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Reactions of Rhodium Carbonyl Clusters with Heterobidentate Ligands. Synthesis and Structural Characterization of the $Rh_6(CO)_{15}[(C_6H_5)_2PC_6H_4N(CH_3)_2]$ and $\{Rh_6(CO)_{15}[(C_6H_5)_2PC_6H_4NH(CH_3)_2]\}[GaX_4]$ Cluster Compounds

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Abstract—The reaction of heterobidentate 4-(dimethylamino)phenyldiphenylphosphine with labile cluster $Rh_6(CO)_{15}(NCMe)$ yielding a new monosubstituted cluster $Rh_6(CO)_{15}(Ph_2PC_6H_4NMe_2)$ was described. The reactions of the resulting cluster with GaX_3 compounds were studied. The structure of all obtained compounds was completely characterized both in a solid phase and in a solution by X-ray diffraction analysis, mass spectrometry, and IR and polynuclear NMR spectroscopy.

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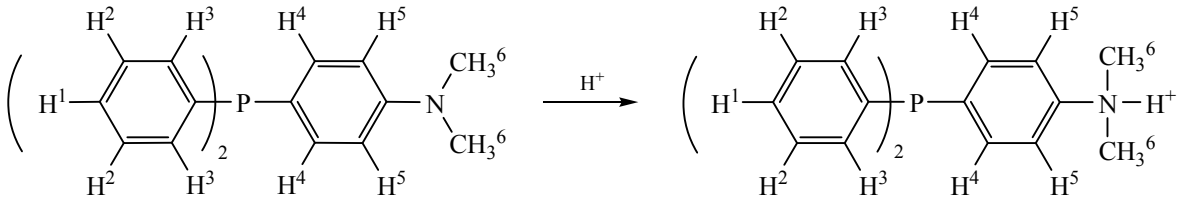
Rapid development of the chemistry of molecular ensembles and active search for paths of their effective synthesis resulted in the fact that the study of the reactivity of multifunctional ligands in relation to metal centers of various nature has become one of the most actual problems in coordination chemistry [1, 2]. The creation of a heterometallic bridged polynuclear complex (coordination heterometallic oligomer) requires a polyfunction bridging ligand with donor functions of different nature to be used. Donor properties of these functions, in turn, should correspond to acceptor properties of metal centres. Not only mononuclear complexes can be used as metal centers, but also polynuclear systems of various nuclearity, in particular carbonyl clusters of transition metals. 4-(Dimethylamino)phenyldiphenylphosphine is a potential bridging ligand carrying two functions, phosphine and amine differing in electronic and steric properties. In the present work the reactions of this multifunctional ligand with the labile cluster $Rh_6(CO)_{15}$·(NCMe) and compounds GaX_3 were studied.

Reaction of the $Ph_2PC_6H_4NMe_2$ compound with the labile $Rh_6(CO)_{15}(NCMe)$ cluster. The heterobidentate compound $Ph_2PC_6H_4NMe_2$ reacts with the cluster $Rh_6(CO)_{15}(NCMe)$ replacing the labile acetonitrile ligand and forming the cluster $Rh_6(CO)_{15}$·$(Ph_2PC_6H_4NMe_2)$ (**I**). The heteroligand in compound **I** is coordinated on the metal skeleton through the phosphorus atom in a terminal position, the amine part



of the ligand remaining free. Thus, cluster **I** as a whole belongs to the well-known family of carbonyl-phosphine rhodium clusters $Rh_6(CO)_{15}(PR_3)$, the synthesis and properties of which are described in the literature [3, 4].

Compound **I** is moderately stable in air and readily dissolved in polar organic solvents such as CH_2Cl_2 and THF. Its solid-phase structure was determined by the X-Ray analysis (Fig. 1); the crystallographic data and certain structural parameters are given in Tables 1 and 2, respectively.

Six rhodium atoms of cluster **I** form an octahedral metal skeleton, which is surrounded by eleven terminal and by four μ_3-bridging carbonyl ligands. The two-electron donor heteroligand $Ph_2PC_6H_4NMe_2$ is coordinated through the phosphorus atom on the rhodium atom in the monodentate mode in a terminal position. Thus, cluster **I** has seven skeletal electronic pairs corresponding to the *closo*-octahedral configuration of the cluster skeleton surrounded by 16 ligands and complies with both the molecular structure of compound **I** and the structures of all cluster complexes $Rh_6(CO)_{15}(PR_3)$ described earlier [3].

Structural parameters of the $Ph_2PC_6H_4NMe_2$ ligand in cluster **I** slightly differ from the parameters of the free compound [5]. All P–C bonds are moderately elongated, their lengths fall into the range from 1.824(10) up to 1.842(11) Å in the case of complex **I**. In the amine part of the molecule no visible changes occur, N–C bond lengths correspond to the bond lengths in the free phosphine, and the $C_6H_4NMe_2$ fragment retains a configuration close to planar. Similar changes of some structural parameters of the $Ph_2PC_6H_4NMe_2$ ligand after coordination on a metal center were described for various gold and silver complexes [6, 7].

