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Rhodium(I) Tristyrylphosphine Cyclooctadiene Complexes

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Abstract — Rhodium complexes with unsaturated phosphines as ligands were studied by NMR spectroscopy. Tris[(*E*,*Z*,*Z*)-styryl)phosphine is a stronger complex-forming agent compared with tris[(*Z*,*Z*,*Z*)-styryl)phosphine in view of the easier accessibility of its lone electron pair. The composition of the complexes and their NMR parameters suggest a square-planar structure with *cis* phosphine ligands.

Metal complexes with mono- and diphosphine ligands are widely used as catalysts (see, for example, [1]). Such complexes are well-documented, however, the range of ligands is limited to aromatic (aliphatic–aromatic) phosphines of the saturated series. No information on metal complexes with unsaturated phosphines is available, since they are hardly accessible. At the same time, complex formation of unsaturated phosphines with metals is interesting to study both theoretically, in view of the possibility to involve the double bond in coordination and/or to trace changes in phosphorus–double bond interaction, and practically as a way to obtain novel metal-complex catalysts. We recently developed a convenient, effective, and selective procedure for synthesis of tris-[(*Z*,*Z*,*Z*)-styryl]phosphine from phosphorus(0) or phosphine and phenylacetylene [2–5], which may help to fill this gap. The *Z*,*Z*,*Z* isomer of tristyrylphosphine was brought into thermal isomerization to obtain the *E*,*Z*,*Z* isomer [5]. Thus complex formation with ligands of different configuration proved possible to study.

In the present work we made use of ^{1}H and ^{31}P NMR spectroscopy to study reaction of tris[(*Z*,*Z*,*Z*)-styryl)]phosphine (**I**) and its mixture with tris[(*E*,*Z*,*Z*)-styryl]phosphine (**II**) with rhodium(I) cyclooctadiene complexes: dimeric chloride complex $[(1,5\text{-COD})\cdot RhCl]_2$ (**III**) and cationic triflate complex $[(1,5\text{-COD})_2\cdot Rh]^{+}CF_3SO_3^{-}$ (**IV**) (here and hereinafter, 1,5-COD stands for 1,5-cyclooctadiene).

Upon mixing of phosphine **I** with chloride complex **III**, the ^{31}P NMR spectrum no longer shows the signal of the starting phosphine at δ_P –60.9 ppm, and a doublet signal of phosphine complex **V** appears at δ_P –28.9 ppm ($^{1}J_{PRh}$ 142.6 Hz). Therewith, in the ^{1}H NMR spectrum we observe changes in the shape and position of the signal of vinyl protons α to the phosphorus atom: The signal shifts downfield by 0.07 ppm, the $^{1}J_{H^{\alpha}H^{\beta}}$ and $^{2}J_{H^{\alpha}P}$ increase from 12.6 and 2.0 Hz, respectively, to the same value of 13.5 Hz, and the signal degenerates into a triplet. In the region of aromatic protons, *meta*- and *para*-proton signals shift downfield by 0.15 ppm.

The reaction of phosphine **I** with cationic triflate complex **IV** produces similar changes in the ^{31}P NMR spectrum: The signal of phosphine **I** disappears and a doublet signal of phosphine complex **VI** appears at δ_P –26.6 ppm ($^{1}J_{PRh}$ 143.3 Hz). The signal of vinyl protons in the α position, too, degenerates into a triplet, but it shifts upfield by 0.21 ppm. Like with the reaction with complex **III**, a downfield shift of the multiplet of aromatic protons is observed. The complex formation with phosphine **I** results in expulsion of one diene molecule from the coordination sphere of rhodium, as evidenced by the observation in the ^{1}H NMR spectrum of signals of free 1,5-cyclooctadiene. The second diene molecule remains in the coordination sphere of the metal. Therewith, the methine and downfield methylene proton signals shift downfield compared with complex **IV**, whereas the upfield methylene proton signal shifts upfield ($\Delta\delta_{CH}$ 0.91, $\Delta\delta_{CH^A}$ 0.28, $\Delta\delta_{CH^B}$ –0.37 ppm). The formation of complex **V** from complex **III** containing one molecule of 1,5-cyclooctadiene per one Rh atom involves no expulsion of the diene with phosphine **I**.

