

Heteroligand substitution in clusters of ruthenium and cobalt

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Abstract

Reactions of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ with tris(2-thienyl)phosphine and dithiacyclohexane have been investigated. $\text{HRuCo}_3(\text{CO})_{12}$ was also tested with tris(2-thienyl)phosphine. The crystal structures of $\text{H}_4\text{Ru}_4(\text{CO})_{11}[\text{P}(\text{SC}_4\text{H}_3)_3]$ (1), $\text{HRuCo}_3(\text{CO})_{11}[\text{P}(\text{SC}_4\text{H}_3)_3]$ (2) and $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{S}_2\text{C}_4\text{H}_8)$ (3) were determined. Both phosphine compounds are monosubstituted and the ligand is bound only from phosphorus. With bidentate dithiacyclohexane the substitution proceeds further forming a disubstituted $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{S}_2\text{C}_4\text{H}_8)$ (3) cluster. © 1998 Elsevier Science S.A.

Keywords: Ruthenium; Carbonyls; Dithiacyclohexane; Tris(2-thienyl)phosphine

1. Introduction

Substitution reactions of tetrahedral metal clusters of Ru, Co and Rh with tertiary alkyl- and arylphosphines have been studied extensively [1–4]. The corresponding substitution products of alkyl- and aryl sulfides usually resemble the structures of phosphine derivatives [5,6], although the sulphur compounds have a greater tendency to form bridges between metal atoms, and site selectivity may be different.

The simultaneous use of different donor atoms produces interesting features in the reactions and compounds achieved. For example, modification of metal centers in metal catalysts will in some cases lead to crucial improvements in activity or stability. One way to achieve these different sites is to use mixed donor ligands. Reactions of phosphine ligands with other active donor atoms have been investigated to some extent. Several chelate structures with mixed donor sites of mono- and dinuclear complexes have been published. The most common combinations are phosphorus and nitrogen or phosphorus and oxygen. Compounds containing a phosphorus/sulphur combination are not common. Those few complexes, in which both phosphorus and sulphur have bonded to a metal atom most commonly appear in rhodium and platinum [7–10].

Bodensieck et al. have reported a reaction between tris(2-thienyl)phosphine and $\text{Ru}_3(\text{CO})_{12}$. In this case the ligand reacts as a simple tertiary phosphine forming the trinuclear disubstituted compound $\text{Ru}_3(\text{CO})_{10}[\text{P}(\text{SC}_4\text{H}_3)_3]$, in which the terminal ligands are situated equatorially in *trans* position along a Ru–Ru bond. However, the thienyl rings seem to interact with the metal core and as a consequence of this the trinuclear compound is labile. This also causes the formation of a mononuclear derivative $\text{Ru}(\text{CO})_3[\text{P}(\text{SC}_4\text{H}_3)_3]_2$, where the phosphine ligands are in *trans* positions.

On the other hand, a work was recently published describing how diphenyl-2-thienylphosphine acts as a bridging ligand in $\text{Ru}_3(\text{CO})_{12}$ [11]. In addition to the phosphorus atom the ligand utilizes either a sulphur atom or the π -electrons of the thienyl ring in coordination [11]. In this work an intermediate with a terminal phosphine ligand was proposed, but the only stable monosubstituted compound involved the μ_3 -bridging mode. Further substitution, however, yielded a compound in which the second ligand is bound terminally via phosphorus. In $\text{Re}_2(\text{CO})_{10}$ the same ligand forms a bridge through the sulphur and phosphorus atoms [11].

Our earlier studies on substitution in tetrahedral clusters with heterodonor ligands have shown the difficulty of activating the ligand at both donor sites without breaking the cluster or the ligand itself. In this article, we report some experiments with tris(2-thienyl)phosphine ligand and the tetrahedral clusters $\text{H}_4\text{Ru}_4(\text{CO})_{12}$

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and $\text{HRuCo}_3(\text{CO})_{12}$. Comparative studies were made with the bidentate homoatomic ligand 1,3-dithiacyclohexane.

2. Results and discussion

2.1. Reactions of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ with tris(2-thienyl)phosphine and dithiacyclohexane

$\text{H}_4\text{Ru}_4(\text{CO})_{12}$ reacts with both tris(2-thienyl)phosphine and dithiacyclohexane in refluxing THF in 3 h. Longer reaction times cause the decomposition of the cluster. In the reaction with tris(2-thienyl)phosphine the reaction mixture contains two main products, which can be separated chromatographically. According to IR spectra the first main product contains the disubstituted tetranuclear compound $\text{H}_4\text{Ru}_4(\text{CO})_{10}[\text{P}(\text{SC}_4\text{H}_3)_3]_2$. Crystallization from CH_2Cl_2 at -40°C , however, yields a monosubstituted product, $\text{H}_4\text{Ru}_4(\text{CO})_{11}[\text{P}(\text{SC}_4\text{H}_3)_3]$, which was also detected in the IR spectrum of the crystals obtained. The second main product is the mononuclear ruthenium complex $\text{Ru}(\text{CO})_3[\text{P}(\text{SC}_4\text{H}_3)_3]_2$ with two tris(2-thienyl)phosphine ligands; the same compound was published by Bodensieck et al. [12]. When the crystallization of the originally disubstituted cluster was carried out at room temperature or even at 4°C , the only product to crystallize was the mononuclear disubstituted complex. Both products thus show the high lability that the ligand brings to the metal compound.

