, washed with ethanol and diethyl ether, and dried. Yield 1.271 g (63%), mp 166°C. IR spectrum, v, cm⁻¹: 530 (0.708), 596 (0.838), 615 (0.847), 656 (0.830), 695 (0.557), 723 (0.783), 741 (0.780), 774 (0.540), 835 (0.896), 853 (0.870), 920 (0.869), 970 (0.893), 1027 (0.889), 1074 (0.873), 1178 (0.908), 1225 (0.929), 1318 (0.928), 1372 (0.940), 1443 (0.773), 1490 (0.774), 1572 (0.795), 1590 (0.741), 2921 (0.940), 3021 (0.802), 3052 (0.882), 3438 (0.836). ¹H NMR spectrum, δ, ppm: 6.26 m (1H, CH=), 6.82 m (1H, CH=), 7.14-7.34 m (5H, Ph). Found, %: C 67.2; H 5.0; Cl 8.3; Pd 12.4. C₄₈H₄₂Cl₂P₂Pd. Calculated, %: C 67.2; H 4.9; Cl 8.3; Pd 12.4.

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