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Crystal structure of $HRu_3[\mu_3,\eta^2\text{-}P(NEt_2)_2](CO)_9$ containing a five-membered cage-like Ru_3PN skeleton

Liu Qiwang, Hu Xiang, Wu Binfang and Liu Shutang

Department of Chemistry, Inner Mongolia University, Huhhot,
Inner Mongolia 010021 (People's Republic of China);
Structural Chemistry Research Laboratory, Fujian Research Institute of Matter Structure,
Chinese Academy of Sciences, Fuzhou, Fujian (People's Rupublic of China)

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Abstract

The reaction of $Ru_3(CO)_{12}$ with $(Et_2N)_2PCl$ results in a brown-yellow crystal compound whose composition is revealed by X-ray crystal structure determination to be $HRu_3[P(NEt_2)_2](CO)_9$ **1**. **1** is a cluster, containing a five-membered Ru_3PN cage-like skeleton. On the skeleton there is a $\mu_3,\eta^2\text{-}P(NEt_2)_2$ ligand which donates five electrons and is bound to the Ru_3 core with its P atom as a μ,three-electron donor and one of its N atoms as a two-electron donor. This crystal has MW = 731.55, monoclinic, $P2_1/n, a = 9.352(4)$, $b = 15.177(2)$, $c = 18.003(3)$ Å, $\beta = 97.13(2)°$, $V = 2535.4$ Å^3, $Z = 4$, $D_c = 1.863$ g cm^{-3}, with 3793 unique observable reflections ($I \geq 3\sigma(I)$) refined by a full-matrix least-squares procedure so that the final $R = 0.026$, $R_w = 0.031$.

Introduction

A bridging ligand or a multidentate ligand coordinates with a metal cluster by more than one bonding atom to form a chelate-like structure which, as has been previously pointed out [1], can increase the stability of the metal atom framework of the cluster, so providing a means of preventing cluster fragmentation during catalytic reactions. Since we know that ligands having soft coordinated atoms C, S and P readily bind to a metal carbonyl cluster, which is in sharp contrast to ligands having hard atoms such as O and N. However, in some cluster compounds of low-oxidation-state metals, owing to chelation or bridging effects, O or N atom can coordinate to the metal core, to give a three-atomed μ_3-bridge. The CCO, NCN, SCN, groups in N- or O-containing ligands form a μ_3,η^2 bridge and bind to three nuclear metal cores to give a six-membered M_3ABC skeleton (A, C being the coordinated atoms). Here we report a new metal carbonyl cluster $HRu_3[P(NEt_2)_2](CO)_9$, which possesses a five-membered Ru_3PN cage-like skeleton and a phosphido- and amine-containing $\mu_3,\eta^2\text{-}P(NEt_2)_2$ ligand as a five-electron donor. This five membered cage-like structure may serve as stabilizing factor for the cluster and enables the hard atom N to become a coordinating atom in the cluster.

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Experimental

Preparation of $HRu_3[\mu_3,\eta^2\text{-}P(NEt_2)_2](CO)_9$, *1*

$Ru_3(CO)_{12}$ (250 mg, 0.39 mmol) and $(Et_2N)_2PCl$ (70 mg, 0.36 mmol) were dissolved in THF (30 ml), the solution was refluxed for 13 h. (under Ar, 62°C) and evacuated to dryness. The resulting brown oil was dissolved in benzene. The mixture was chromatographed on silica-gel column. The separation and crystallization yielded brownish yellow prismatic crystals of **1** which are moderately stable in the air.

X-Ray crystallography

The brownish yellow prismatic crystal (0.20 × 0.30 × 0.20 mm) was measured at room temperature on an Enraf–Nonius CAD-4 diffractometer through graphite monochromated Mo-K_α radiation and diffraction data to $2\theta \leqslant 50°$ were collected in an $\omega/2\theta$ scan mode. The 3793 unique reflections ($I \geqslant 3\sigma(I)$) observed were corrected for Lorentz polarization and empirical absorption. The crystal is monoclinic with unit cell parameters $a = 9.352(4)$, $b = 15.177(2)$, $c = 18.003(3)$ Å, $\beta = 97.13(2)°$, $V = 2535.4$ Å^3, $Z = 4$, $D_c = 1.863$ g cm^{-3}. Space group $P2_1/n$.