Earlier we studied the reactions of some sulphur compounds with nitrogen or oxygen as heteroatoms and in those cases, although some intermediates with a metal–nitrogen bond are found, the sulphur atom in the final product is the most reactive component in metal

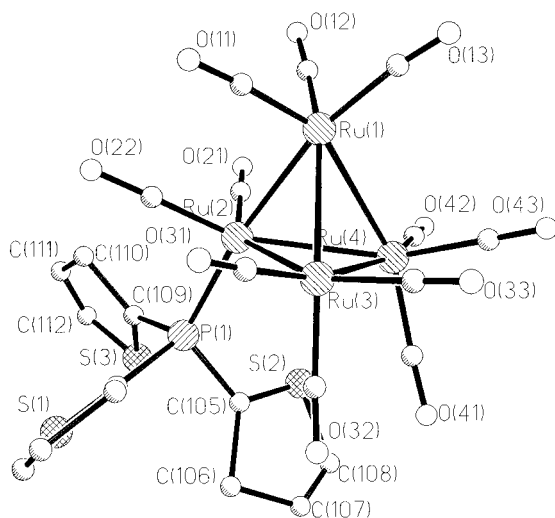


Fig. 1. Structure and numbering scheme for $\text{H}_4\text{Ru}_4(\text{CO})_{11}[\text{P}(\text{SC}_4\text{H}_3)_3]$ (1).

Table 1

Atomic coordinates ($\times 10^4$) for $\text{H}_4\text{Ru}_4(\text{CO})_{11}[\text{P}(\text{SC}_4\text{H}_3)_3]$ (1)

Atom	x	y	z
Ru1	385.7 (2)	308.5 (2)	897.07 (7)
Ru2	333.7 (2)	326.3 (2)	768.78 (7)
Ru3	45.1 (2)	413.7 (2)	856.79 (7)
Ru4	276.7 (2)	84.7 (2)	846.63 (7)
P1	253.3 (6)	337.7 (6)	666.5 (2)
S1	62.4 (13)	581.3 (12)	563.3 (5)
S2	304.9 (14)	-15.6 (13)	659.0 (6)
S3	452.7 (13)	184.0 (12)	545.1 (5)
S1A	-54.5 (14)	663.4 (13)	682.8 (6)
S2A	2.3 (15)	248.1 (14)	614.8 (6)
S3A	525.5 (19)	390.5 (18)	606.4 (8)
C101	82.7 (24)	534.9 (23)	636.1 (9)
C103	-163.7 (35)	780.9 (34)	628.7 (14)
H103	-259.9 (35)	877.4 (34)	637.6 (14)
C104	-122.0 (33)	744.7 (31)	579.0 (14)
H104	-189.8 (33)	805.4 (31)	546.2 (14)
C105	187.4 (25)	193.0 (23)	644.8 (10)
C107	29.4 (37)	56.2 (35)	615.8 (14)
H107	-52.7 (37)	33.3 (35)	602.8 (14)
C108	165.7 (31)	-58.0 (31)	635.0 (12)
H108	185.5 (31)	-167.0 (31)	635.2 (12)
C109	414.2 (23)	301.0 (22)	606.5 (9)
C111	625.1 (40)	313.8 (36)	540.7 (15)
H111	704.9 (40)	337.9 (36)	522.0 (15)
C112	579.8 (40)	218.5 (40)	519.0 (17)
H112	633.4 (40)	164.8 (40)	482.4 (17)
C11	368.1 (29)	519.7 (25)	899.6 (11)
O11	348.6 (33)	641.6 (25)	904.4 (11)
C12	615.7 (22)	211.6 (26)	884.1 (10)
O12	756.7 (20)	153.6 (20)	878.8 (9)
C13	394.4 (27)	272.8 (26)	988.5 (12)
O13	395.8 (23)	245.6 (29)	1038.3 (8)
C21	557.9 (24)	185.1 (24)	750.2 (10)
O21	692.3 (19)	97.6 (23)	736.7 (8)
C22	348.5 (26)	519.5 (25)	758.6 (9)
O22	369.2 (24)	633.4 (21)	750.1 (10)
C31	-59.1 (25)	653.5 (26)	864.0 (12)
O31	-114.6 (25)	787.5 (21)	867.3 (12)
C32	-107.5 (26)	402.8 (22)	802.9 (11)
O32	-207.6 (21)	396.5 (19)	773.2 (9)
C33	-54.7 (25)	365.4 (37)	928.4 (14)
O33	-116.0 (24)	345.1 (25)	972.5 (11)
C41	127.8 (21)	36.4 (23)	804.2 (9)
O41	35.6 (17)	2.0 (19)	781.0 (8)
C42	470.8 (27)	-118.7 (27)	825.2 (11)
O42	576.9 (19)	-235.0 (20)	811.3 (9)
C43	220.2 (28)	17.2 (26)	926.8 (12)
O43	193.8 (25)	-17.4 (22)	972.9 (10)

bonding [13]. In this case the metal–phosphorus bond is more stable than the metal–sulphur bond and the thienyl rings probably result in the lability of the products.

In the reaction with dithiacyclohexane the main product is a disubstituted tetranuclear compound in which both sulphur atoms of the ligand are bound to adjacent ruthenium atoms. The product can be purified chromatographically and recrystallized from CH_2Cl_2 . The dithiacyclohexane derivative and the tris(2-thienyl)phosphine derivative obtained by chromato-

graphic separation have similar IR spectra. The dithia-cyclohexane compound has six peaks in the terminal carbonyl area: 2096m, 2067s, 2060s, 2028s, 2007m and 1966w. The tris(2-thienyl)phosphine derivative also has six peaks: 2098m, 2071s, 2060s, 2026s, 2009m and 1953w. In the $\text{Ru}_3(\text{CO})_{12}$ derivative with tris(2-thienyl)phosphine the phosphine ligands are situated equatorially in *trans* position along the Ru–Ru bond [12]. The triphenylphosphine derivative of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ also prefers the *trans* position in the disubstituted product [1]. If the ligands are at the opposite site of the cluster, there is a different symmetry than when the ligands are in the axial position. This should also be observed in the IR spectra. The axial position would be sterically limited and probably labile.

