

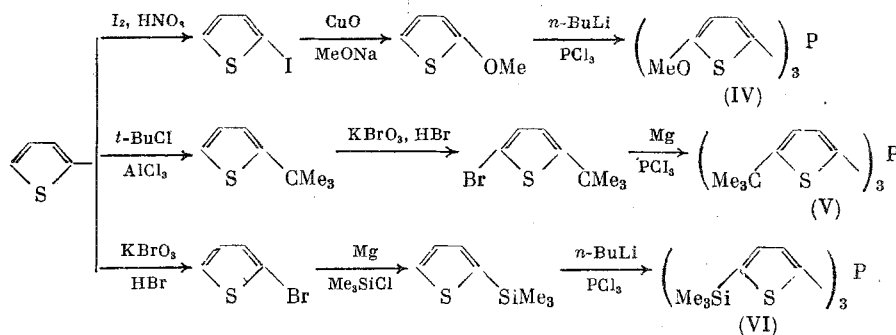
SYNTHESIS OF SOME TRITHIENYLPHOSPHINE-CARBONYL COMPLEXES
OF RHODIUM

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We previously demonstrated the practical applicability of the concept of isosterism to the search for new catalytic systems in the example case of the thiophene analog of Wilkinson's catalyst [1]. In this context it seemed to us that it would be useful to synthesize carbonyl hydride compounds of Rh containing trithioenylphosphine ligands and to investigate their catalytic activity, since the analogous complex hydridocarbonyltris(triphenylphosphine)-rhodium(I) displays high activity in homogeneous hydrogenation and isomerization reactions of unsaturated compounds [2]. The starting compounds for the synthesis of carbonyl hydride complexes of Rh were stable chlorocarbonyl complexes of Rh [3]. It is known that the catalytic activity of Rh complexes is dependent to a considerable extent on the electron density on the central metal atom, which, in turn, is determined by the donor-acceptor properties of the ligands surrounding the metal [4].

The main method for the synthesis of the trithienylphosphines was based on the use of organolithium or organomagnesium compounds. Tri(2-thienyl)phosphine (I) was obtained by reacting 2-thienylmagnesium bromide with PCl_3 [5]. Tri(3-thienyl)phosphine (II) and tri(5-methyl-2-thienyl)phosphine (III) were obtained by treating the corresponding organolithium derivatives with PCl_3 [6, 7]. In addition, the syntheses of tri(5-methoxy-2-thienyl)phosphine (IV), tri(5-tert-butyl-2-thienyl)phosphine (V), and tri(5-trimethylsilyl-2-thienyl)phosphine (VI) were carried out for the first time. Phosphines (IV) and (VI) were obtained by the metallation of 2-methoxythiophene and 2-trimethylsilylthiophene followed by the treatment of the Li derivatives with PCl_3 . The starting compound for the synthesis of phosphine V was 2-tert-butylthiophene, which was obtained according to the method in [8]. According to the GLC data, the sample of 2-tert-butylthiophene contained <3.5% 3-tert-butylthiophene; the further bromination of this mixture under the action of a KBrO_3 -HBr mixture results in the formation of a dibromo derivative from the β isomer and a monobromo derivative from the α isomer, which are easily separated by ordinary distillation. The treatment of the Grignard reagent obtained from 2-bromo-5-tert-butylthiophene with PCl_3 gives phosphine (V). The synthesis of phosphines (IV), (V), and (VI) is described in the following scheme:



The purity of phosphines (I)-(IV) was verified by gas-chromatographic-mass spectrometry; the values of the molecular ions (M^+) corresponded to the calculated. The structures of phosphines (IV)-(VI) were confirmed by data from elemental analysis, mass spectrometry, and PMR spectroscopy.

*Deceased.

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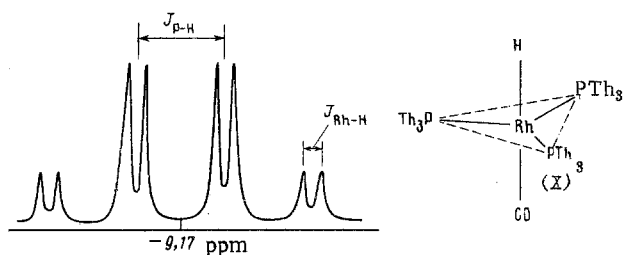


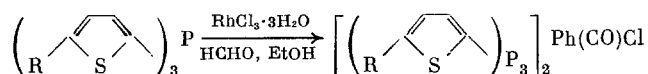
Fig. 1. PMR spectrum of hydridocarbonyl complex (X) (the hydride part of the spectrum). Here, Th stands for 2-thienyl.

