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**Dichloro- and Dibromo-
[N-(2-pyridylmethylidene)-2-thienylmethyl-
amine-*N,N'*]copper(II) Complexes, [CuCl₂-
(C₁₁H₁₀N₂S)] and [CuBr₂(C₁₁H₁₀N₂S)]**

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Abstract

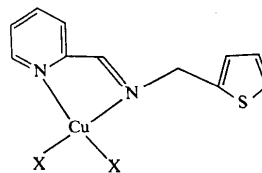
The crystal structures of dichloro- (2) and dibromo- [N-(2-pyridylmethylidene)-2-thienylmethylamine-*N,N'*]copper(II) (1) have been determined to investigate the coordination of the metal centre. In both cases, the two N atoms and two halogen anions are coordinated to the copper(II) and the S atom is free. For the dibromo complex, the structure is monomeric, while the dichloro complex forms dimers (di- μ -chloro-bis{chloro[N-(2-pyridylmethylidene)-2-thienylmethylamine-*N,N'*]copper(II)})

Comment

The results presented here form part of a project directed towards the synthesis and study of ligands designed to

bind two metal ions in close proximity. The ligand *N*-(2-pyridylmethylidene)-2-thienylmethylamine has been prepared in the hope that it might show enhanced affinity, compared with analogous ligands containing N and/or O donor atoms, for 'soft' cations, in particular those of the second and third transition series (Manzur *et al.*, 1993).

The copper(II) complexes, (1) and (2), of the ligand were prepared and the crystal structures determined to verify that the copper centres are each coordinated to the two N atoms and the S atom is free to bond to another metal centre.



- (1) X = Br
(2) X = Cl

The structure of the bromo complex (1) consists of monomeric units linked in the crystal by intermolecular hydrogen bonds. The copper centre is bonded to two Br anions and to two N atoms of the organic chelate (Fig. 1). The geometry around the metal centre can be described as distorted tetrahedral, with Cu—Br(1) = 2.360 (1), Cu—Br(2) = 2.348 (1), Cu—N(1) = 2.001 (3) and Cu—N(2) = 2.016 (4) Å. The dihedral angle between the planes N(1)—Cu—N(2) and Br(1)—Cu—Br(2) is 137.1°. The S heterocycle is quite planar, with C(7) and N(2) -0.0188 and 1.3466 Å, respectively, out of the plane. The bidentate moiety in the organic ligand is much less planar, with the Cu atom 0.0233 Å out of the plane. The dihedral angle between

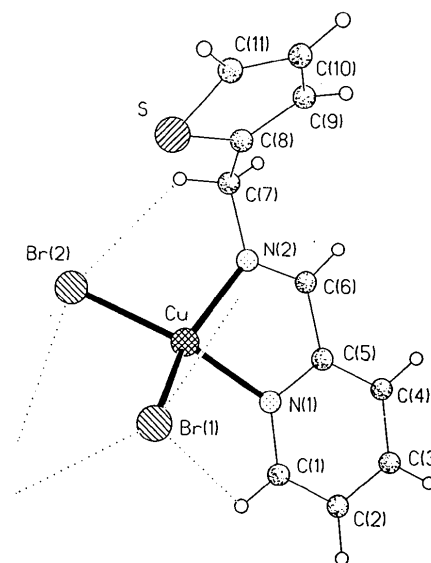


Fig. 1. View of a molecule of [CuBr₂(C₁₁H₁₀N₂S)] (1).

these two mean planes is 64.5° . The structure is stabilized by short nonbonding contacts [Br(1)··H(1)—C(1) = 2.985 and Br(2)··H(7B)—C(7) = 2.916 Å] and intermolecular bonds [Br(2)··H(1)—C(1) = 2.914, Br(2)··H(3)—C(3) = 2.964 and Br(1)··H(7A)—C(7) = 2.918 Å].