2.2. Reaction of $\text{HRuCo}_3(\text{CO})_{12}$ with tris(2-thienyl)phosphine

The mixed metal cluster $\text{HRuCo}_3(\text{CO})_{12}$ reacts with tris(2-thienyl)phosphine in CH_2Cl_2 solution at room temperature in 20 h. A higher reaction temperature or a more reactive solvent, like THF, causes the breakdown of the cluster. The monosubstituted cluster is the main product, but other products such as a disubstituted

Table 2
Selected bond lengths for $\text{H}_4\text{Ru}_4(\text{CO})_{11}\text{P}(\text{SC}_4\text{H}_3)_3$ (1)

Ru1–Ru2	2.786 (2)
Ru1–Ru3	2.963 (2)
Ru1–Ru4	2.938 (2)
Ru2–Ru3	2.982 (3)
Ru2–Ru4	2.943 (3)
Ru3–Ru4	2.769 (2)
Ru1–C11	1.87 (2)
Ru1–C12	1.88 (2)
Ru1–C13	1.96 (3)
Ru2–P1	2.319 (5)
Ru2–C21	1.88 (2)
Ru2–C22	1.85 (2)
Ru3–C31	1.95 (2)
Ru3–C32	1.89 (2)
Ru3–C33	1.89 (4)
Ru4–C41	1.90 (2)
Ru4–C42	1.93 (2)
Ru4–C43	1.93 (3)
O11–C11	1.06 (3)
O12–C12	1.15 (2)
O13–C13	1.08 (3)
O21–C21	1.14 (2)
C22–O22	1.15 (3)
C31–O31	1.09 (2)
C32–O32	1.17 (2)
C33–O33	1.13 (4)
O41–C41	1.17 (2)
O42–C42	1.10 (2)
C43–O43	1.07 (3)
P1–C105	1.79 (2)
P1–C109	1.83 (2)
P1–C101	1.86 (2)

Table 3
Selected bond angles for $\text{H}_4\text{Ru}_4(\text{CO})_{11}\text{P}(\text{SC}_4\text{H}_3)_3$ (1)

C11–Ru1–Ru2	94.6 (7)
C12–Ru1–Ru2	92.0 (6)
C13–Ru1–Ru2	168.2 (8)
C11–Ru1–Ru4	149.5 (6)
C12–Ru1–Ru4	107.3 (6)
C13–Ru1–Ru4	106.9 (8)
Ru2–Ru1–Ru4	61.83 (6)
C11–Ru1–Ru3	97.0 (7)
C12–Ru1–Ru3	153.4 (6)
C13–Ru1–Ru3	109.1 (7)
Ru2–Ru1–Ru3	62.40 (6)
Ru4–Ru1–Ru3	55.96 (5)
C22–Ru2–Ru1	92.3 (6)
C21–Ru2–Ru1	92.8 (6)
P1–Ru2–Ru1	171.0 (2)
C22–Ru2–Ru4	151.8 (6)
C21–Ru2–Ru4	96.1 (8)
P1–Ru2–Ru4	111.6 (2)
Ru1–Ru2–Ru4	61.63 (6)
C22–Ru2–Ru3	104.1 (7)
C21–Ru2–Ru3	147.9 (8)
P1–Ru2–Ru3	109.84 (14)
Ru1–Ru2–Ru3	61.72 (6)
Ru4–Ru2–Ru3	55.71 (6)
C33–Ru3–Ru4	91.4 (8)
C32–Ru3–Ru4	95.1 (5)
C31–Ru3–Ru4	162.9 (7)
C33–Ru3–Ru1	103.1 (7)
C32–Ru3–Ru1	152.0 (6)
C31–Ru3–Ru1	102.4 (6)
Ru4–Ru3–Ru1	61.56 (5)
C33–Ru3–Ru2	150.7 (7)
C32–Ru3–Ru2	100.6 (7)
C31–Ru3–Ru2	105.6 (9)
Ru4–Ru3–Ru2	61.44 (6)
Ru1–Ru3–Ru2	55.89 (5)
C41–Ru4–Ru3	92.0 (5)
C43–Ru4–Ru3	94.9 (6)
C42–Ru4–Ru3	163.9 (9)
C41–Ru4–Ru1	153.8 (6)
C43–Ru4–Ru1	95.8 (7)
C42–Ru4–Ru1	108.1 (6)
Ru3–Ru4–Ru1	62.47 (5)
C41–Ru4–Ru2	107.9 (7)
C43–Ru4–Ru2	149.7 (7)
C42–Ru4–Ru2	101.1 (9)
Ru3–Ru4–Ru2	62.84 (6)
Ru1–Ru4–Ru2	56.54 (5)

cluster and some mononuclear complexes are also formed to a minor extent. Chromatographic separation on silica plates produces several fractions. The largest is the monosubstituted compound $\text{HRuCo}_3(\text{CO})_{11}\text{P}(\text{SC}_4\text{H}_3)_3$; another large fraction is the same ruthenium complex that was found in the $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ reaction. In this reaction as well, the ligand tends to fragment the cluster. The IR and ^1H NMR spectra are very similar to the corresponding spectra of the triphenylphosphine derivative of $\text{HRuCo}_3(\text{CO})_{12}$ [14,15].

Both phosphine and sulphide ligands have a greater tendency to bond with a cobalt atom than a ruthenium atom. This has also been observed in disubstituted derivatives where Co–Co isomers are more common than Co–Ru isomers, although the latter is also possible. Amines and tellurides, on the other hand, prefer Co–Ru isomers [4]. It has been proven that sulphide ligands bound to cobalt can easily be replaced by phosphine ligands [4]. Thus, the Co–P bond is stronger than the Co–S bond and in the case of tris(2-thienyl)phosphine the phosphorus atom is also more available to sterically bond with the cobalt atom than with sulphur atoms from thienyl groups. Axial site occupancy is well-known for a large number of mono-substituted tetranuclear clusters having C_{3v} symmetry [14,15]. In reactions of $HRuCo_3(CO)_{12}$ the monosubstituted products seem to be more favoured.