The P–Rh distance in **I** is 2.373(3) Å that fits well to the value found in all other $Rh_6(CO)_{15}(PR_3)$ derivatives. The insertion of $Ph_2PC_6H_4NMe_2$ in the coordination environment of Rh_6 results in a distortion of the octahedral cluster skeleton as compared with $Rh_6(CO)_{16}$. The range of values of Rh-Rh bond lengths increases, they vary from 2.7268(16) up to 2.8491(16) Å, the metal-metal distance in immediate proximity of the site of the heteroligand coordination (the average value of 2.8251 Å) being longer than remaining distances (the average value of 2.7763 Å) (Table 2). The phenomenon of non-uniform distortion of the Rh_6 skeleton owing to the coordination of a σ-donor and π-acceptor heteroligand is well-known and is described in detail for various substituted derivates of the $Rh_6(CO)_{16}$ cluster [3, 8–10].

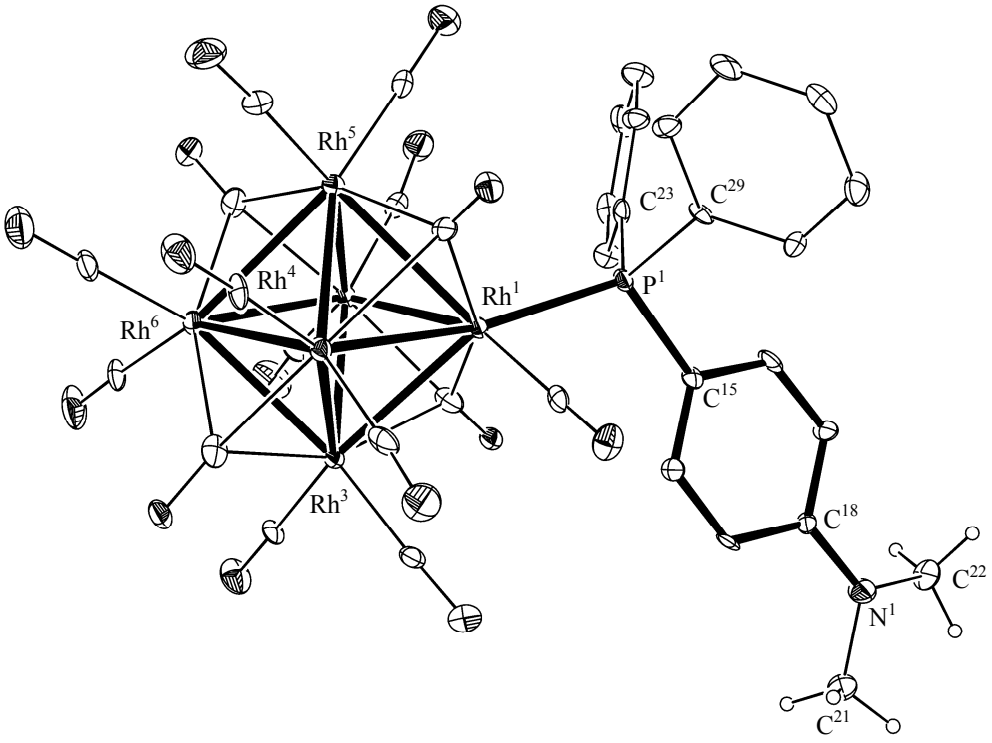


Fig. 1. ORTEP view of the cluster **I** molecule. Protons of phenyl group are omitted.

Table 1. Crystallographic data for compounds **I–III**

Parameter	N		
	I	**II**	**III**
Formula	$C_{35}H_{20}NO_{15}PRh_6$	$C_{35}H_{21}Cl_4GaNO_{15}PRh_6 \cdot 4.5\ C_6H_6$	$C_{35}H_{21}Br_4GaNO_{15}PRh_6 \cdot 0.5\ C_6H_6$
M	1342.95	1906.9	1772.4
Temperature, K	200	200	200
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, E	982.9(2)	966.2(2)	2793.7(6)
b, E	1229.1(3)	1681.4(3)	1021.0(2)
c, E	1773.7(4)	2204.6(4)	1871.9(4)
α, deg	83.79(3)	80.78(3)	
β, deg	80.83(3)	89.95(3)	103.05(3)
γ, deg	76.99(3)	88.07(3)	
V, Å^3	2055.3(7)	3533(1)	5201(2)
Number of formula units	2	2	4
Calculated density, g cm^{-3}	2.170	1.792	2.263
Extinction coefficient, mm^{-1}	2.459	1.976	5.530
2θ range, deg	3 – 48	4 – 48	4 – 48
Index range	±10±14±20	±10±19±25	±31±11±21
Reflections, collected	13067	22533	32641
Reflections, unique	6026	10358	8198
Reflections, number with $I > 2\sigma(I)$	2941	7015	4024
R factor[a]	$R_1 = 0.040$, $wR_2 = 0.079$	$R_1 = 0.032$, $wR_2 = 0.071$	$R_1 = 0.054$, $wR_2 = 0.123$
Residual electronic density, e Å^{-3}	–1.07/0.88	–0.56/0.64	–1.17/1.25

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR_2 = \{\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$.