The reactions of rhodium complexes **III** and **IV** with a mixture of isomeric phosphines **I** and **II** (7 : 3) gives rise to two types of complexes. With chloride complex **III**, the ^{31}P NMR spectrum acquires two doublets at δ_P –28.9 ppm ($^{1}J_{PRh}$ 141.8 Hz) (complex **V**) and δ_P –15.0 ppm ($^{1}J_{PRh}$ 142.6 Hz) (complex **VII**). Comparison with the above results for complex **III** with phosphine **I** suggests that isomeric phosphines **I** and **II** give different complexes, and the upfield signal

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at δ_P –28.9 ppm belongs to the rhodium complex with *Z,Z,Z* isomer **I**, and the downfield signal at δ_P –15.0 ppm, to the complex with *E,Z,Z* isomer **II**.

The complex-forming power of isomers **I** and **II** proved to be essentially different. Thus, the signal of the minor *E,Z,Z* isomer **II** at δ_P –46.7 ppm completely disappears from the ^{31}P NMR spectrum, and the signal of the major *Z,Z,Z* isomer **I** at δ_P –60.9 ppm is preserved; the ratio of complexes **V** and **VII** (from the integral intensities of their signals) is 2:3, which implies that *E,Z,Z* isomer **II** is much more active with respect to rhodium chloride complex **III**.

Along with above changes in the ^{1}H NMR spectrum, associated with the formation of complex **V**, the reaction with a mixture of isomers **I** and **II** gives rise to new signals assignable to complex **VII**. These are the α-vinyl proton signal shifted upfield by 0.19 ppm with respect to that of free ligand, as well as the signal of *ortho* protons of the benzene ring, shifted downfield by 0.5 ppm. The reaction of a mixture of isomers **I** and **II** with cationic complex **IV**, too, yields two complexes that appear at δ_P –26.6 ppm (complex **VI**) and δ_P –8.6 ppm ($^1J_{PRh}$ 137.4 Hz) (complex **VIII**). The ratio of complexes **VI** and **VIII**, as determined from the ^{31}P NMR spectrum, is 1:5, i.e. *E,Z,Z* isomer **II**, like with chloride complex **III**, is more active, and the selectivity of the complex formation in the case of the cationic complex is higher. Table 1 lists the ^{1}H NMR spectra of complexes **III**–**VIII**.

The downfield shift of the signal of the 1,5-cyclooctadiene methine proton suggests that its coordination with the metal is weakened. The same effect is characteristic of other rhodium(I) phosphine cyclooctadiene complexes [6–8]. The H^A and H^B methylene proton signals of 1,5-cyclooctadiene, rather than coming close together, as we observed earlier in the complexes $[(1,5\text{-COD})Rh(DIOP)]^+CF_3SO_3^-$ [7] and $[(1,5\text{-COD})Rh(PPh_3)_2]^+CF_3SO_3^-$ [8], shift in different directions, which implies enhanced nonequivalence of these protons. A plausible explanation for this phenomenon is that the phenyl groups remote from phosphorus in phosphines **I** and **II** exert different through-space effects on axial and equatorial protons of 1,5-cyclooctadiene.

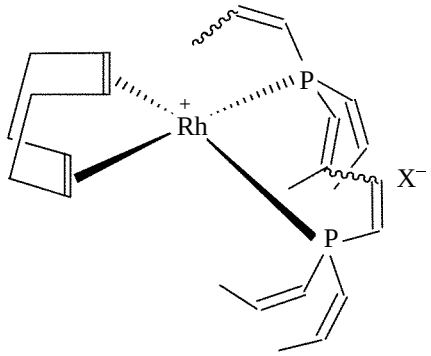
The different complex-forming powers of *E,Z,Z* and *Z,Z,Z* isomers **II** and **I** relate to their structural features. Molecular mechanics (MM2) and quantum-chemical (AM1) calculations give for *Z,Z,Z* isomer **I** a "*closed bud*" conformation (see Fig. 1a) in which the phosphorus lone electron pair is unavailable for complex formation. When one of the phenyl groups comes into the *trans* position, a "*half-open bud*" conformation is formed (see Fig. 1b), thus rendering the phosphorus lone pair more available for complex formation.

Table 1. Chemical shifts in the ^{1}H NMR spectra of 1,5-cyclooctadiene (δ, ppm) for complexes **III**–**VIII** (acetone-d_6)

Comp. no.	H^A in CH_2	H^B in CH_2	=CH
III	1.77	2.49	4.21
IV	1.77	2.50	4.16
V	1.45	2.94	5.01
VI	1.40	2.78	5.07
VII	1.47	2.92	5.06
VIII	1.40	2.77	4.93, 5.10
[a]	2.30	2.30	5.50

[a] Individual 1,5-cyclooctadiene.