2.3. Characterization and structures of the substituted clusters

2.3.1. $H_4Ru_4(CO)_{11}P(SC_4H_3)_3$ (1)

The parent cluster core remains unchanged and the ligand replaces one terminal carbonyl. Corresponding structures have reported for PR_3 and $P(OR)_3$ derivatives of $H_4Ru_4(CO)_{12}$ [16,17]. The molecular structure is presented in Fig. 1. The atomic coordinates are given in Table 1, selected bond lengths appear in Table 2 and bond angles in Table 3. The phosphine ligand is coordinated via the phosphorus atom to Ru(2). Like the parent cluster, all the other metals have three terminal carbonyls. The carbonyls adjacent to the phosphine ligand bend slightly away from the phosphine due to sterical reasons. The metal–metal distances to Ru(2) are significantly longer than those without the influence of the

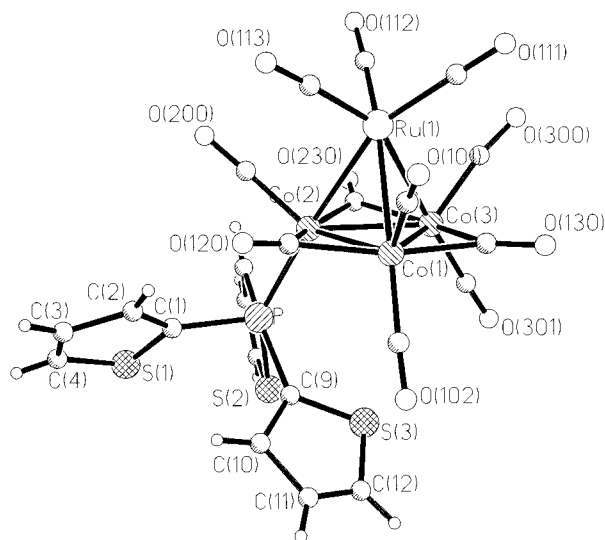


Fig. 2. Structure and numbering scheme for $HRuCo_3(CO)_{11}P(SC_4H_3)_3$ (2).

Table 4

Atomic coordinates ($\times 10^4$) for $HRuCo_3(CO)_{11}P(SC_4H_3)_3$ (2)

Atom	x	y	z
Ru1	715.42 (11)	46.63 (3)	824.56 (6)
Co1	464.5 (2)	54.34 (5)	692.89 (8)
Co2	624.9 (2)	138.20 (5)	739.33 (8)
Co3	741.3 (2)	64.58 (5)	650.58 (9)
P	534.9 (3)	211.25 (9)	658.0 (2)
S1	437.0 (5)	328.33 (15)	687.0 (2)
S2	654.0 (6)	281.1 (2)	509.7 (3)
S3	427.5 (5)	164.7 (2)	465.9 (3)
C101	404.2 (15)	4.5 (5)	765.4 (8)
O101	348.5 (12)	-27.4 (4)	806.0 (6)
C102	288.5 (13)	59.1 (4)	607.3 (7)
O102	174.3 (10)	58.7 (4)	554.6 (6)
C111	744.5 (15)	-29.9 (5)	841.2 (8)
O111	768.2 (16)	-74.1 (4)	850.3 (8)
C112	924.8 (17)	62.2 (5)	885.7 (9)
O112	1049.6 (15)	72.0 (5)	928.3 (8)
C113	618.3 (18)	57.2 (5)	931.2 (9)
O113	553.8 (16)	63.8 (5)	993.8 (6)
C120	419.5 (13)	115.6 (4)	771.3 (7)
O120	322.0 (9)	126.4 (3)	817.0 (5)
C130	587.7 (14)	4.0 (4)	627.7 (7)
O130	580.5 (12)	-38.4 (3)	595.9 (6)
C200	694.4 (16)	169.5 (4)	844.7 (8)
O200	736.2 (14)	190.9 (4)	912.0 (6)
C230	843.1 (16)	132.8 (5)	707.6 (9)
O230	971.8 (10)	151.2 (3)	718.6 (7)
C300	904.0 (16)	21.0 (5)	688.6 (9)
O300	1011.3 (12)	-7.9 (4)	700.7 (8)
C301	773.2 (15)	76.4 (5)	534.5 (9)
O301	793.3 (12)	82.2 (4)	461.1 (6)
C1	429.6 (11)	261.9 (4)	716.4 (6)
C2	323.9 (10)	253.3 (4)	785.0 (6)
H2	298.0 (10)	220.6 (4)	810.0 (6)
C3	266.8 (15)	306.7 (5)	806.8 (9)
H3	199.0 (15)	312.0 (5)	850.6 (9)
C4	315.9 (14)	345.6 (5)	761.8 (8)
H4	286.1 (14)	381.2 (5)	770.3 (8)
C5	684.7 (12)	251.2 (4)	611.7 (7)
C6	850.6 (8)	269.5 (3)	675.0 (5)
H6	893.3 (8)	260.1 (3)	735.0 (5)
C7	915.4 (17)	306.2 (5)	608.4 (9)
H7	1015.5 (17)	323.0 (5)	623.1 (9)
C8	824.7 (15)	313.5 (5)	528.3 (9)
H8	857.0 (15)	336.2 (5)	484.2 (9)
C9	386.1 (11)	197.3 (4)	560.1 (6)
C10	209.6 (10)	205.4 (3)	552.0 (6)
H10	155.6 (10)	222.6 (3)	594.7 (6)
C11	135.5 (20)	181.8 (6)	466.3 (10)
H11	24.1 (20)	181.0 (6)	447.5 (10)
C12	237.1 (16)	162.2 (5)	418.7 (9)
H12	205.0 (16)	147.4 (5)	360.7 (9)

phosphine ligand. The thienyl rings are disordered so that they can rotate 180° in the direction of the P–C axis. When the sulphur atoms are directed towards the metals there is a possibility of interaction between the sulphur and ruthenium. Unfortunately, this possible interaction is not detectable with ^{31}P NMR. The positions of the hydrides are deduced from the lengthening of the

Ru–Ru bonds (an average of 296 pm for a hydrogen-bridged bond and 278 pm for a non-bridged bond) and the opening of the Ru–Ru–C angles. The ^1H NMR supports this conclusion.

