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Reactions of Carbonyl Clusters with Heterobidentate Ligands. Synthesis and Structural Characterization of $H_4Ru_4(CO)_{10}[k^2(P,S)\text{-}Ph_2P(2\text{-}CH_3SC_6H_4)]$ and $Rh_6(CO)_{14}[k^2(P,S)\text{-}Ph_2P(2\text{-}CH_3SC_6H_4)]$ Clusters

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Abstract — Two new disubstituted derivatives of the clusters $Rh_6(CO)_{16}$ and $H_4Ru_4(CO)_{12}$ with the heterobidentate ligand $[Ph_2P(2\text{-}CH_3SC_6H_4)]$ were synthesized. Structures of these compounds were completely characterized both in solid phase and solution. The $H_4Ru_4(CO)_{10}[k^2(P,S)\text{-}Ph_2P(2\text{-}CH_3SC_6H_4)]$ cluster is an example of a structure, in which a chelating coordination of a heterobidentate ligand results in the occurrence of a center of asymmetry associated with the substituted metal atom. This type of polynuclear complexes is of interest for obtaining essentially new catalysts for asymmetric synthesis on the basis of cluster compounds.

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In the last few years functionalized phosphines find increasing application in coordination chemistry, namely, in homogeneous catalysis including asymmetric catalysis [1, 2]. Study of coordination modes of the various nature complexes of these ligands is of significant theoretical and practical interest, as the behavior of the ligands in the coordination sphere of potential catalyst determines both its activity and selectivity. Among the polynuclear carbonyl complexes the clusters $H_4Ru_4(CO)_{12}$ and $Rh_6(CO)_{16}$ and their derivatives are the most widely used as catalysts of practically important hydrogenation [3–6] and hydroformylation [7–9] reactions. In this communication we report on the results of study coordinating properties of the $[Ph_2P(2\text{-}MeSC_6H_4)]$ phosphine ligand in its reactions with the carbonyl clusters $H_4Ru_4(CO)_{12}$ and $Rh_6(CO)_{16}$.

In the presence of trimethylamine *N*-oxide both the clusters react with the ligand to form disubstituted derivatives: $H_4Ru_4(CO)_{10}[k^2(P,S)\text{-}Ph_2P(2\text{-}MeSC_6H_4)]$–$[k^2(P,S)\text{-}Ph_2P$(2-methylsulfanylphenylphenylphophine]tetrahydridododecacarbonyltetraruthenium (**I**) and $Rh_6(CO)_{14}[k^2(P,S)\text{-}Ph_2P(2\text{-}MeSC_6H_4)]$–$[k^2(P,S)\text{-}Ph_2P$(2-methylthiophenyl)]diphenylphophine(μ_3-tetracarbonyl)dodecacarbonylhexarhodium (**II**). Structures of compounds **I** and **II** in solid phase have been established by the X-ray structural analysis, and ORTEP diagrams of these molecules are shown in Figs. 1 and 2, respectively. Position of hydride ligands in cluster **I** was determined by the method of difference synthesis. In the both clusters the chelating ligand is coordinated to one of metal atoms to form a five-membered metallacycle.

Selected bond lengths and angles in the structures of clusters **I** and **II** are given in the Table. The Ru–Ru bond lengths in cluster **I** fall to the region typical for the substituted derivatives of the $H_4Ru_4(CO)_{12}$ cluster [10, 11]. Hydride atoms are coordinated on the edges, which are somewhat elongated as compared with other Ru–Ru bonds, that also agrees with the published data. An examination of the cluster **I** structure shows that the geometry of the ligand donor functions is the most suitable for the chelating coordination on the cluster framework Ru_4 with the formation of a nonstrained five-membered metallacycle. Bond lengths in the metallacycle agree well with the parameters found for mononuclear coordination compounds containing the same ligand [12, 13]. The SRuP angle (86.39°) in the metallacycle is less than the (O)CRuC(O) angle (93.68°) in the starting cluster, but it fully agrees with the values of PRuP angles (84°–94°), which were observed previously in