TABLE 1. Chemical Shifts (δ , ± 0.01 ppm) and Spin-Spin Coupling Constants (J , ± 0.3 Hz) of 5-Substituted Tri(2-thienyl)phosphines

Compound	δ_{H^3}	δ_{H^4}	$\delta_{H_{sub}}$	$J_{H^3-H^4}$	J_{H^3-P}	J_{H^4-P}
(IV)	7,08	6,22	3,91	3,9	7,8	1,3
(V)	7,24	6,86	1,45	3,5	7,0	1,9
(VI)	7,49	7,29	0,39	3,4	5,9	1,2
(VII)	7,18	6,95	—	3,6	6,9	1,3

The PMR spectra of phosphines (IV)-(VI) and tri(5-chloro-2-thienyl)phosphine (VII), which we previously described in [9], consist of a spin system of the AMX type, where A and M are the protons of the aromatic heterocycle, and X is ^{31}P . The signals of the H^3 and H^4 protons were assigned on the basis of the effects of the substituents in position 5 of the thiophene ring. The spin-spin coupling constants $J_{H^3-H^4}$, J_{P-H^3} , and J_{P-H^4} were determined from the doublet of doublets in the spectra for the H^3 and H^4 protons. The data from the analysis of the PMR spectra are presented in Table 1.

The trans-chlorocarbonyl complexes of Rh were obtained according to [3]:



where R - H, Me, Me_3C , and Me_3Si .

The great differences between the solubilities of the complex compounds obtained should be noted. For example, trans-carbonylchlorobis[tri(2-thienyl)phosphine]rhodium(I) (VIII) is moderately soluble in benzene and insoluble in hexane, while trans-carbonylchlorobis[tri(5-tert-butyl-2-thienyl)phosphine]rhodium(I) (IX) is readily soluble in hexane.

The treatment of complex (VIII) with NaBH_4 in ethanol in the presence of phosphine (I) gives hydridocarbonyltris[tri(2-thienyl)phosphine]rhodium(I) (X). It could be postulated that the structure of the complex obtained is similar to the structure of hydridocarbonyltris(triphenylphosphine)rhodium(I), whose structure has been investigated by x-ray diffraction analysis and consists of a trigonal bipyramid with H and CO ligands in the apical positions [10]. This hypothesis was confirmed by PMR spectroscopy. In contrast to the triphenylphosphine analog, whose hydride H atom is manifested at -20°C in the form of a broadened singlet with a chemical shift of -9.9 ppm and at -30°C in the form of a doublet of quartets [11], the hydride H atom of complex X (in the form of a solution in CDCl_3) is manifested in the form of a doublet of quartets already at -20°C [$\delta(\text{H}) = -9.17$ ppm, the intensity ratio of the signals in each quartet is 1:3:3:1, $J_{P-H} = 15.9 \pm 0.6$, $J_{\text{Rh-H}} = 1.8 \pm 0.6$ Hz], attesting to the greater stereochemical rigidity of the structure of (X) in comparison to the triphenylphosphine analog. In addition, the equivalence of the P atoms and, consequently, the correctness of the assignment of the structure of complex (X), were confirmed.

Complex (X) displayed activity as a catalyst of the homogeneous hydrogenation of allylbenzene, although it was somewhat lower than that of the corresponding triphenylphosphine analog.