2.3.2. $\text{HRuCo}_3(\text{CO})_{11}\text{P}(\text{SC}_4\text{H}_3)_3$ (2)

In $\text{HRuCo}_3(\text{CO})_{11}\text{P}(\text{SC}_4\text{H}_3)_3$ (Fig. 2), the ligand is bound to one of the cobalt atoms replacing one terminal carbonyl. The other carbonyls are unchanged. $\text{HRuCo}_3(\text{CO})_{12}$ has three terminal carbonyls at the ruthenium, two terminal carbonyls at each cobalt and three bridging carbonyls situated between the cobalts. The final atomic positional parameters are listed in Table 4, selected bond distances are in Table 5 and bond angles in Table 6.

The cobalt phosphorus distance is 224 pm, which is typical for phosphine derivatives of $\text{HRuCo}_3(\text{CO})_{12}$. The small changes in close carbonyl geometry are also similar to the triphenylphosphine derivative [14,15]. The metal hydride exhibits a broad ^1H NMR signal at -19.7 ppm, which is typical for $\mu_3\text{-H}$ bridging. The hydride is situated at the bottom of the cobalt triangle as

Table 5
Selected bond lengths for $\text{HRuCo}_3(\text{CO})_{11}\text{P}(\text{SC}_4\text{H}_3)_3$ (2)

Ru1–Co1	2.636 (2)
Ru1–Co2	2.6465 (15)
Ru1–Co3	2.640 (2)
Co1–Co2	2.510 (2)
Co1–Co3	2.496 (2)
Co2–Co3	2.522 (2)
Ru1–C111	1.923 (12)
Ru1–C112	1.881 (14)
Ru1–C113	1.891 (14)
Co1–C101	1.756 (12)
Co1–C102	1.789 (12)
Co1–C120	1.977 (10)
Co1–C130	1.958 (11)
Co2–P	2.236 (3)
Co2–C120	1.929 (11)
Co2–C200	1.752 (12)
Co2–C230	1.952 (12)
Co3–C300	1.760 (13)
Co3–C301	1.793 (12)
Co3–C130	1.969 (11)
Co3–C230	2.016 (14)
C111–O111	1.117 (13)
O112–C112	1.158 (15)
O113–C113	1.15 (2)
O101–C101	1.132 (13)
O102–C102	1.135 (12)
O120–C120	1.164 (11)
O130–C130	1.148 (12)
O200–C200	1.130 (12)
O230–C230	1.157 (14)
O300–C300	1.139 (13)
O301–C301	1.126 (13)
P–C1	1.821 (10)
P–C5	1.808 (10)
P–C9	1.788 (10)

Table 6
Selected bond angles for $\text{HRuCo}_3(\text{CO})_{11}\text{P}(\text{SC}_4\text{H}_3)_3$ (2)

C112–Ru1–Co1	156.1 (4)
C113–Ru1–Co1	101.9 (4)
C111–Ru1–Co1	103.7 (4)
C112–Ru1–Co3	102.8 (4)
C113–Ru1–Co3	152.9 (4)
C111–Ru1–Co3	105.2 (4)
Co1–Ru1–Co3	56.47 (5)
C112–Ru1–Co2	103.2 (4)
C113–Ru1–Co2	98.5 (3)
C111–Ru1–Co2	158.0 (4)
Co1–Ru1–Co2	56.74 (4)
Co3–Ru1–Co2	57.00 (4)
C101–Co1–Co3	125.8 (4)
C102–Co1–Co3	120.7 (3)
C130–Co1–Co3	50.7 (3)
C120–Co1–Co3	109.4 (3)
C101–Co1–Co2	127.4 (4)
C102–Co1–Co2	119.0 (3)
C130–Co1–Co2	111.2 (3)
C120–Co1–Co2	49.2 (3)
Co3–Co1–Co2	60.51 (5)
C101–Co1–Ru1	76.8 (4)
C102–Co1–Ru1	177.5 (3)
C130–Co1–Ru1	84.0 (3)
C120–Co1–Ru1	80.0 (3)
Co3–Co1–Ru1	61.84 (5)
Co2–Co1–Ru1	61.84 (4)
C200–Co2–Co1	134.3 (4)
C120–Co2–Co1	50.9 (3)
C230–Co2–Co1	110.9 (4)
P–Co2–Co1	113.70 (8)
C200–Co2–Co3	132.6 (4)
C120–Co2–Co3	110.1 (3)
C230–Co2–Co3	51.7 (4)
P–Co2–Co3	115.64 (8)
Co1–Co2–Co3	59.47 (5)
C200–Co2–Ru1	85.9 (4)
C120–Co2–Ru1	80.6 (3)
C230–Co2–Ru1	81.1 (3)
P–Co2–Ru1	174.97 (8)
Co1–Co2–Ru1	61.42 (5)
Co3–Co2–Ru1	61.37 (5)
C300–Co3–C301	100.6 (5)
C300–Co3–Co1	123.9 (4)
C301–Co3–Co1	122.1 (4)
C130–Co3–Co1	50.3 (3)
C230–Co3–Co1	109.2 (3)
C300–Co3–Co2	128.2 (4)
C301–Co3–Co2	120.0 (4)
C130–Co3–Co2	110.3 (3)
C230–Co3–Co2	49.4 (3)
Co1–Co3–Co2	60.02 (5)
C300–Co3–Ru1	76.1 (4)
C301–Co3–Ru1	176.2 (4)
C130–Co3–Ru1	83.7 (3)
C230–Co3–Ru1	80.1 (3)
Co1–Co3–Ru1	61.69 (5)
Co2–Co3–Ru1	61.64 (5)

in the parent cluster and in other phosphine and sulfide monosubstituted clusters. The thienyl rings in this structure are also disordered so that the ring can rotate