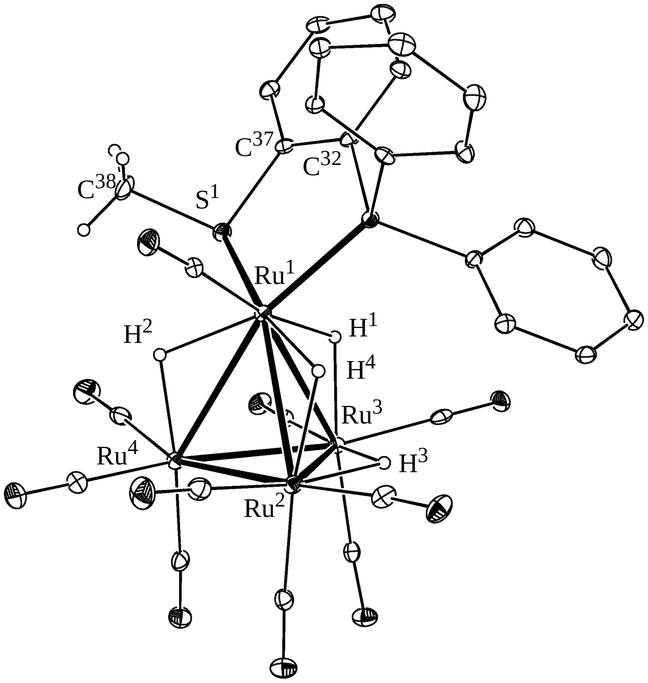


Fig. 1. ORTEP diagram of a cluster **I** molecule. Protons of phenyl rings of the ligand are omitted for simplicity of representation.

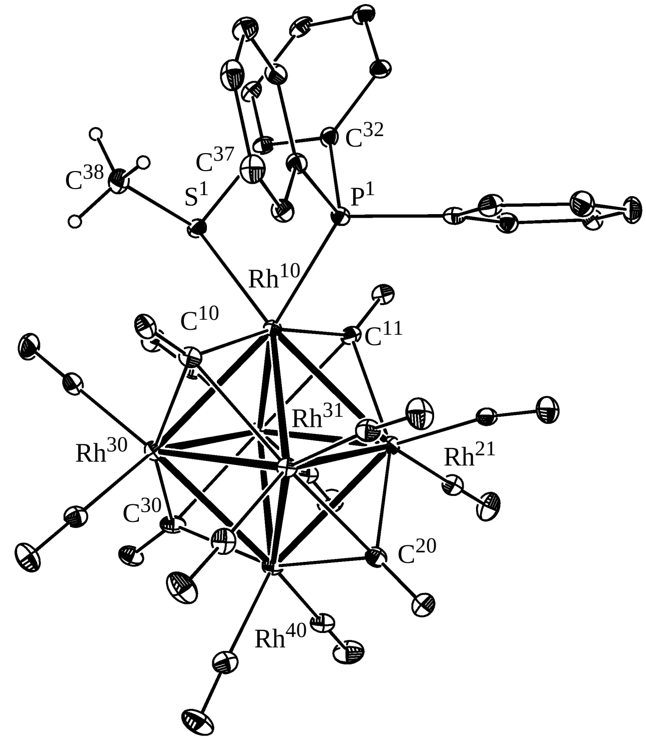


Fig. 2. ORTEP diagram of a cluster **II** molecule. Protons of phenyl rings of the ligand are omitted for simplicity of representation.

the derivatives of $H_4Ru_4(CO)_{12}$ cluster with various chelate-coordinated diphosphine ligands [6, 14–16]. These data point to a rigidity of the ligand fragment P–C–C–S which takes part in the formation of the chelated structure, and also to a certain strain in the metallacycle leading to a change in the bond angles at the substituted ruthenium atom. The Ru–P bond length is close to the average value (2.33 Å) observed in phosphine derivatives of the $H_4Ru_4(CO)_{12}$ cluster [6, 14–16]. The other bond lengths in the chelated metallacycle only slightly differ from the parameters found for cluster (II) and for mononuclear complexes of the [$Ph_2P(2\text{-}MeSC_6H_4)$] ligand [12].