The composition of complexes **V**–**VIII**, as given by the intensity ratio of the signals of coordinated 1,5-cyclooctadiene and phosphine **I** or **II**, corresponds to the formula [(1,5-COD)Rh(phosphine)$_2$]. The $^1J_{PRh}$ value and chemical shifts of coordinated 1,5-cyclooctadiene are close for those observed earlier for 1,5-cyclooctadiene cationic rhodium(I) complexes with other phosphines [6–8]. On this basis, complexes **VI** and **VIII** can be assigned a square-planar structure **A** with two tristyrylphosphine ligands in the *cis* position.



A

The probable structure of chloride complexes **V** and **VII** is a tetragonal pyramid with an apical chlorine atom.

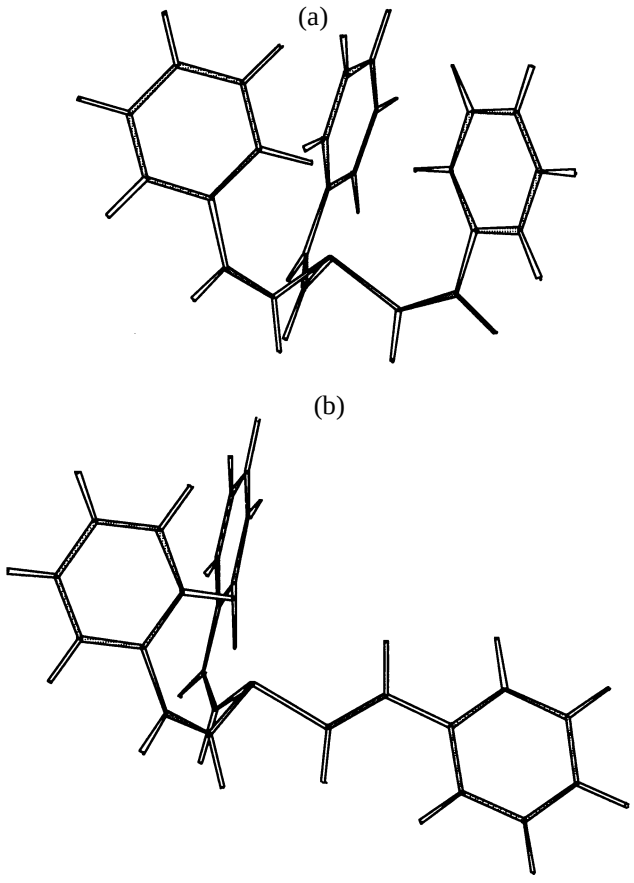
Analysis of the ^{1}H and ^{31}P NMR spectra (Table 2) allows certain conclusions as to the strength of bonding of phosphine ligands **I** and **II** with the metal atom in chloride and triflate rhodium complexes **V**–**VIII**. *A priori* various criteria can be used, namely, displacement of the α-and β-vinyl proton signals, changes in the $^2J_{H^\alpha P}$, $^3J_{H^\alpha P}$, or $^1J_{RhP}$ constants, as well as

Table 2. Chemical shifts (δ, ppm) and coupling constants (*J*, Hz) in phosphines **I** and **II**, complexes **V**–**VIII**, and tris[-(*Z*,*Z*,*Z*)-styryl]phosphine oxide (**IX**)

Parameter	**I**	**II**	**V**	**VI**	**VII**	**VIII**	**IX**
$\delta(=CH^{\alpha})$[a]	6.28	6.31[b]	6.35 (+0.07)	6.07 (–0.21)	6.12 (–0.19)[b]	6.08 (–0.23)[b]	5.95 (–0.33)
δ_P[a]	–60.9	–46.7	–28.9 (32)	–26.6 (34.4)	–15.0 (31.8)	–8.6 (38.1)	
$^2J_{PRh}$			142.6	143.3	142.6	137.4	
$^2J_{H^{\alpha}P}$	2.0	2.6	13.5	13.9	4.9	137.4	19.3
$^3J_{H^{\beta}P}$	23.4		33.3				40.4

[a] Parenthesized are displacements of signals relative to the signal of the corresponding free phosphine. [b] H^{α} signal in (*Z*)-P–CH=CHPh.