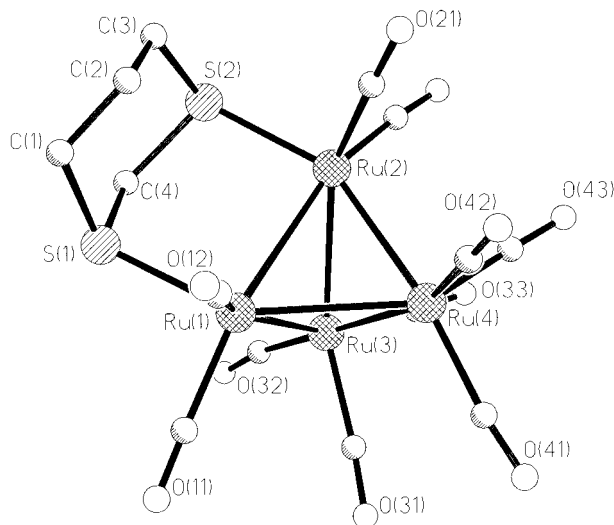


Fig. 3. Structure and numbering scheme for $H_4Ru_4(CO)_{10}(S_2C_4H_8)(3)$.

Table 7

Atomic coordinates ($\times 10^4$) for $H_4Ru_4(CO)_{10}(S_2C_4H_8)(3)$

Atom	x	y	z
Ru1	0.70958 (7)	0.22517 (5)	0.39199 (4)
Ru2	0.89387 (7)	0.34871 (6)	0.30741 (4)
Ru3	0.63545 (8)	0.43342 (6)	0.34116 (4)
Ru4	0.64528 (8)	0.29122 (6)	0.22239 (4)
S1	0.8682 (2)	0.2428 (2)	0.51755 (13)
S2	1.0573 (3)	0.3677 (2)	0.43084 (15)
C11	0.5574 (10)	0.1945 (8)	0.4436 (6)
O11	0.4668 (8)	0.1729 (8)	0.4718 (5)
C12	0.7444 (11)	0.0880 (8)	0.3799 (7)
O12	0.7579 (11)	0.0058 (6)	0.3730 (6)
C21	0.9953 (11)	0.2642 (7)	0.2512 (6)
O21	1.0568 (10)	0.2155 (7)	0.2151 (6)
C22	0.9523 (12)	0.4537 (8)	0.2510 (7)
O22	0.9916 (12)	0.5176 (7)	0.2132 (6)
C31	0.4415 (10)	0.4047 (8)	0.3217 (6)
O31	0.3289 (8)	0.3904 (7)	0.3135 (5)
C32	0.6287 (11)	0.5319 (9)	0.2584 (6)
O32	0.6279 (11)	0.5915 (7)	0.2115 (6)
C33	0.6280 (11)	0.5232 (8)	0.4294 (6)
O33	0.6102 (9)	0.5781 (7)	0.4785 (5)
C41	0.4538 (11)	0.2791 (8)	0.1774 (6)
O41	0.3457 (9)	0.2757 (7)	0.1462 (5)
C42	0.6912 (12)	0.3793 (8)	0.1469 (6)
O42	0.7158 (10)	0.4338 (6)	0.0962 (5)
C43	0.6990 (12)	0.1758 (8)	0.1693 (7)
O43	0.7266 (12)	0.1076 (6)	0.1369 (6)
C1	1.0104 (11)	0.1564 (8)	0.5231 (6)
H1A	1.0723 (11)	0.1673 (8)	0.5740 (6)
H1B	0.9743 (11)	0.0897 (8)	0.5245 (6)
C2	1.0915 (11)	0.1620 (8)	0.4560 (7)
H2A	1.0301 (11)	0.1509 (8)	0.4049 (7)
H2B	1.1588 (11)	0.1091 (8)	0.4628 (7)
C3	1.1650 (11)	0.2586 (8)	0.4509 (7)
H3A	1.2203 (11)	0.2531 (8)	0.4084 (7)
H3B	1.2273 (11)	0.2687 (8)	0.5017 (7)
C4	0.9648 (11)	0.3559 (7)	0.5145 (6)
H4A	0.9018 (11)	0.4113 (7)	0.5126 (6)
H4B	1.0301 (11)	0.3612 (7)	0.5647 (6)

Table 8

Selected bond lengths for $H_4Ru_4(CO)_{10}(S_2C_4H_8)(3)$

Ru1–Ru2	2.9960 (12)
Ru1–Ru3	2.9942 (12)
Ru1–Ru4	2.9356 (11)
Ru2–Ru3	2.9382 (12)
Ru2–Ru4	2.7310 (13)
Ru3–Ru4	2.7762 (11)
Ru1–S1	2.406 (2)
Ru1–C11	1.901 (10)
Ru1–C12	1.902 (11)
Ru2–S2	2.406 (3)
Ru2–C21	1.874 (11)
Ru2–C22	1.850 (11)
Ru3–C31	1.927 (10)
Ru3–C32	1.912 (12)
Ru3–C33	1.921 (11)
Ru4–C41	1.919 (10)
Ru4–C42	1.846 (11)
Ru4–C43	1.913 (11)
O11–C11	1.119 (12)
O12–C12	1.127 (13)
O21–C21	1.136 (13)
O22–C22	1.174 (13)
O31–C31	1.114 (12)
O32–C32	1.123 (14)
O33–C33	1.141 (13)
O41–C41	1.106 (12)
O42–C42	1.178 (13)
O43–C43	1.126 (13)

180° around the Co–P axis, and the sulphur atoms are not so clearly turned towards the metal atoms as in structure 1.