The data of IR and NMR spectroscopy for compound **I** confirm the retention of the solid-phase structure in solution. Frequencies and relative intensities of bands in the region of carbonyl ligand vibrations in the IR spectrum exactly correspond to the data obtained earlier for the $Rh_6(CO)_{15}(PR_3)$ clusters [3, 4]. The coordination of the heteroligand to the rhodium atom in cluster **I** through the phosphorus atom is confirmed by the downfield shift of the P atom signal in the ^{31}P NMR spectrum to 23.9 ppm, which corresponds to the region of chemical shifts characteristic of mono- and disubstituted

$Rh_6(CO)_{16-x}P_x$ clusters [3, 4, 11–22]. The signal of the ^{31}P atom appears at room temperature as a well resolved doublet of quintets with the coupling constants $^1J_{P-Rh} = 132.6$ and $^2J_{P-Rh} = 1.7$ Hz. A similar structure of signals is characteristic of $Rh_6(CO)_{15}(PAr_3)$ clusters and is an indirect prove of the fact that the coordination environment in cluster **I** is stereochemically nonrigid at room temperature [4].

The assignments of signals in the ^1H NMR spectrum of compound **I** was based on the ^1H–^1H COSY (Fig. 2) and $^1H\{^{31}P\}$ spectral (Fig. 3) data. The presence of spin–spin coupling visualized by cross peaks in the COSY spectrum and the change in the shapes of signals on suppression of splitting on phosphorus have allowed us to select the signals corresponding to various protons of the aromatic part of the $Ph_2PC_6H_4NMe_2$ heteroligand. The number of signals in the ^1H NMR spectrum of compound **I**, their chemical shifts, relative intensity, and multiplicity confirm the fact that the structure of the fragment $Ph_2PC_6H_4NMe_2$ does not change on the coordination on the metal skeleton as compared with the free compound. The singlets at 2.28 ppm in C_6D_6 belong to the methyl protons of the $N(CH_3)_2$ group. In the

Table 2. Selected bond lengths (Å) of clusters **I–III**

Parameter	N		
	I	**II**	**III**
Rh−Rh for metal atoms bound with heteroligand	Rh^1–Rh^3 2.7971(15) Rh^1–Rh^2 2.8198(15) Rh^1–Rh^4 2.8346(17) Rh^1–Rh^5 2.8491(16) Average value 2.8251 (0.0192)	Rh^1–Rh^2 2.8138(8) Rh^1–Rh^3 2.8201(10) Rh^1–Rh^4 2.8316(9) Rh^1–Rh^5 2.7882(11) 2.8134 (0.0159)	Rh^1–Rh^5 2.7802(17) Rh^1–Rh^4 2.8163(16) Rh^1–Rh^2 2.8188(18) Rh^1–Rh^6 2.8330(17) 2.8121 (0.0195)
Average Rh−Rh length for metal atoms not bound to heteroligand	Rh^2–Rh^5 2.7865(15) Rh^4–Rh^5 2.7268(16) Rh^3–Rh^4 2.8042(14) Rh^2–Rh^3 2.7509(16) Rh^2–Rh^6 2.7737(17) Rh^3–Rh^6 2.7636(16) Rh^4–Rh^6 2.8004(15) Rh^5–Rh^6 2.8043(16) Average value 2.7763 (0.0262)	Rh^2–Rh^6 2.7668(10) Rh^2–Rh^5 2.7723(10) Rh^2–Rh^3 2.7775(12) Rh^3–Rh^4 2.7606(10) Rh^3–Rh^6 2.8018(11) Rh^4–Rh^5 2.7773(11) Rh^4–Rh^6 2.7843(9) Rh^5–Rh^6 2.7815(10) 2.7778 (0.0116)	Rh^2–Rh^5 2.7603(17) Rh^2–Rh^3 2.7732(18) Rh^2–Rh^6 2.7856(18) Rh^3–Rh^4 2.7816(18) Rh^3–Rh^5 2.7887(18) Rh^3–Rh^6 2.8026(18) Rh^4–Rh^6 2.7383(17) Rh^4–Rh^5 2.7773(18) 2.7759 (0.0183)
Rh−P	Rh^1–P^1 2.373(3)	Rh^1–P^8 2.3666(15)	Rh^1–P^1 2.368(4)
N−C_6H_4	N^1–C^{18} 1.374(13)	N^1–C^{16} 1.514(7)	N^1–C^{19} 1.50(2)
N−CH_3	N^1–C^{22} 1.445(13) N^1–C^{21} 1.474(14)	N^1–C^{19} 1.504(7) N^1–C^{20} 1.516(8)	N^1–C^{23} 1.46(2) N^1–C^{24} 1.55(2)
Ga–X, average value	–	2.1904 (0.0247)	2.3410 (0.0181)

downfield part of the spectrum there are two multiplets (at 6.33 and 7.64 ppm) corresponding to the H^5 and H^4 protons of the phenyl spacer and three multiplets (at 6.97, 7.06, and 7.84 ppm) corresponding to the H^1, H^2, and H^3 protons of the phenyl groups, respectively. The number of signals in the ^{1}H NMR spectrum of compound **I**, their relative intensity and multiplicity are retained in the spectra obtained for solutions in $CDCl_3$, but in this case a significant change of chemical shifts is observed (a singlet of methyl protons at 3.02 ppm and multiples of protons of aromatic rings at 6.69, 7.42, and 7.62 ppm).