The chloro complex (2) forms a dimer, comprising two [CuCl₂(C₁₁H₁₀N₂S)] monomers held together by two Cu—Cl bonds. The [CuCl]₂ unit, defined by Cl(1)—Cu = 2.254 (1), Cl(1)—Cuⁱ = 2.698 (1) Å, Cu—Cl(1ⁱ)—Cuⁱ = 88.9 (1)°, is planar with an inversion centre. Each Cu atom is bonded to two N atoms of the organic moiety and to three Cl ions, two belonging to the monomeric unit and a third from the neighbouring monomeric species. The geometry of the first coordination sphere is well described as square pyramidal, with the basal plane formed by N(1), N(2), Cl(1) and Cl(2), which deviate from the best mean plane by -0.169 (3), 0.168 (3), -0.133 (1) and 0.134 (1) Å, respectively. The apical site is occupied by Cl(1ⁱ) (belonging to the basal plane of a neighbouring monomer) at 2.844 (1) Å from the plane, with the Cu atom deviating 0.155 (2) Å in the same direction as Cl(1ⁱ). The N chelate is planar. The S heterocycle is disordered over two well defined unequally occupied orientations (occupation factors 0.625 and 0.375), nearly related by a twofold rotation almost parallel to the C(7)—C(8) bond (Fig. 2). The interatomic distances in the group were constrained in accordance with the structure of the homologous Br complex. The constrained refinement led to some oscillations and, thus, rather large final Δ/σ values for the positional parameters in the refinement cycle. Convergence for the rest of the structure was quite good.

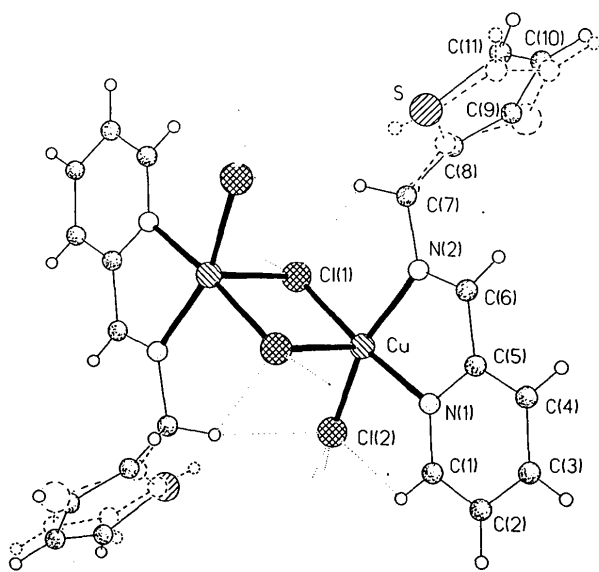


Fig. 2. View of the dimer of [CuCl₂(C₁₁H₁₀N₂S)] (2).

As for the Br complex, the structure is stabilized by short nonbonding contacts [Cl(2)··H(1)—C(1) = 2.662, Cl(2)··H(7A)—C(7) = 2.782 Å] and interdimeric contacts [Cl(1)··H(4)—C(4) = 2.810, Cl(1)··H(7A)—C(7) = 2.869 Å]. There is an extra interdimeric contact from Cl(2) towards two almost coincident H-atom sites of the disordered S heterocycle [H(11) in one of the orientations and H(10ⁱ) in the other], shown in Fig. 2 as a pair of dotted lines. This prevents any possibility of free rotation around C(7)—C(8) and anchors the hetero group to either of the two possible orientations compatible with the Cl(2)··H bond.

Experimental

The ligand, prepared from 2-pyridylcarboxaldehyde and 2-thienylmethylamine, was added to a solution of CuX₂ (X = Cl, Br; molar ratio 1:1). The resulting microcrystalline solid was recrystallized from an acetonitrile-water solution.