Cluster **II** has a stable 86-electron configuration corresponding to a closo-octahedral structure of the cluster framework [17]. The Rh–Rh bond lengths fall to the range typical for other $Rh_6(CO)_{16}$ substituted derivates [18–22]. Bridging carbonyl groups $C^{10}O$ and $C^{11}O$ in cluster (II) are strongly shifted from symmetric positions above the centers of corresponding octahedron sides to the Rh^{10} vertex that completely corresponds to the influence of the heteroligand on the structural parameters of the carbonyl environment of $Rh_6(CO)_{16-x}(L)_x$ clusters [18, 20, 22]. As well as in cluster **I**, the SRhP angle (83.38) in the metallacycle of cluster **II** is essentially less than the average values of (O)CRhC(O) angles (94.28) in the starting $Rh_6(CO)_{16}$ cluster [22].

The data of the NMR and IR spectroscopy point to retention of the solid-phase structure of clusters **I** and **II** on passing into solution. Thus, the ^{31}P NMR spectrum of cluster **I** contains a singlet (68.0 ppm) shifted downfield as compared to the signal of the starting ligand. In the ^{1}H NMR spectrum of cluster **I** the signal of ligand methyl group is also shifted downfield (2.87 ppm) as compared to the phosphine not bound in the [$Ph_2P(2\text{-}MeSC_6H_4)$] complex (2.45 ppm), which points to the retaining of the ligand coordination involving phosphorus and sulfur atoms in solution. At room temperature the ligand surrounding cluster **I** is stereochemically nonrigid, however cooling a solution to 223 K “freezes out” the exchange of hydride ligands and allows us to give full assignment of signals in the hydride spectral region. The signal at –15.08 ppm has $^2J_{PH}$ of 35 Hz. This value of a spin–spin coupling constant (SSCC) is characteristic for a mutual transarrangement of hydride and phosphine ligands that allows the corresponding signal to be assigned to the H^2 atom, whereas the doublets at –18.48 and –18.94 ppm with SSCC $^2J_{PH}$ 14 Hz

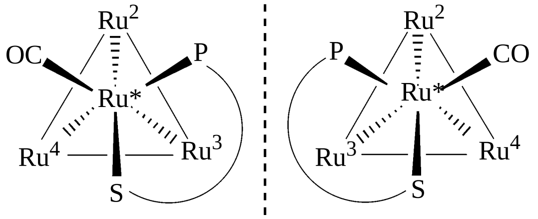
Selected bond lengths (Å) and angles (deg) in clusters **I** and **II**