Reactions of cluster I with GaX_3 compounds. Reactions of tertiary amines NR_3 with compounds GaX_3 result in the formation of stable coordination compounds $[GaX_3(NR_3)]$ [23, 24], however the reaction of cluster **I** with a small excess of a GaX_3 compound (X = Cl, Br, I) in toluene does not result in the formation of significant amounts of a heterometallic bridging complex $[Rh_6(CO)_{15}(Ph_2PC_6H_4{\cdot}NMe_2)GaX_3]$. We managed to record signals of the $[Rh_6(CO)_{15}(Ph_2PC_6H_4NMe_2)GaX_3]$ molecular ions in the FAB^+ mass spectra of the reaction mixture, but the main result of the reaction is the formation of the ion pairs $[Rh_6(CO)_{15}(Ph_2PC_6H_4NMe_2H)][GaX_4]$ [X = Cl (**II**), Br (**III**), I (**IV**)], in which the amine part of a ligand is protonated. The formation of free protons owing to the reactions of GaX_3 with an aromatic solvent, in particular, with toluene, in the systems containing gallium halides is described in the literature [25–27]. These processes have a complicated mechanism and result in the formation of $[ArH][GaX_4]$ ion pairs. Probably the presence of a rhodium cluster in the reaction mixture promotes this process, and a high susceptibility of amines toward protonation leads to the formation of compounds **II–IV**.

Compounds **II–IV** are moderately resistant to air oxygen and are readily soluble in polar organic solvents (CH_2Cl_2 and THF). The solubility in benzene, toluene, and chloroform noticeably decreases from compound **II** to **IV**. The solid-phase structure of complexes **II** and **III** was determined by X-ray analysis (Figs. 4 and 5); the crystallographic data and certain structural parameters are given in Tables 1 and 2, respectively.

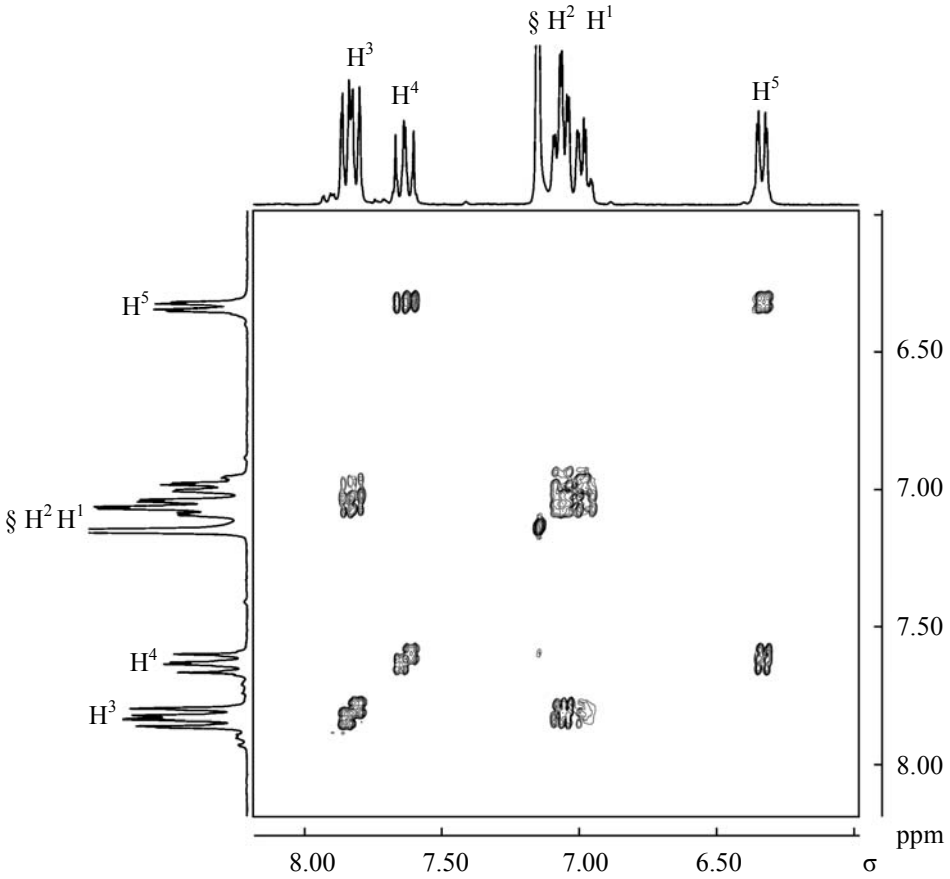


Fig. 2. ^{1}H–^{1}H NMR spectrum of compound **I** (range of phenyl protons), C_6D_6, 293 K. Residual solvent signals are marked by the sign §. Assignment of the signals is given according to numbering of atom in Fig. 1.