Compound (1)

Crystal data

[CuBr₂(C₁₁H₁₀N₂S)]

M_r = 425.6

Monoclinic

*P*2₁/*n*

a = 8.110 (1) Å

b = 11.848 (1) Å

c = 13.832 (2) Å

β = 95.69 (1)°

V = 1322.5 (3) Å³

Z = 4

D_x = 2.138 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 5–10°

μ = 7.829 mm⁻¹

T = 293 K

Polyhedra

0.40 × 0.20 × 0.16 mm

Brownish

Data collection

Siemens R3m diffractometer

$\theta/2\theta$ scans

(4.19–29.3° min⁻¹)

Absorption correction:

empirical

T_{min} = 0.428, *T_{max}* =

0.804

1880 measured reflections

1735 independent reflections

1355 observed reflections

[*F* > 4.0σ(*F*)]

R_{int} = 0.034

θ_{\max} = 22.5°

h = 0 → 8

k = 0 → 12

l = -14 → 14

2 standard reflections

monitored every 48

reflections

intensity variation: none

Refinement

Refinement on *F*

R = 0.024

wR = 0.034

S = 0.57

1355 reflections

154 parameters

H-atom parameters not

refined

Calculated weights

$w = 1/[\sigma^2(F) + 0.0022F^2]$

(Δ/σ)_{max} = 0.001

$\Delta\rho_{\max}$ = 0.34 e Å⁻³

$\Delta\rho_{\min}$ = -0.44 e Å⁻³

Atomic scattering factors

from *International Tables for Crystallography* (1992),

Vol. C, Tables 6.1.1.4 and

6.1.1.5)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (1)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
Cu	-0.0599 (1)	0.8364 (1)	0.6089 (1)	0.029 (1)
Br(1)	0.1505 (1)	0.8439 (1)	0.5028 (1)	0.041 (1)
Br(2)	-0.2871 (1)	0.7779 (1)	0.5023 (1)	0.045 (1)
N(1)	0.0479 (4)	0.9460 (3)	0.7055 (3)	0.027 (1)
N(2)	-0.1329 (4)	0.7677 (3)	0.7310 (3)	0.027 (1)
C(1)	0.1360 (5)	1.0367 (4)	0.6886 (3)	0.033 (2)
C(2)	0.1994 (5)	1.1076 (4)	0.7626 (4)	0.037 (2)
C(3)	0.1776 (5)	1.0810 (4)	0.8575 (4)	0.040 (2)
C(4)	0.0890 (5)	0.9849 (4)	0.8751 (3)	0.035 (2)
C(5)	0.0233 (5)	0.9204 (4)	0.7992 (3)	0.026 (1)
C(6)	-0.0789 (5)	0.8198 (4)	0.8077 (3)	0.026 (1)
C(7)	-0.2385 (5)	0.6664 (4)	0.7380 (3)	0.031 (1)
C(8)	-0.1421 (5)	0.5612 (4)	0.7306 (3)	0.030 (2)
C(9)	-0.0724 (6)	0.4954 (4)	0.8056 (4)	0.036 (2)
C(10)	0.0106 (6)	0.3984 (4)	0.7721 (4)	0.040 (2)
C(11)	-0.0002 (6)	0.3926 (4)	0.6747 (4)	0.044 (2)
S	-0.1072 (2)	0.5026 (1)	0.6196 (1)	0.042 (1)

2396 measured reflections
1707 independent reflections
1563 observed reflections
[*F* > 4.0σ(*F*)]

2 standard reflections
monitored every 48
reflections
intensity variation: none

Refinement

Refinement on *F**R* = 0.027*wR* = 0.044*S* = 1.02

1563 reflections

200 parameters

H-atom parameters not
refined

Calculated weights

$$w = 1/[\sigma^2(F) + 0.0022F^2]$$

(Δ/σ)_{max} = 0.96Δρ_{max} = 0.28 e Å⁻³Δρ_{min} = -0.54 e Å⁻³

Atomic scattering factors

from *International Tables*
for *Crystallography* (1992),
Vol. C, Tables 6.1.1.4 and
6.1.1.5)

Table 2. Selected geometric parameters (Å, °) for (1)