TABLE 2. Chlorocarbonyl Complexes of Rhodium

Com- pound	Decomposition temperature, °C	Empirical formula	Found						IR spec- trum, νCO, cm ⁻¹	UV spectrum (CH ₂ Cl ₂) λ _{max} , nm	lg ε
			Calculated, %								
			C	H	Cl	P	Rh	S			
(VIII)	>171 (from benzene)	C ₂₃ H ₁₈ ClOP ₂ RhS ₆	44.49 41.30	2.66 2.49	4.81 4.88	8.13 8.52	13.51 14.15	26.14 26.46	1974	247 281 sh 366	4.77 4.61 3.58
(IX)	>169 (from hexane)	C ₄₃ H ₆₆ ClOP ₂ RhS ₆	55.88 55.32	6.63 6.25	3.27 3.33	6.03 5.82	10.01 9.67	17.77 18.08	1982	249 276 366	4.62 4.61 3.43
(XI)	>181 (from benzene)	C ₂₃ H ₁₈ ClOP ₂ RhS ₆	41.82 41.30	2.32 2.49	4.74 4.88	8.36 8.52	13.89 14.15	25.75 26.46	1962	245 278 sh 365	4.59 4.24 3.42
(XII)	>160 (from hexane)	C ₃₁ H ₃₀ ClOP ₂ RhC ₆	45.30 45.90	3.75 3.73	4.30 4.37	7.26 7.64	12.06 12.68	23.30 23.71	1973	248 276 366	4.57 4.53 3.45
(XIII)*	mp 153-166 (from ethanol)	C ₄₃ H ₆₆ ClOP ₂ RhS ₆ Si ₆	44.48 44.59	5.91 5.74	3.10 3.06	5.33 5.35	8.86 8.88	16.81 16.61	1980	256 278 sh 365	4.67 4.60 3.46

*Si: found, %: 14.51; calculated, %: 14.38.

EXPERIMENTAL

The gas-chromatographic-mass spectrometry was carried out on a Varian MAT-111 instrument in a column measuring 150 × 0.2 cm with 3% OV-1 on Chromosorb W. The mass spectra were recorded on a Varian MAT-CH-6 spectrometer, and the GLC analysis of the mixtures of α - and β -tert-butylthiophenes was carried out on an LKhM-8MD chromatograph (with a capillary column measuring 50 m × 0.25 mm, Carbowax 40M/KF, and N₂ as the carrier gas). The PMR spectra were recorded on a Bruker WM-250 instrument with CDCl₃ as the solvent and TMS as an internal reference. The UV spectra were recorded on a Specord UV-VIS spectrophotometer with CH₂Cl₂ as the solvent, and the IR spectra were recorded on a Perkin-Elmer model 577 instrument with the use of samples molded with CsI. The melting points and the temperatures for the beginning of decomposition were determined on a Boetius hot-stage apparatus.

Tri(2-thienyl)phosphine was obtained according to the method in [5], tri(3-thienyl)phosphine was obtained according to the method in [6], and tri(5-methyl-2-thienyl)phosphine was obtained according to the method in [7].

Tri(5-methoxy-2-thienyl)phosphine (IV). A solution of 13.7 g of 2-methoxythiophene [12] in 70 ml of absolute ether was given an addition of 75 ml of a solution of n-BuLi in ether (with a concentration equal to 0.1056 g/ml) with stirring over the course of 15 min at 0°C in an inert atmosphere. After 1 h, the mixture was cooled to -60°C, a solution of 3 ml of PCl₃ in 6 ml of absolute ether was added, and the resultant mixture was held for 1 h at -20°C, cooled to -30°C, and decomposed by an aqueous solution of NH₄Cl. The organic layer was separated, the aqueous layer was extracted by three 30-ml portions of ether, the combined organic phases were washed with water and dried with MgSO₄, the ether was removed, and 3.11 g (28%) of (IV) with mp 59.0-61.5°C were recovered by chromatography of the residue in a column with SiO₂ (40-100 μ , the eluent was a 6:1 mixture of hexane and ether). Found, %: C 48.62, H 4.20, P 8.25, S 26.27. C₁₅H₁₅O₃PS₃. Calculated, %: C 48.64, H 4.08, P 8.36, S 25.96. M⁺ 370.

2-Trimethylsilylthiophene. A 6.05-g portion of metallic Mg in 95 ml of absolute ether was given an addition of a solution of 33.15 g of 2-bromothiophene [13] in 100 ml of absolute ether at a rate which provided for moderate boiling of the mixture. After completion of the reaction and cooling of the mixture by ice water, 28 g of freshly distilled Me₃SiCl were slowly added in a dropwise manner, the mixture obtained was held for 12 h at -20°C and decomposed by 5% aqueous HCl, the organic layer was separated, and the aqueous layer was extracted by two 50-ml portions of ether. The combined ethereal phases were washed by a solution of NaHCO₃ and water and dried with MgSO₄. Afterwards the ether was driven off, and 16.3 g (53%) of 2-trimethylsilylthiophene with bp 165-170°C were recovered by distillation of the residue. Repeated distillation gave a product with bp 165-168°C and n_D²² 1.4971 (compare [14]).