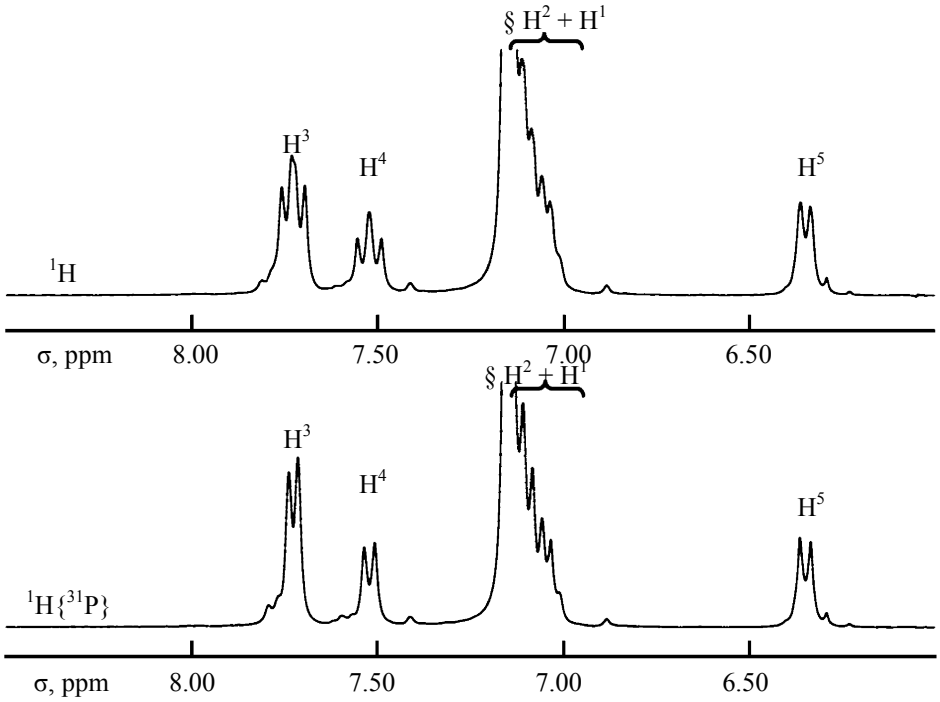


Fig. 3. ^{1}H and ^{1}H{^{31}P} NMR spectra of compound **I** (range of phenyl protons), C_6D_6 + CCl_4, 293 K. Residual solvent signals are marked by the sign §.

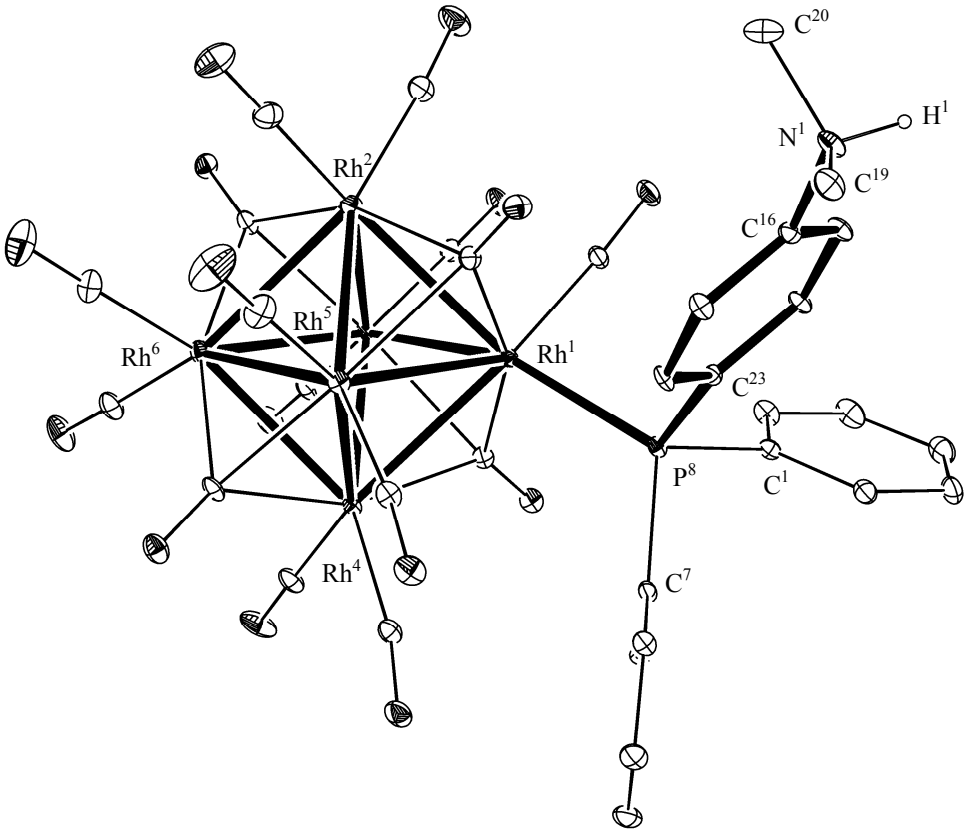


Fig. 4. ORTEP view of cluster **II**. Protons of phenyl and methyl groups and the $[GaCl_4]^-$ anion are omitted.

The protonation of the amine part of the heteroligand in compound **I** does not result in noticeable changes in the solid-phase structure. The N–C bonds are elongated, and the fragment $\{Ph_2PC_6H_4NMe_2H^+\}$ takes a configuration close to tetrahedral (Table 2). The attachment of a proton does not change donor properties of the fragment $Ph_2PC_6H_4NMe_2$ in relation to the cluster skeleton, which also has seven skeletal electronic pairs in complexes **II** and **III** and corresponds to the *closo* octahedral configuration of the cluster skeleton carrying 16 ligands. Acceptor properties of the fragment $Ph_2PC_6H_4NMe_2H^+$ correspond to the deprotonated form. Owing to the coordination of the σ-donor and π-acceptor heteroligand, a non-uniform distortion of the Rh_6 skeleton takes place in clusters **II** and **III**, as well as in compound **I** (Table 2). The arrangements of the $[Rh_6(CO)_{15}(Ph_2PC_6H_4{\cdot}NMe_2H^+)]$ cation and the $[GaX_4]^-$ anion relative to each other for solid-phase complexes **II** and **III** strongly differ. The NH–X distance in compound **II** is longer than 11 Å, whereas in complex **III** this value varies within the limits from 2.568 up to 6.172 Å. Most likely, such arrangement of counterions is caused by special features of the solid-phase packaging.