Structure determination and refinement

All calculations were performed on a PDP 11/44 computer with the SDP programs. At first, a number of coordinate parameters of non-hydrogen atoms were obtained by the direct methods from the electron density map. Then difference-Fourier syntheses were used to reveal the positions of all remaining non-hydrogen

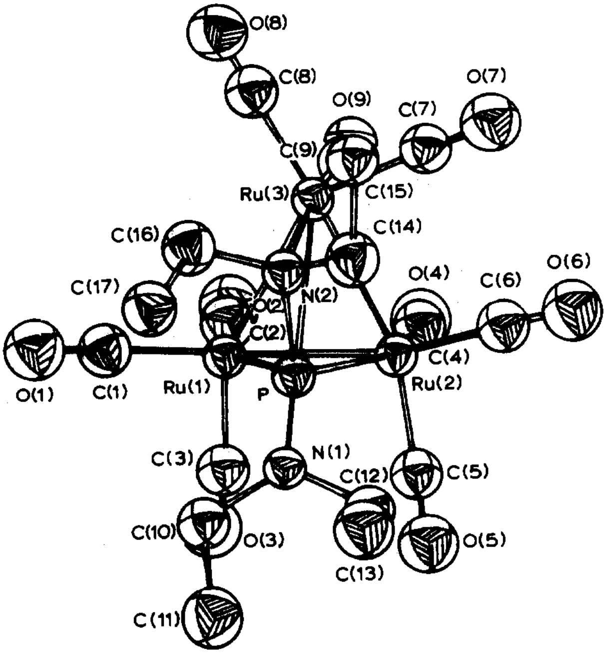


Fig. 1. Molecular structure of $HRu_3(\mu_3,\eta^2\text{-}P(NEt)_2)_2(CO)_9$.

Table 1

Atomic coordinates and thermal parameters of non-hydrogen atoms for 1

Atom	x	y	z	B_{eq} [a]
Ru(1)	0.45043(4)	0.11720(3)	0.61664(2)	2.832(8)
Ru(2)	0.25078(4)	0.25293(3)	0.63200(2)	2.773(7)
Ru(3)	0.35489(4)	0.16124(3)	0.76228(2)	2.621(7)
P	0.4956(1)	0.25885(8)	0.66004(7)	2.44(2)
O(1)	0.7306(5)	0.0119(4)	0.6334(3)	7.3(1)
O(2)	0.2305(6)	−0.0294(3)	0.5703(3)	7.8(1)
O(3)	0.4618(6)	0.1648(4)	0.4543(2)	6.7(1)
O(4)	−0.0162(5)	0.1395(4)	0.5804(3)	7.1(1)
O(5)	0.2603(6)	0.3474(4)	0.4850(3)	7.0(1)
O(6)	0.1093(6)	0.4046(3)	0.7053(3)	6.8(1)
O(7)	0.1763(4)	0.2878(3)	0.8433(2)	5.3(1)
O(8)	0.4758(5)	0.0590(3)	0.9036(2)	5.8(1)
O(9)	0.0975(5)	0.0415(3)	0.7352(3)	6.5(1)
N(1)	0.5971(4)	0.3329(3)	0.6223(2)	3.37(9)
N(2)	0.5429(4)	0.2522(3)	0.7592(2)	2.43(7)
C(1)	0.6271(6)	0.0511(4)	0.6283(3)	4.3(1)
C(2)	0.3119(7)	0.0235(4)	0.5879(4)	4.7(1)
C(3)	0.4573(6)	0.1477(4)	0.5160(3)	4.1(1)
C(4)	0.0807(6)	0.1814(4)	0.6013(4)	4.4(1)
C(5)	0.2529(6)	0.3107(4)	0.5393(3)	4.2(1)
C(6)	0.1632(6)	0.3474(4)	0.6789(3)	4.2(1)
C(7)	0.2433(5)	0.2421(4)	0.8121(3)	3.5(1)
C(8)	0.4380(6)	0.0964(4)	0.8505(3)	3.7(1)
C(9)	0.1929(6)	0.0872(4)	0.7450(3)	4.2(1)
C(10)	0.7272(6)	0.3074(5)	0.5882(4)	5.4(1)
C(11)	0.7176(9)	0.3348(7)	0.5056(4)	8.2(2)
C(12)	0.5503(7)	0.4261(4)	0.6157(4)	4.7(1)
C(13)	0.6669(9)	0.4918(5)	0.6496(5)	6.9(2)
C(14)	0.5317(6)	0.3399(3)	0.7976(3)	3.1(1)
C(15)	0.5492(6)	0.3338(4)	0.8832(3)	4.0(1)
C(16)	0.6830(5)	0.2058(4)	0.7856(3)	3.5(1)
C(17)	0.8201(6)	0.2591(5)	0.7783(4)	5.3(2)