Cu—Br(1)	2.360 (1)	C(3)—C(4)	1.380 (7)
Cu—Br(2)	2.348 (1)	C(4)—C(5)	1.364 (6)
Cu—N(1)	2.001 (3)	C(5)—C(6)	1.463 (6)
Cu—N(2)	2.016 (4)	C(7)—C(8)	1.480 (6)
N(1)—C(1)	1.324 (6)	C(8)—C(9)	1.374 (6)
N(1)—C(5)	1.365 (5)	C(8)—S	1.733 (5)
N(2)—C(6)	1.268 (5)	C(9)—C(10)	1.432 (7)
N(2)—C(7)	1.483 (6)	C(10)—C(11)	1.344 (8)
C(1)—C(2)	1.383 (7)	C(11)—S	1.704 (5)
C(2)—C(3)	1.378 (7)		
Br(1)—Cu—Br(2)	101.0 (1)	C(2)—C(3)—C(4)	118.4 (4)
Br(1)—Cu—N(1)	95.5 (1)	C(3)—C(4)—C(5)	119.8 (4)
Br(2)—Cu—N(1)	151.0 (1)	N(1)—C(5)—C(4)	121.6 (4)
Br(1)—Cu—N(2)	145.8 (1)	N(1)—C(5)—C(6)	113.2 (4)
Br(2)—Cu—N(2)	97.4 (1)	C(4)—C(5)—C(6)	125.2 (4)
N(1)—Cu—N(2)	81.2 (1)	N(2)—C(6)—C(5)	118.8 (4)
Cu—N(1)—C(1)	128.0 (3)	N(2)—C(7)—C(8)	111.4 (4)
Cu—N(1)—C(5)	113.2 (3)	C(7)—C(8)—C(9)	127.2 (4)
C(1)—N(1)—C(5)	118.7 (4)	C(7)—C(8)—S	122.2 (3)
Cu—N(2)—C(6)	113.5 (3)	C(9)—C(8)—S	110.6 (3)
Cu—N(2)—C(7)	127.0 (3)	C(8)—C(9)—C(10)	112.4 (5)
C(6)—N(2)—C(7)	119.6 (4)	C(9)—C(10)—C(11)	112.4 (4)
N(1)—C(1)—C(2)	121.9 (4)	C(10)—C(11)—S	112.9 (4)
C(1)—C(2)—C(3)	119.5 (4)	C(8)—S—C(11)	91.8 (2)

Compound (2)

Crystal data

[CuCl₂(C₁₁H₁₀N₂S)]*M_r* = 336.7

Triclinic

*P*1*a* = 8.115 (1) Å*b* = 8.772 (1) Å*c* = 10.226 (1) Å

α = 79.21 (1)°

β = 75.27 (1)°

γ = 67.92 (1)°

V = 649.0 (2) Å³*Z* = 2

Data collection

Siemens *R3m* diffractometer

θ/2θ scans

(4.19–29.3° min⁻¹)

Absorption correction:

none

D_x = 1.723 Mg m⁻³Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 5–10°

μ = 2.231 mm⁻¹*T* = 293 K

Needles

0.50 × 0.20 × 0.10 mm

Green

*R*_{int} = 0.012θ_{max} = 22.5°*h* = 0 → 8*k* = -8 → 9*l* = -10 → 11Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
Cu	0.2120 (1)	0.5201 (1)	0.4715 (1)	0.034 (1)
Cl(1)	-0.0627 (1)	0.6939 (1)	0.5623 (1)	0.041 (1)
Cl(2)	0.2310 (1)	0.6804 (1)	0.2717 (1)	0.050 (1)
N(1)	0.4590 (3)	0.3494 (3)	0.4119 (2)	0.034 (1)
N(2)	0.2597 (3)	0.3964 (3)	0.6567 (3)	0.033 (1)
C(1)	0.5543 (4)	0.3261 (4)	0.2858 (3)	0.047 (1)
C(2)	0.7131 (5)	0.1943 (4)	0.2588 (4)	0.055 (2)
C(3)	0.7785 (5)	0.0823 (4)	0.3621 (4)	0.056 (2)
C(4)	0.6810 (4)	0.1058 (4)	0.4935 (4)	0.048 (1)
C(5)	0.5232 (4)	0.2395 (4)	0.5150 (3)	0.036 (1)
C(6)	0.4070 (4)	0.2739 (4)	0.6493 (3)	0.038 (1)
C(7)	0.1324 (4)	0.4351 (3)	0.7896 (3)	0.040 (1)
C(8)	0.1907 (19)	0.3200 (12)	0.9086 (10)	0.037 (5)
C(9)	0.276 (3)	0.3317 (17)	1.0043 (15)	0.065 (7)
C(10)	0.2975 (17)	0.1945 (10)	1.1075 (9)	0.051 (4)
C(11)	0.2172 (17)	0.0914 (10)	1.0930 (8)	0.049 (4)
S	0.1211 (6)	0.1498 (5)	0.9533 (3)	0.060 (1)
C(8')	0.173 (3)	0.3135 (18)	0.9093 (14)	0.039 (8)
C(9')	0.135 (3)	0.170 (2)	0.9547 (19)	0.068 (13)
C(10')	0.232 (3)	0.0718 (15)	1.0582 (18)	0.062 (7)
C(11')	0.331 (3)	0.1454 (13)	1.0924 (15)	0.048 (6)
S'	0.3163 (18)	0.3318 (9)	1.0007 (8)	0.059 (2)

Table 4. Selected geometric parameters (Å, °) for (2)

Cu—Cl(1')	2.698 (1)	N(2)—C(7)	1.492 (3)
Cu—Cl(2)	2.259 (1)	C(1)—C(2)	1.375 (4)
Cu—N(1)	2.023 (2)	C(2)—C(3)	1.367 (5)
Cu—N(2)	2.050 (2)	C(3)—C(4)	1.384 (5)
Cu—Cl(1)	2.254 (1)	C(4)—C(5)	1.374 (4)
N(1)—C(1)	1.333 (4)	C(5)—C(6)	1.467 (4)
N(1)—C(5)	1.354 (4)	C(7)—C(8)	1.482 (10)
N(2)—C(6)	1.268 (3)		
Cl(1')—Cu—Cl(2)	105.5 (1)	Cu—N(2)—C(6)	113.7 (2)
Cl(1')—Cu—N(1)	88.1 (1)	Cu—N(2)—C(7)	125.1 (2)
Cl(2)—Cu—N(1)	92.9 (1)	C(6)—N(2)—C(7)	121.1 (2)
Cl(1')—Cu—N(2)	90.8 (1)	N(1)—C(1)—C(2)	121.8 (3)
Cl(2)—Cu—N(2)	162.1 (1)	C(1)—C(2)—C(3)	120.5 (3)
N(1)—Cu—N(2)	80.2 (1)	C(2)—C(3)—C(4)	118.2 (3)
Cl(1')—Cu—Cl(1)	91.1 (1)	C(3)—C(4)—C(5)	119.0 (3)
Cl(2)—Cu—Cl(1)	93.7 (1)	N(1)—C(5)—C(4)	122.4 (3)
N(1)—Cu—Cl(1)	173.3 (1)	N(1)—C(5)—C(6)	114.0 (2)
N(2)—Cu—Cl(1)	93.2 (1)	C(4)—C(5)—C(6)	123.6 (3)
Cu—Cl(1')—Cu ¹	88.9 (1)	N(2)—C(6)—C(5)	118.4 (3)
Cu—N(1)—C(1)	128.0 (2)	N(2)—C(7)—C(8)	115.1 (4)
Cu—N(1)—C(5)	113.6 (2)	N(2)—C(7)—C(8')	117.4 (6)
C(1)—N(1)—C(5)	118.1 (2)		

Symmetry code: (i) -*x*, 1 - *y*, 1 - *z*.