Parameter	Value	Parameter	Value
Metal–metal bonds			
	cluster **I**		cluster **II**
Ru^1–Ru^2	2.9439(7)	Rh^{10}–Rh^{20}	2.7533(7)
Ru^1–Ru^4	2.9684(7)	Rh^{10}–Rh^{21}	2.7704(7)
Ru^1–Ru^3	3.0290(7)	Rh^{10}–Rh^{30}	2.7766(7)
Ru^2–Ru^3	2.9095(7)	Rh^{10}–Rh^{31}	2.7919(7)
Ru^2–Ru^4	2.7930(7)	Rh^{20}–Rh^{21}	2.7429(7)
Ru^3–Ru^4	2.7831(8)	Rh^{20}–Rh^{30}	2.7768(7)
		Rh^{20}–Rh^{40}	2.7784(7)
		Rh^{21}–Rh^{40}	2.7753(7)
		Rh^{30}–Rh^{40}	2.7646(7)
		Rh^{30}–Rh^{31}	2.7310(7)
		Rh^{31}–Rh^{21}	2.7712(7)
		Rh^{31}–Rh^{40}	2.7508(7)
Rh–μ_3-CO bonds (only for cluster **II**)			
Rh^{10}–C^{10}	2.051(7)	Rh^{20}–C^{10}	2.303(7)
Rh^{30}–C^{10}	2.303(7)	Rh^{20}–C^{20}	2.193(7)
Rh^{21}–C^{20}	2.200(6)	Rh^{40}–C^{20}	2.163(7)
Rh^{10}–C^{11}	2.090(7)	Rh^{21}–C^{11}	2.238(6)
Rh^{31}–C^{11}	2.316(7)	Rh^{30}–C^{30}	2.134(7)
Rh^{31}–C^{30}	2.183(7)	Rh^{40}–C^{30}	2.175(7)
Bonds in metallocycle			
S^1–Ru^1	2.3445(17)	Rh^{10}–S^1	2.3429(17)
P^1–Ru^1	2.3068(17)	Rh^{10}–P^1	2.2960(16)
C^{37}–S^1	1.791(6)	S^1–C^{37}	1.782(7)
C^{32}–P^1	1.835(6)	P^1–C^{32}	1.826(6)
C^{32}–C^{37}	1.386(9)	C^{32}–C^{37}	1.396(9)
C^{38}–S^1	1.806(7)	S^1–C^{38}	1.825(7)
Angles in metallocycle			
$P^1Ru^1S^1$	86.39(6)	$P^1Rh^{10}S^1$	83.38(6)
$C^{32}P^1Ru^1$	107.0(2)	$C^{32}P^1Rh^{10}$	104.8(2)
$C^{37}C^{32}P^1$	119.1(5)	$C^{37}C^{32}P^1$	117.0(5)
$C^{32}C^{37}S^1$	120.3(5)	$C^{32}C^{37}S^1$	118.9(5)
$C^{37}S^1Ru^1$	106.8(2)	$C^{37}S^1Rh^{10}$	104.3(2)
$C^{37}S^1C^{38}$	101.4(3)	$C^{37}S^1C^{38}$	98.8(3)

should be assigned to H^1 and H^4 atoms arranged in the *cis* position to phosphorus. The singlet at –16.51 ppm obviously belongs to the H^3 atom, which is located in three bonds from the phosphorus atom in the *cis*,*cis* position that completely suppresses its spin–spin interaction with the phosphorus nucleus.

In the ^{31}P NMR spectrum of cluster **II** there is a doublet (17.0 ppm) with a typical SSCC $^1J_{RhP}$ of 146 Hz, whereas an upfield shift of the methyl group (2.15 ppm) as compared to the starting ligand is observed in the ^1H NMR spectrum, which points to the retaining of the heteroligand bidentate coordination in solution. We point out that in all phosphine derivatives of the $Rh_6(CO)_{16}$ cluster both with diphosphine [18, 23] and functionalized phosphine ligands synthesized previously the heteroligand was coordinated only in the bridgehead mode to form five- or hexaatomic dimetallacycles [19, 20, 24]. Thus, cluster (II) is the first example of the chelating phosphine coordination on the Rh_6 framework. Saturation of solutions of clusters **I** and **II** with carbon monoxide under atmospheric pressure does not result in the decoordination of sulphide sulphur. The heteroligand remains coordinated in the bidentate mode that points to the inertness of this coordination function and to the inability of the ligand to show hemilabile properties in clusters **I** and **II**.

It is necessary to note that chelating coordination of a heterobidentate ligand on the Ru_4 framework of cluster (I) results in the asymmetry of the molecule as a whole. This asymmetry is associated with the substituted metal atom representing a classical chiral tetrahedron with P, S, and C(O) functions in three vertexes, whereas the fourth vertex is occupied by the $[Ru_3(CO)_9]$ cluster fragment.