[a] $B_{eq} = 8\pi^2(u_1 + u_2 + u_3)/3$ where u_1, u_2, u_3 (in Å^2) are the principal axes of the thermal ellipsoid.

atoms. Final refinement was conducted through four runs of full-matrix least-squares procedure with positional parameters of non-hydrogen atoms corrected and anisotropic thermal parameters adjusted. Resulting values were $R = 0.026$, $R_w = 0.031$. Final difference-Fourier syntheses were done without anomalous structural features.

The structure of 1 is shown in Fig. 1, the final positions and thermal parameters of non-hydrogen atoms are listed in Table 1 and selected bond lengths and angles in Table 2. The crystal and refinement data of 1 are shown in Table 3.

Results and discussion

The molecule is formally derived from $Ru_3(CO)_{12}$ by replacing three terminal CO ligands with a one-electron donating μ-H ligand and a five-electron donating μ_3,η^2-$P(NEt_2)_2$ ligand (P atom as μ, three-electron donor and N atom as two-electron donor). The three Ru atoms form a triangle with Ru(1)–Ru(2) = 2.8169(6), Ru(2)–Ru(3) = 2.7961(6), Ru(1)–Ru(3) = 2.9497(6) Å. The hydride H may be de-

Table 2

Selected bond lengths (Å) and angles (°) for 1

Ru(1)-Ru(2)	2.8169(6)	Ru(3)-C(7)	1.905(6)
Ru(1)-Ru(3)	2.9497(6)	Ru(3)-C(8)	1.946(5)
Ru(1)-P	2.308(1)	Ru(3)-C(9)	1.881(6)
Ru(1)-C(1)	1.922(7)	P-N(1)	1.670(5)
Ru(1)-C(2)	1.949(6)	P-N(2)	1.787(4)
Ru(1)-C(3)	1.879(6)	O(1)-C(1)	1.130(8)
Ru(2)-Ru(3)	2.7961(6)	O(2)-C(2)	1.125(9)
Ru(2)-P	2.285(1)	O(3)-C(3)	1.146(7)
Ru(2)-C(4)	1.948(6)	O(4)-C(4)	1.133(7)
Ru(2)-C(5)	1.887(6)	O(5)-C(5)	1.136(8)
Ru(2)-C(6)	1.899(6)	O(6)-C(6)	1.138(8)
Ru(3)-N(2)	2.241(4)	O(7)-C(7)	1.131(7)
O(8)-C(8)	1.131(7)	O(9)-C(9)	1.125(7)
N(1)-C(10)	1.481(8)	N(1)-C(12)	1.481(7)
N(2)-C(14)	1.510(6)	N(2)-C(16)	1.511(7)
C(10)-C(11)	1.54(1)	C(12)-C(13)	1.55(1)
C(14)-C(15)	1.531(7)	C(16)-C(17)	1.537(8)
Ru(2)-Ru(1)-Ru(3)	57.95(1)	P-Ru(2)-C(5)	93.3(2)
Ru(2)-Ru(1)-P	51.78(4)	P-Ru(2)-C(6)	110.3(2)
Ru(2)-Ru(1)-C(1)	160.4(2)	C(4)-Ru(2)-C(5)	96.1(3)
Ru(2)-Ru(1)-C(2)	97.6(2)	C(4)-Ru(2)-C(6)	99.5(3)