Tri(5-trimethylsilyl-2-thienyl)phosphine (VI). A solution of 26.14 g of 2-trimethylsilylthiophene in 75 ml of absolute ether was given an addition of 107 ml of a solution of n-BuLi in ether (with a concentration equal to 0.1 g/ml) with stirring at -20°C in an inert atmosphere, the mixture was heated for ~2 h with maintenance of the gentle boiling of the ether and cooled to -68°C, and a solution of 4.9 ml of PCl₃ in 20 ml of absolute ether was added dropwise at -68°C to -60°C. The reaction mass was held for 1 h at -20°C, heated to boiling, cooled to -30°C, and decomposed by an NH₄Cl-HCl mixture. The organic layer was separated, the aqueous layer was extracted by two 50-ml portions of ether, the combined organic phases were washed with a solution of NaHCO₃ and water and dried with MgSO₄, and the ether was driven off. The viscous residue was chromatographed in a column with SiO₂ (the eluent was a 7:1 mixture of hexane and ether). The eluates were combined and evaporated, and the residue was dried in a vacuum. This gave 13.44 g (48.4%) of (VI), mp 55-57°C. Found, %: C 51.30, H 6.82, P 6.07, S 18.95, Si 16.52. C₂₁H₃₃O₃Si₃. Calculated, %: C 50.76, H 6.69, P 6.23, S 19.36, Si 16.96. M⁺ 496. UV spectrum: λ_{\max} = 252 nm, log ϵ = 4.28; λ_{\max} = 285 nm, log ϵ = 4.16.

2-Tert-Butylthiophene was obtained according to the method in [8]; the content of the β isomer was <3.5% (GLC).

2-Bromo-5-tert-butylthiophene was obtained according to a method similar to that in [13]. The yield was 85.6%, and the bp was 102-103°C (14 mm Hg).

Tri(5-tert-butyl-2-thienyl)phosphine (V) was obtained according to a method similar to that in [6]. The yield was 68.3%, and the mp was 138.5-140.0°C (from ethanol). Found, %: C 64.28, H 7.43, P 7.23, S 20.60. $C_{24}H_{33}PS_3$. Calculated, %: C 64.24, H 7.41, P 6.90, S 21.44. UV spectrum: $\lambda_{max} = 246$ nm, $\log \epsilon = 4.10$; $\lambda_{max} = 285$ nm, $\log \epsilon = 4.00$. M^+ 448.

Complex Compounds of Rhodium. Trans-chlorocarbonylbis[tri(2-thienyl)phosphine]rhodium(I) (VIII), trans-chlorocarbonylbis[tri(5-tert-butyl-2-thienyl)phosphine]rhodium(I) (IX), trans-chlorocarbonylbis[tri(3-thienyl)phosphine]rhodium(I) (XI), trans-chlorocarbonylbis[tri(5-methyl-2-thienyl)phosphine]rhodium(I) (XII), and trans-chlorocarbonylbis[tri(5-trimethylsilyl-2-thienyl)phosphine]rhodium(I) (XIII) were obtained according to a method similar to that in [3] by the successive treatment of $RhCl_3 \cdot 3H_2O$ in ethanol with the corresponding phosphine and formaldehyde. The amorphous precipitate formed was filtered out, washed with water, ethanol, and a small quantity of ether, and dried, and the pure complex compounds were obtained by crystallization from a suitable solvent (Table 2).

Hydridocarbonyltris[tri(2-thienyl)phosphine]rhodium(I) was obtained according to a method similar to that in [3]. The yield was 42.3%, and the decomposition temperature was $>119^\circ C$ (from ether). Found, %: C 45.74, H 3.28, P 9.04, Rh 10.01. $C_{37}H_{28}OP_3RhS_9$. Calculated, %: C 45.67, H 2.90, P 9.55, Rh 10.58. IR spectrum (ν , cm^{-1}): 2014 (RhH), 1934 (CO).

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CONCLUSIONS

New carbonyl complexes of rhodium with trithienylphosphine ligands have been synthesized.

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