We note that the whole Ru_4 tetrahedral metal framework also becomes chiral as all four ruthenium atoms are stereochemically nonequivalent. In particular, the metal atoms in the nonsubstituted $[Ru_3 \cdot (CO)_9]$ fragment differ by their positions relatively to the S and P functions of the ligand: Ru^2: *cis*-P, *trans*-S, Ru^3: *cis*-P, *cis*-S, and Ru^4: *trans*-P, *cis*-S. The extension of the asymmetry in cluster **I** to the metal framework as a whole makes molecules of this type perspective catalysts of asymmetric synthesis, in which both ligands and a cluster framework of a molecule can be chiral inductors.

EXPERIMENTAL

The IR spectra were taken on a Specord M-80 instrument. The NMR spectra were recorded on a Bruker DX-300 spectrometer for solutions in $CDCl_3$. The X-ray structural analysis was carried out on a Nonius Kappa-CCD device. The $H_4Ru_4(CO)_{12}$ [25] and $Rh_6(CO)_{15}NCMe$ [26] starting carbonyl clusters and the (2-methylsulfanylphenyl)diphenylphosphine functionalized heteroligand [12] were synthesized according to previously published techniques. The structural data for clusters **I** and **II** are deposited in the Cambridge Structural Database (nos. 280 702 and 280701, respectively).

$H_4Ru_4(CO)_{10}[k^2(P,S)$-$Ph_2P(2$-$CH_3SC_6H_4)]$ (I). A dry nitrogen flow was passed through a solution of a mixture of 63.5 mg of $H_4Ru_4(CO)_{12}$ and 26.3 mg of $[Ph_2P(2$-$MeSC_6H_4)]$ in 30 ml of chloroform for 15 min with vigorous stirring. Then a solution of 14.0 mg of $Me_3NO \cdot 2H_2O$ in a mixture of 0.5 ml of ethanol and 5 ml of chloroform was added dropwise to the reaction mixture. The reaction product was isolated by flash chromatography on silica gel (5–40 mesh), using a hexane–chloroform mixture (2 : 1 volume ratio) as an eluent. Yield 49 mg (58%). IR spectrum (hexane), ν(CO), cm^{-1}: 2078 m, 2068 w, 2048 s, 2026 s, 2008 m, 1984 w. ^{1}H NMR spectrum (223 K), δ, ppm: 7.36.37.94 m (14H, Ph), 2.87 s (3H, SMe), –15.08 d (1H, H^2, $^2J_{PH}$ 35 Hz), –16.51 s (1H, H^3), –18.48 d [1H, H^1(H^4), $^2J_{PH}$ 14 Hz], –18.94 d [1H, H^4(H^1), $^2J_{PH}$ 14 Hz]. ^{31}NMR spectrum, δ_P, ppm: 68.0 s.

$Rh_6(CO)_{14}[k^2(P,S)$-$Ph_2P(2$-$CH_3SC_6H_4)]$ (II). A solution of 54.0 mg of $Rh_6(CO)_{15}$NCMe in 10 ml of dichloromethane was degased at a single-pass freezing in vacuum. A solution of a mixture of 15.4 mg of $[Ph_2P(2$-$MeSC_6H_4)]$ and 5.5 mg of $Me_3NO \cdot 2H_2O$ in 4 ml of dichloromethane was added dropwise to the frozen reaction mixture. At vigorous stirring the reaction mixture heated spontaneously up to room temperature. The reaction product was isolated by flash chromatography on silica gel (5–40 mesh), using a hexane–dichloromethane mixture (1 : 1 volume ratio) as an eluent. Yield 44 mg (63%). IR spectrum (hexane), ν(CO), cm^{-1}: 2088 s, 2074 s, 2050 v. s, 2038 w, 2028 w, 2026 w, 2020 w, 2010 w, 2002 w, 1816 v. s, 1798 m, 1792 m, 1774 m, 1764 m, 1734 v. s. ^{1}H NMR spectrum (223 K), δ, ppm: 7.36–7.94 m (14H, Ph), 2.15 s (3H, SMe). ^{31}NMR spectrum, δ_P, ppm: 17.0 d ($^1J_{PRhi}$ *146 Hz).*

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