2.3.3. $H_4Ru_4(CO)_{10}(S_2C_4H_8)(3)$

$H_4Ru_4(CO)_{10}(\text{dithiacyclohexane})$ has a conformation in which the bidentate ligand replaces two carbonyls in the parent cluster. The molecular structure is presented in Fig. 3. The atomic coordinates are given in Table 7, selected bond lengths in Table 8 and bond angles in Table 9. All the remaining carbonyls are terminal. The ^1H NMR spectra show that there are four $\mu_2\text{-H}$ metal hydrides present and their positions can be determined from the distances of the ruthenium atoms and the openings in the metal–carbonyl angles. Three of them bridge the Ru(1)–Ru(2)–Ru(3) triangle and the fourth bridges the Ru(1)–Ru(4) bond. This is similar to the disubstituted trithiacyclohexane derivative of $H_4Ru_4(CO)_{12}$ [18]. The bidentate phosphine (dppe and dppm) derivatives also have a similar hydride geometry [19,20]. The phosphine and phosphite ligands prefer the *trans* position to one another along the unbridged Ru–Ru bond. The sulphur ligands favour the bridged Ru–Ru bond. The dithiacyclohexane ring is located in such a way that the three carbon atoms are turned away from Ru(3) when the hydrides in Ru(1)–Ru(2)–Ru(3) triangle have sufficient space. The fourth hydride in the Ru(1)–Ru(4) bond has the least space, but the carbonyls bend away enough to provide room for it.

Table 9
Selected bond angles for $H_4Ru_4(CO)_{10}(S_2C_4H_8)_3$ (3)

C11–Ru1–Ru4	116.5 (3)
C12–Ru1–Ru4	101.9 (3)
S1–Ru1–Ru4	144.40 (7)
C11–Ru1–Ru3	99.2 (3)
C12–Ru1–Ru3	157.7 (3)
S1–Ru1–Ru3	104.22 (7)
Ru4–Ru1–Ru3	55.82 (3)
C11–Ru1–Ru2	157.8 (3)
C12–Ru1–Ru2	110.9 (3)
S1–Ru1–Ru2	89.93 (6)
Ru4–Ru1–Ru2	54.82 (3)
Ru3–Ru1–Ru2	58.75 (3)
C22–Ru2–Ru4	106.5 (4)
C21–Ru2–Ru4	94.3 (3)
S2–Ru2–Ru4	152.66 (7)
C22–Ru2–Ru3	99.0 (4)
C21–Ru2–Ru3	152.9 (3)
S2–Ru2–Ru3	105.76 (7)
Ru4–Ru2–Ru3	58.51 (3)
C22–Ru2–Ru1	159.3 (4)
C21–Ru2–Ru1	108.5 (3)
S2–Ru2–Ru1	91.59 (7)
Ru4–Ru2–Ru1	61.47 (3)
Ru3–Ru2–Ru1	60.60 (3)
C32–Ru3–Ru4	88.0 (3)
C33–Ru3–Ru4	175.4 (3)
C31–Ru3–Ru4	84.0 (3)
C32–Ru3–Ru2	93.2 (3)
C33–Ru3–Ru2	122.8 (3)
C31–Ru3–Ru2	139.5 (3)
Ru4–Ru3–Ru2	57.01 (3)
C32–Ru3–Ru1	146.7 (3)
C33–Ru3–Ru1	114.6 (3)
C31–Ru3–Ru1	92.7 (3)
Ru4–Ru3–Ru1	61.02 (3)
Ru2–Ru3–Ru1	60.66 (3)
C42–Ru4–Ru2	82.4 (3)
C43–Ru4–Ru2	100.2 (3)
C41–Ru4–Ru2	165.1 (3)
C42–Ru4–Ru3	94.9 (3)
C43–Ru4–Ru3	160.4 (3)
C41–Ru4–Ru3	100.8 (3)
Ru2–Ru4–Ru3	64.48 (3)
C42–Ru4–Ru1	144.9 (3)
C43–Ru4–Ru1	99.7 (3)
C41–Ru4–Ru1	112.9 (3)
Ru2–Ru4–Ru1	63.72 (3)
Ru3–Ru4–Ru1	63.16 (3)

The Ru–S distances lie in a normal range (both bonds are 241 pm), and the corresponding distance in the trithiacyclohexane derivative is nearly the same (average 242 pm) [18]. The dithiacyclohexane ring causes a slight bending in the nearby carbonyls.

3. Conclusion

The tris(2-thienyl)phosphine derivatives of $H_4Ru_4(CO)_{12}$ and $HRuCo_3(CO)_{12}$ were characterized

by X-ray structure determination. Both these compounds are rather labile, especially the $H_4Ru_4(CO)_{12}$ derivative. Although the yields of the products are moderate, they break down very easily. In both compounds the ligand is bonded to the metal atom through the phosphorus atom. The position of the thienyl rings indicates some interactions between the metal and the sulphur atoms. The reaction of $H_4Ru_4(CO)_{12}$ with dithiacyclohexane forms the disubstituted cluster 3. The IR spectra of 1 prior to crystallization indicates the possibility of a disubstituted product in this reaction as well.

The same ligands were observed to form complexes with bonds to the metal from both phosphorus and sulphur atoms. Further experiments are required to determine whether the same kind of bonding is also possible with tris(2-thienyl)phosphine.

4. Experimental

4.1. General comments

If not otherwise stated, all manipulations were carried out under nitrogen atmosphere with deoxygenated solvents. Dithiacyclohexane and 2,2,2-tris(thienyl)phosphine were of commercial origin (Aldrich Chemie). $H_4Ru_4(CO)_{12}$ [21] and $HRuCo_3(CO)_{12}$ [22] were prepared by published methods.

Infrared spectra were recorded in dichloromethane on a Nicolet 750 spectrometer. 1H NMR spectra were measured on a Bruker AM-250 spectrometer with $CDCl_3$ as solvent and TMS as reference.

4.1.1. Synthesis of $H_4Ru_4(CO)_{10}[P(C_4H_3S)_3]_2$ (1)

The compound tris(thienyl)phosphine $P(C_4H_3S)_3$ (0.5 ml, 0.18 mmol) was added to a solution of $H_4Ru_4(CO)_{12}$ (100 mg, 0.13 mmol) in THF (40 ml). The mixture was refluxed for 4 h and the solvent evaporated in vacuo. The residue was chromatographed on a silica column. Elution with hexane gave a yellow band containing impurities of the starting material and some byproducts. Further elution with hexane–dichloromethane 3:2 mixture produced the orange band of the disubstituted product. A 1:4 mixture gave another orange band of the product (62 mg, 48%). Recrystallization from CH_2Cl_2 yielded red rectangular crystals. IR: 2079w, 2063m, 2029s, 2010s, 1996m, 1970m. 1H NMR: 7.3 ppm (m, CH), –16.7 ppm (s, H) Calc. for $Ru_4PS_3O_{11}C_{23}H_{13}$: C 27.71%, H 1.31%. Found: C 27.75%, H 1.56%.