We were not able to obtain crystals of compound **IV** suitable for the X-ray crystal analysis, and its structure was determined on the basis of the IR and NMR spectra and the FAB^+ mass-spectrometry data. The spectroscopic data for complexes **II–IV** are rather similar to each other. Frequencies and relative intensities of bands in the region of carbonyl ligand vibrations in the IR spectra of compounds **II–IV** exactly correspond to the data found for cluster **I**. It means that the symmetry of the carbonyl environment is the same for all the compounds. The chemical shift and the multiplicity of the P atom signal in the ^{31}P NMR spectra of compounds **II–IV**, and also the coupling constants are practically identical to those of cluster **I**, which means that the heteroligand is coordinated to the rhodium atom through the phosphorus atom, and the properties of the phosphine part have not undergone changes owing to the protonation of the amine part.

The number of ^1H NMR signals of compounds **II–IV**, their chemical shifts, relative intensities, and multiplicity confirm the fact that the amine part of the heteroligand is not deprotonated in solution. The signal

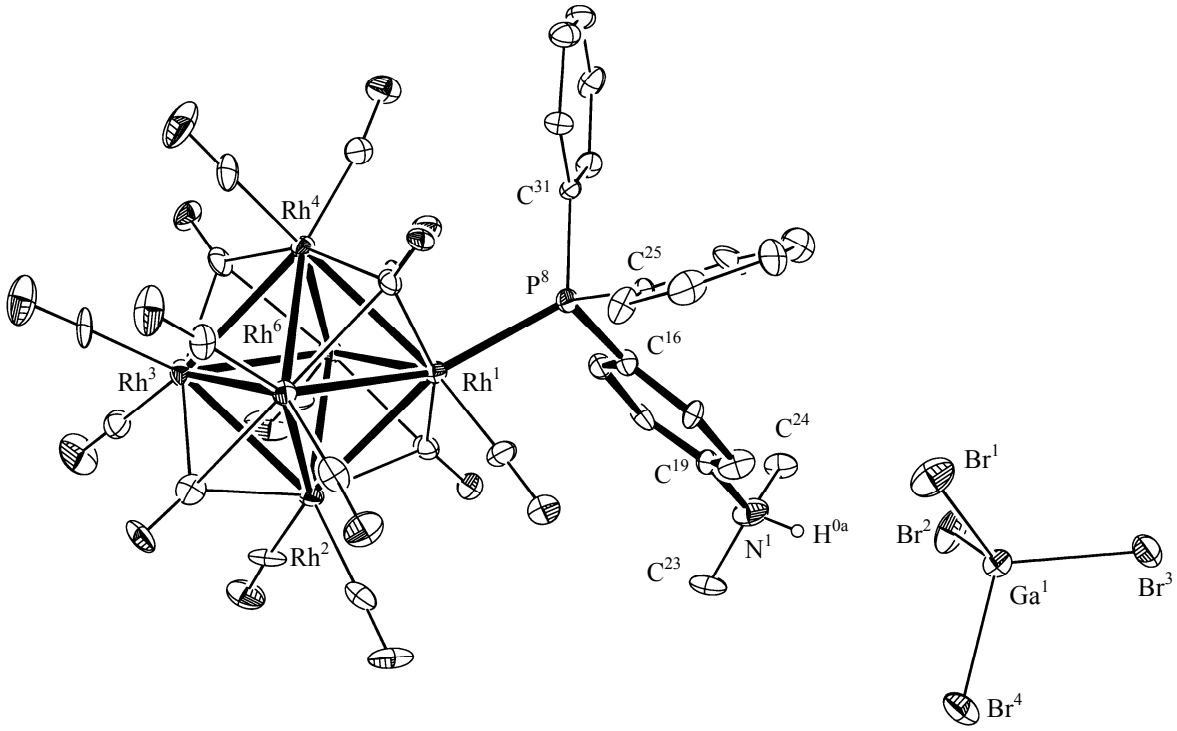


Fig. 5. ORTEP view of cluster **III**. Protons of phenyl and methyl groups are omitted.

corresponding to the N–H proton in the ^{1}H NMR spectra of complexes **II–IV** appears in the weak field, which agrees with the published data for protonated amines, in particular, for N,N-dimethylaniline [28]. The chemical shifts and multiplicity of the signals corresponding to the H^1, H^2, and H^3 protons of phenyl groups are practically identical to those observed in the spectrum of compound **I**. The protonation of the $Ph_2PC_6H_4NMe_2$ fragment results in a drastically low-field shift of the H^5 and H^4 proton signals of the phenylene spacer as compared to complex **I**. The exact chemical shift value depends on the nature of a solvent and a $[GaX_4]^-$ anion. The signal of the H^6 protons of methyl groups in complexes **II–IV** is shifted into the weak field compared to cluster **I**, and also it is split into two separate singlets corresponding to two methyl groups. This phenomenon seems to be caused by a weak interaction of the protonated amine part of the ligand with the $[GaX_4]^-$ anion, which is sufficiently close to block the free rotation around of the C–N bond.