Data collection: *P3/P4-PC* (Siemens, 1991). Cell refinement: *P3/P4-PC*. Data reduction: *XDISK* in *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *XS* in *SHELXTL-Plus*. Program(s) used to refine structure: *XLS* in *SHELXTL-Plus*. Molecular graphics: *XP* in *SHELXTL-Plus*. Software used to prepare material for publication: *XPUBL* in *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71805 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1080]

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A Tri- μ -chloro Dirhodium(III) Complex $[\text{Rh}_2(\mu\text{-Cl})_3(\text{triphos})_2](\text{CF}_3\text{SO}_3)_3$ \text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3

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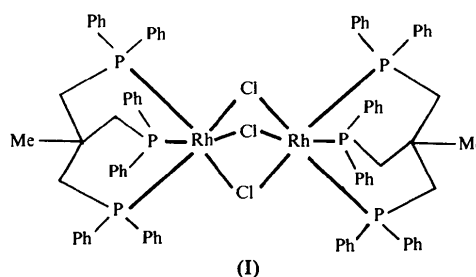
Abstract

The crystal structure of tri- μ -chloro-bis{2-[(diphenylphosphino)methyl]-2-methyl-1,3-propanediyl}bis(diphenylphosphine)-*P,P',P''*dirhodium(III) tris(trifluoromethanesulfonate), $[\text{Rh}_2(\mu\text{-Cl})_3(\text{triphos})_2](\text{CF}_3\text{SO}_3)_3$, where triphos is the tripod-like tridentate ligand $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$, has been determined by X-ray diffraction.

The tri-cationic complex $[\text{Rh}_2(\mu\text{-Cl})_3(\text{triphos})_2]$ has a distorted cofacial bioctahedral geometry with two Rh atoms sharing a triangular face formed by three bridging Cl atoms. It is characterized by a long Rh...Rh distance of 3.414 (4) Å and by a consequent elongation of the coordination polyhedron. The coordination geometry is also distorted by a 34° rotation of both [(triphos)Rh] units around the *M*...*M* direction.

Comment

In the course of studies of the reactivity of the Rh^{III} complex $[\text{RhCl}_3(\text{triphos})]$, where triphos is the tripod-like tridentate ligand $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$, a number of mono- and polynuclear compounds were obtained, depending on the reaction conditions and the ratio of reagents. Some of the products display diverse and novel structural properties. One of them, the di- μ -chloro complex $[\text{Rh}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{triphos})_2]^{2+}$ was found to form in a methanol solution of $[\text{RhCl}_3(\text{triphos})]$ and then to react slowly yielding the tri- μ -chloro complex $[\text{Rh}_2(\mu\text{-Cl})_3(\text{triphos})_2]^{3+}$, (1) (Ott, 1986). This latter reaction occurred under the crystallization conditions, as the X-ray analysis showed.



The crystal structure of the title compound consists of discrete $[\text{Rh}_2(\mu\text{-Cl})_3(\text{triphos})_2]^{3+}$ cations and $(\text{CF}_3\text{SO}_3)^-$ anions with no short contacts between atoms of different ions. A perspective view of the cation is shown in Fig. 1.

Each Rh atom is octahedrally coordinated by the three P atoms of the triphos ligand and by the three bridging Cl atoms. The two octahedra share the face formed by the Cl atoms to form a cofacial bioctahedral polyhedron. The elongation axis of the polyhedron lies on the threefold axis of the cubic cell. Thus the whole complex has crystallographic C_{3v} symmetry and only one third of it is symmetry independent (Fig. 2).

The geometry of the cofacial bioctahedron presents severe distortions. The two [(triphos)Rh] units are rotated around the Rh...Rh direction by 34.0 (2)° with respect to each other. As a result of this rotation each P atom does not lie on the plane defined by Rh(1), Rh(2) and its Cl_{trans} atom, but is rotated away from the plane, by 16° for the P atoms of the [(triphos)Rh(1)] unit and by -18° for those of the [(triphos)Rh(2)] unit (Fig. 3). This type of distortion has been found in two other triphos complexes: $[\text{Fe}_2(\mu\text{-H})_3(\text{triphos})_2]^+$ and $[\text{Co}_2(\mu\text{-H})_3(\text{triphosAs})_2]^+$ (Dapporto,