4.1.2. Synthesis of $HRuCo_3(CO)_{11}[P(C_4H_3S)_3]_2$ (2)

Tris(2-thienyl)phosphine (0.5 ml, 0.18 mmol) was added to a solution of $HRuCo_3(CO)_{12}$ (100 mg, 0.16 mmol) in dichloromethane (40 ml). The solution was stirred at room temperature for 24 h. Chromatographic

Table 10

Crystal data and collection parameters for $\text{H}_4\text{Ru}_4(\text{CO})_{11}\text{P}(\text{SC}_4\text{H}_3)_3$ (1), $\text{HRuCo}_3(\text{CO})_{11}\text{P}(\text{SC}_4\text{H}_3)_3$ (2) and $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{S}_2\text{C}_4\text{H}_8)$ (3)

	1	2	3
Formula	$\text{Ru}_4\text{PS}_3\text{O}_{11}\text{C}_{23}\text{H}_{13}$	$\text{RuCo}_3\text{PS}_3\text{O}_{11}\text{C}_{23}\text{H}_{10}$	$\text{Ru}_4\text{S}_2\text{O}_{10}\text{C}_{14}\text{H}_{12}$
Formula weight (g mol^{-1})	996.75	867.34	808.62
Colour, habit	orange	black	red
Crystal size (mm)	$0.2 \times 0.2 \times 0.4$	$0.2 \times 0.2 \times 0.6$	$0.15 \times 0.2 \times 0.5$
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> (Å)	9.191(2)	8.351(2)	9.876(2)
<i>b</i> (Å)	9.191(2)	24.775(5)	13.514(3)
<i>c</i> (Å)	21.350(4)	14.717(3)	16.710(3)
α (°)	87.47(3)	90	90
β (°)	87.47(3)	98.73(3)	99.83(3)
γ (°)	61.83(3)	90	90
<i>V</i> (Å ³)	1587.8(6)	3009.6(11)	2197.4(8)
<i>Z</i>	2	4	4
μ (mm ⁻¹)	2.166	2.433	2.933
Calculated density (g cm^{-3})	2.085	1.914	2.432
Number of centring reflections	23	29	25
Centring 2θ (°)	5–30	11–25	10–25
2θ limits deg	5–50	5–55	5–55
Scan speed (°min ⁻¹)	3–30	3–30	3–30
<i>h</i> , <i>k</i> , <i>l</i> range	19, ± 12 , ± 25	9, 29, ± 17	11, 16, ± 19
Number of unique reflections	3495	5154	3715
Number of observed data ($F > 4\sigma(F)$)	2323	2843	2753
Number of parameters	304	304	271
<i>R</i>	0.0799	0.0599	0.0576
<i>R</i> _w	0.2307	0.1497	0.1353
GOOF	1.980	1.028	1.030

$$w = 1/[\sigma^2(F_0^2) + (0.0600 * p)^2 + 0.15 * p].$$

$$p = (\max(F_0^2) + 2 * F_c^2)/3.$$

separation on silica plates with 1:1 hexane– CH_2Cl_2 as eluent yielded five bands. The first fraction was a byproduct and the second and largest fraction contained product (2), yield 28 mg, 21%. The other three fractions contained some minor products such as disubstituted $\text{HRuCo}_3(\text{CO})_{12}$ and a ruthenium complex as characterized by IR spectra. Black crystals for the X-ray study were obtained from CH_2Cl_2 . IR: 2084m, 2049s, 1865m, 1847m. ¹H NMR: 7.4 ppm (m, CH), –19.7 ppm (s, H). Calc. for $\text{RuCo}_3\text{PS}_3\text{O}_{11}\text{C}_{23}\text{H}_{13}$: C 31.85%, H 1.16%. Found: C 31.30%, H 1.23%.

4.1.3. Synthesis of $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{S}_2\text{C}_4\text{H}_8)$ (3)

A mixture of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ (150 mg, 0.20 mmol) and $\text{S}_2\text{C}_4\text{H}_8$ (24 mg, 0.20 mmol) in 40 ml of THF was refluxed for 3 h. The mixture was dried in vacuo and the residue chromatographed on a silica column in air. Elution with hexane gave a yellow fraction of the unreacted starting cluster. Further elution with hexane–dichloromethane 1:1 mixture produced a red fraction of the main product (62 mg, 48%). Red crystals were obtained from CH_2Cl_2 . IR: 2096m, 2067s, 2060s, 2028s, 2007m, 1966w. ¹H NMR: 3.7 ppm (s, CH₂), 2.7 ppm (t, CH₂), 2.0 ppm (m, CH₂), –17.3 ppm (br., H). Calc.

for $\text{Ru}_4\text{PS}_2\text{O}_{10}\text{C}_{14}\text{H}_{12}$: C 20.79%, H 1.50%. Found: C 21.35%, H 1.75%.

4.1.4. X-ray crystallography

Data were collected on a Nicolet R3m diffractometer using Mo–K α radiation ($\lambda = 71.073$ pm). Intensities were corrected for background, polarization and Lorentz factors. Empirical absorption correction was made from ψ -scan data for 3. Empirical absorption correction did not produce any improvement in structures 1 and 2. Table 10 presents further crystallographic data. All structures were solved with the use of the SHELXL93 program [23]. Anisotropic refinement was carried out for all non-hydrogen atoms. The protons were placed in idealized positions with C–H distances of 96 pm and isotropic temperature factors of 0.08 \AA^2 .

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