EXPERIMENTAL

All operations were carried out in a dry argon atmosphere using standard Schlenk technique or in a Glove-Box Braun Inertgas-Systeme GmbH, Labmaster 130. All solvents, including deuterated solvents for NMR experiments, were distilled in an argon flow above appropriate drying agents and then held no less than a weak above molecular sieves A4. The initial cluster $Rh_6(CO)_{15}(MeCN)$ was obtained according to the published procedure [29]. 4-(Dimethylamino)-phenyldiphenylphosphine (Aldrich, CAS 739-58-2) was recrystallized from anhydrous benzene directly before use. Gallium halides GaX_3 (Aldrich; X = Cl, CAS 13450-90-3; X = Br, CAS 13450-88-9; X = I, CAS 13450-91-4) were sublimated directly before use and sealed in glass capillaries in a Glove-Box.

Infrared spectra were recorded on Perkin Elmer 16PC and BIORAD Excalibur FTS 3000 FT-IR spectrometers. ^{1}H, ^{1}H{^{31}P}, ^{1}H–^{1}H COSY, and ^{31}P{^{1}H} NMR spectra were recorded in C_6D_6 and $CDCl_3$ using Bruker DPX-300 and AV400 instruments. Chemical shifts were referenced to residual signals of solvents in ^{1}H NMR spectra; 85% H_3PO_4 aqueous solution was used as the standard for ^{31}P spectra.

We used aluminum plates covered by a 0.5 mm layer of silica gel 60 (Merck) for the thin-layer analytical chromatography (TLC), and silica gel 5/40 mesh (Merck) for preparative column chromatography.

The FAB^+ mass-spectra were recorded on a JEOL JMS-700 instrument (Institute of organic chemistry, University of Heidelberg), applying 1-nitro-2-(octyl-oxy)benzene as a matrix.

X-ray crystal analysis of compounds I–III. Crystals suitable in quality were mounted with a perfluorinated polyether oil on the tip of a glass fibre and cooled immediately on a goniometer head. A three-dimensional set of diffraction data was obtained on a STOE IPDS I diffractometer (MoK_α radiation). Structures were solved and refined with the Bruker AXS SHELXTL 5.1 program package. All hydrogen atoms were arranged in calculated positions. The crystallographic data are summarized in Table 1; the structures are registered at the Cambridge Crystallographic Data Center (CCDC 725043, 725044, 725045 for compounds **I–III**, respectively).

$Rh_6(CO)_{15}(Ph_2PC_6H_4NMe_2)$ (I). $Rh_6(CO)_{15}(NCMe)$ (75 mg) was dissolved in 15 ml of CH_2Cl_2, and solid $Ph_2PC_6H_4NMe_2$ (23 mg) was added under vigorous stirring. The reaction was completed within few minutes, and the reaction mixture color changed from brown to dark red. The solvent was removed in vacuo of an oil pump, an oily brown residue was dissolved in 2 ml of CH_2Cl_2, diluted with 2 ml of hexane, and transferred to a chromatographic column. The reaction product (a red-brown band) was isolated by slow eluating with a CH_2Cl_2/hexane (1/2 by volume) mixture. In addition to the reaction product small amounts of the $Rh_6(CO)_{16}$ cluster and a bright red non-identified compound were eluted from the column. After removing solvents the yield of compound **I** was 73 mg (0.054 mmol, 78%). Red-brown crystalline powder. IR spectrum, (CH_2Cl_2), ν(CO), cm^{-1}: 2097 w, 2061 s, 2032 w, 1798 br.m. ^1H NMR spectrum (C_6D_6, 293 K), δ, ppm: 2.28 s (6H, H^6), 6.33 m (2H, H^5), 6.97 m (2H, H^1), 7.06 m (4H, H^2), 7.64 m (2H, H^4), 7.84 m (4H, H^3); ($CDCl_3$, 293 K), δ, ppm: 3.02 s (6H, H^6), 6.69 m (2H, H^5), 7.42 m (8H, $H^{1–4}$), 7.62 m (4H, $H^{1–4}$); (C_6D_6 + CCl_4, 293 K), δ, ppm: 2.40 s (6H, H^6), 6.36 d (2H, H^5), 7.07 m (6H, $H^{1–2}$), 7.53 m (2H, H^4), 7.74 m (4H, H^3). $^1H\{^{31}P\}$ NMR spectrum (C_6D_6 + CCl_4, 293 K), δ, ppm: 2.40 s (6H, H^6), 6.36 d (2H, H^5), 7.07 m (6H, $H^{1–2}$), 7.53 d (2H, H^4), 7.74 d (4H, H^3). $^{31}P\{^1H\}$ NMR spectrum (C_6D_6, 293 K), δ, ppm: 24.0 d.q ($^1J_{PRh}$ 132.6, $^2J_{PRh}$ 1.7 Hz); ($CDCl_3$, 293 K), δ, ppm: 23.9 dq ($^1J_{PRh}$ 132.6, $^2J_{PRh}$ 1.7 Hz). FAB^+ mass spectrum (*m/z*): 1343 $[M]^+$. $C_{35}H_{20}N_1O_{15}P_1Rh_6$. Calculated *M* 1342. Signals of sequential loss of carbonyl ligands [$M^+ - n$CO], n = 1–15 were also fixed.

Crystals of compound **I** suitable for the X-ray analysis were grown from a CH_2Cl_2-cyclohexane mixture at 4°C by the method of slow diffusion in a closed system.