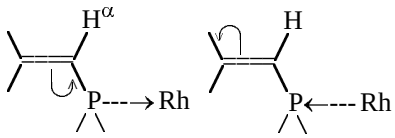
coordination-induced displacement of the ^{31}P NMR signal. The latter criterion seems to be preferred, since the position of the ^{31}P signal is directly related to the electron density on the phosphorus atom. The largest downfield shift is characteristic of complexes **VI** and **VIII**, which reflects stronger bonding of the ligand in the more ionic triflate complexes. Therewith, the shift for complex **VIII** is markedly larger than for complex **VI**, which is associated with the above-mentioned stronger complex-forming power of the conformationally more open *E*,*Z*,*Z* isomer **II**. The changes in the $^2J_{H^{\alpha}P}$ constants are generally consistent with these conclusions. The $^2J_{H^{\alpha}P}$ value that is known to increase on complex formation almost an order of magnitude with increasing coordination degree of phosphorus [9] and attains a maximum for the strongest complex **VIII**, approaching the respective value for tris[(*Z*,*Z*,*Z*)-styryl]phosphine oxide (**IX**).



Molecular structures of (a) tris[(*Z*,*Z*,*Z*)-styryl]phosphine (**I**) and (b) tris[(*E*,*Z*,*Z*)-styryl]phosphine (**II**).

Data for tris[(*E*,*Z*,*Z*)-styryl]phosphine oxide are lacking, but the $^2J_{H^{\alpha}P}$ value for structurally related diphenyl[(*E*)-styryl]phosphine oxide is close to that for compound **IX** (22.5 Hz) [10]. The $^2J_{H^{\alpha}P}$ value for complex **VII** fails to fully fit in the this series, comprising only double that for free phosphine.

The position of the H^{α} signal shows interesting trends on complex formation. Coordination of phosphines **I** and **II** with the triflate rhodium(I) complex produces an appreciable upfield shift (–0.2 ppm). The same shift is observed on coordination of phosphine **II** with the chloride complex, as well as on oxidation of phosphine **I** to phosphine oxide **IX**. With complex **V**, a small (+0.07 ppm) downfield shift is observed. The opposite coordination-induced shifts of the H^{α} signal may result from different contributions into bonding of two components: σ-donor (P→Rh) and back π-donation (P←Rh). The first type of bonding should shift the H^{α} signal upfield because of polarization of the double bond and is observed in complexes **VI**–**VIII**, as well as in going from phosphines to phosphine oxides [10]. In the weakest coordinated complex **V**, direct π-donation **B** is weaker and can be compensated for by back π-donation **C** that polarizes the double bond in the opposite direction and shifts the H^{α} signal downfield.



B **C**

The β-vinyl proton signal most frequently overlaps with aromatic proton signals, but in complex **V** it locates in a stronger field and makes it possible to reveal coordination-induced changes in the vicinal $^3J_{H^\beta P}$ constant. Like $^2J_{H^\alpha P}$, this coupling constant much increases (from 23 to 33 Hz) and approaches the $^3J_{H^\beta P}$ value for phosphine oxide.

Unlike 1,5-cyclooctadiene Rh(I) complexes with triphenylphosphine, whose 1,5-cyclooctadiene ligand is readily hydrogenated to cyclooctane [8], complexes **V**–**VIII** are inert toward molecular hydrogen: Its 40-min passing through solutions of the complexes gave no cyclooctane (by ^{1}H NMR data).

EXPERIMENTAL

The ^{1}H and ^{31}P NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 and 162 MHz, respectively) for solutions in anhydrous and degassed acetone-d_6, internal reference HMDS; the chemical shifts are given relative to TMS and 85% H_3PO_4, respectively. Chloride and triflate 1,5-cyclopentadiene rhodium(I) complexes **III** and **IV** were prepared as described in [11] and [7], respectively; moisture- and oxygen-free argon and hydrogen were used.

1,5-Cyclooctadienebis(bis(tristyryl)phosphine rhodium(I) complexes *in situ*. A solution of phosphine **I** or **II** was added to a solution of 0.05 mmol of complex **III** or **IV** is degassed acetone-d_6 (1.5 ml) under argon (P/Rh ratio 2 : 1). The resulting solution was transferred into an NMR ampule filled with argon, after which hydrogen was bubbled through it.

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