$\{Rh_6(CO)_{15}[Ph_2P(C_6H_4NH(CH_3)_2)]\}[GaX_4]$ (II–IV). In a typical experiment a solution of cluster **I** (73 mg) in 15 ml of toluene was cooled to −78°C, then a capillary with solid GaX_3 (0.075–0.085 mmol) was broken immediately in a reaction mixture under active stirring. The reaction mixture was cooled for about 2 h more, then slowly heated up to room temperature. On termination of the reaction a solvent and all volatile components were removed in vacuo of an oil pump, and a resulting brown oily substance was washed out by cyclohexane and dried *in vacuo*. The resulting material was treated by small portions of C_6D_6 to obtain a transparent red-brown solution (except for compound **IV**). The residue after extraction by deuterobenzene was dissolved in 1 ml of $CDCl_3$. Solubility of the obtained compounds decreases from **II** to **IV**. After removal of solvents, compounds **II–IV** were isolated as brown crystalline powders. Admixtures of $[ArH][GaX_4]$ have not allowed us to estimate accurately yields of compounds **II–IV**, the approximate estimate is 70–80% in relation to cluster **I**.

$\{Rh_6(CO)_{15}[Ph_2P(C_6H_4NH(CH_3)_2)]\}[GaCl_4]$ (II). IR spectrum (C_6H_6), ν(CO), cm^{-1}: 2099 w, 2064 s, 2034 w, 1798 br.m; (CH_2Cl_2), ν(CO), cm^{-1}: 2100 w, 2065 s, 2034 w, 1794 brm. ^1H NMR spectrum (C_6D_6, 293 K), δ, ppm: 2.23 s (3H, H^6), 2.24 s (3H, H^6), 6.75 m (2H, H^5), 7.01 m (2H, H^1), 7.13 m (4H, H^2), 7.72 m (4H, H^3), 7.79 m (3H, H^4 + NH); ($CDCl_3$, 293 K), δ, ppm: 3.48 s (3H, H^6), 3.50 s (3H, H^6), 7.52 m (6H, $H^{1–3,5}$), 7.64 m (6H, $H^{1–3,5}$), 7.89 m (2H, H^4), 8.74 s (1H, NH). $^{31}P\{^1H\}$ NMR spectrum (C_6D_6, 293 K), δ, ppm: 24.8 d.q ($^1J_{PRh}$ 137.4, $^2J_{PRh}$ 1.9 Hz). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, 293 K), δ, ppm: 24.8 dq ($^1J_{PRh}$ 137.9, $^2J_{PRh}$ 1.9 Hz). FAB^+ mass spectrum, (*m/z*) 1344 $[M]^+$. $C_{35}H_{21}N_1O_{15}P_1Rh_6$, 1343 $[M^+ - H]$.

Crystals of compound **II** suitable for X-ray analysis were grown from a saturated C_6D_6 solution in a closed system at room temperature.

$\{Rh_6(CO)_{15}[Ph_2P(C_6H_4NH(CH_3)_2)]\}[GaBr_4]$ (III). IR spectrum (C_6H_6), ν(CO), cm^{-1}: 2099 w, 2064 s, 2034 w, 1798 brm; (CH_2Cl_2), ν(CO), cm^{-1}: 2100 w, 2065 s, 2033 w, 1794 brm. ^1H NMR spectrum (C_6D_6, 293 K), δ, ppm: 2.25 s (3H, H^6), 2.26 s (3H, H^6), 6.80 m (2H, H^5), 7.01 m (2H, H^1), 7.12 m (4H, H^2), 7.72 m (4H, H^3), 7.80 m (2H, H^4), 7.90 s (1H, NH); ($CDCl_3$,

293 K), δ, ppm: 3.47 s (3H, H^6), 3.48 s (3H, H^6), 7.56 m (6H, $H^{1-3,5}$), 7.67 m (6H, $H^{1-3,5}$), 7.94 m (2H, H^4), 8.83 s (1H, NH). $^{31}P\{^1H\}$ NMR spectrum (C_6D_6, 293 K), δ, ppm: 24.8 d.q ($^1J_{PRh}$ 137.3, $^2J_{PRh}$ 1.8 Hz); ($CDCl_3$, 293 K), δ, ppm: 24.9 dq ($^1J_{PRh}$ 137.9, $^2J_{PRh}$ 1.8 Hz). FAB^+ mass spectrum (*m/z*) 1344 $[M]^+$. $C_{35}H_{21}N_1O_{15}P_1Rh_6$, 1343 $[M^+ - H]$.

Crystals of complex **III** suitable for X-ray analysis were grown from a saturated C_6D_6 solution in a closed system at room temperature.

$\{Rh_6(CO)_{15}[Ph_2P(C_6H_4NH(CH_3)_2)]\}[GaI_4]$ IV. IR spectrum (CH_2Cl_2), ν(CO), cm^{-1}: 2100w, 2066 s, 2035 w, 2025 sh, 1795 brm. ^1H NMR spectrum ($CDCl_3$, 293 K), δ, ppm: 3.55 s (3H, H^6), 3.56 s (3H, H^6), 7.52 m (6H, H^{1-3}), 7.63 m (4H, H^{1-3}), 7.76 m (2H, H^5), 7.91 m (2H, H^4), 9.25 s (1H, NH). $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, 293 K), δ, ppm: 24.8 dq ($^1J_{PRh}$ 137.9, $^2J_{PRh}$ 2.0 Hz). FAB^+ mass spectrum, (*m/z*) 1344 $[M]^+$. $C_{35}H_{21}N_1O_{15}P_1Rh_6$. 1343 $[M^+ - H]$.

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