Ru(2)-Ru(1)-C(3)	91.0(2)	C(5)-Ru(2)-C(6)	95.4(3)
Ru(3)-Ru(1)-P	63.31(3)	Ru(1)-Ru(3)-Ru(2)	58.64(1)
Ru(3)-Ru(1)-C(1)	111.8(2)	Ru(1)-Ru(3)-N(2)	78.0(1)
Ru(3)-Ru(1)-C(2)	97.8(3)	Ru(1)-Ru(3)-C(7)	143.9(2)
Ru(3)-Ru(1)-C(3)	148.4(2)	Ru(1)-Ru(3)-C(8)	118.4(2)
P-Ru(1)-C(1)	109.4(2)	Ru(1)-Ru(3)-C(9)	92.5(2)
P-Ru(1)-C(2)	148.9(2)	Ru(2)-Ru(3)-N(2)	82.26(9)
P-Ru(1)-C(3)	94.0(2)	Ru(2)-Ru(3)-C(7)	85.4(2)
C(1)-Ru(1)-C(2)	100.5(3)	Ru(2)-Ru(3)-C(8)	176.7(2)
C(1)-Ru(1)-C(3)	95.9(3)	Ru(2)-Ru(3)-C(9)	88.2(2)
C(2)-Ru(1)-C(3)	91.4(3)	N(2)-Ru(3)-C(7)	95.4(2)
Ru(1)-Ru(2)-Ru(3)	63.40(1)	N(2)-Ru(3)-C(8)	95.5(2)
Ru(1)-Ru(2)-P	52.56(3)	N(2)-Ru(3)-C(9)	169.1(2)
Ru(1)-Ru(2)-C(4)	95.3(2)	C(7)-Ru(3)-C(8)	97.4(2)
Ru(1)-Ru(2)-C(5)	100.0(2)	C(7)-Ru(3)-C(9)	89.2(2)
Ru(1)-Ru(2)-C(6)	157.4(2)	C(8)-Ru(3)-C(9)	93.8(2)
Ru(3)-Ru(2)-P	66.36(3)	Ru(1)-P-Ru(2)	75.67(4)
Ru(3)-Ru(2)-C(4)	98.5(2)	Ru(1)-P-N(1)	125.4(2)
Ru(3)-Ru(2)-C(5)	158.7(2)	Ru(1)-P-N(2)	107.4(1)
Ru(3)-Ru(2)-C(6)	97.3(2)	Ru(2)-P-N(1)	122.9(2)
P-Ru(2)-C(4)	147.7(2)	Ru(2)-P-N(2)	109.7(1)
N(1)-P-N(2)	111.2(2)	P-N(1)-C(10)	122.0(5)
P-N(1)-C(12)	119.9(4)	C(10)-N(1)-C(12)	117.8(5)
Ru(3)-N(2)-P	87.8(1)	Ru(3)-N(2)-C(14)	115.6(3)
Ru(3)-N(2)-C(16)	110.9(3)	P-N(2)-C(14)	112.6(3)
P-N(2)-C(16)	116.0(4)	C(14)-N(2)-C(16)	111.9(3)
Ru(1)-C(1)-O(1)	178.4(6)	Ru(1)-C(2)-O(2)	178.6(6)
Ru(1)-C(3)-O(3)	178.8(6)	Ru(2)-C(4)-O(4)	177.0(6)
Ru(2)-C(5)-O(5)	176.7(5)	Ru(2)-C(6)-O(6)	178.4(5)
Ru(3)-C(7)-O(7)	177.6(6)	Ru(3)-C(8)-O(8)	174.5(5)
Ru(3)-C(9)-O(9)	178.7(5)	N(1)-C(10)-C(11)	112.2(5)
N(1)-C(12)-C(13)	113.4(6)	N(2)-C(14)-C(15)	113.7(5)
N(2)-C(16)-C(17)	115.3(5)		

Table 3

Crystal and refinement data of 1

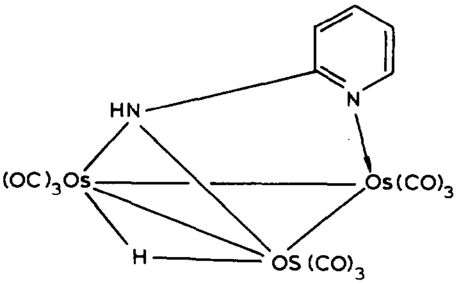
Formula	$C_{17}H_{21}Ru_3PN_2O_9$
MW	710.38
Crystal system	monoclinic
Crystal size, mm	0.2 × 0.30 × 0.20
Space group	$P2_1/n$ [a]
a, Å	9.352(4)
b, Å	15.177(2)
c, Å	18.003(3)
β,	97.13(2)°
V, Å^3	2535.4
Z	4
ρ(calcd), g cm^{-3}	1.861
μ, cm^{-1}	18.364 (for Mo-K_α radiation)
Radiation	Mo-K_α, graphite monochromator $\lambda = 0.71073$ Å
Diffractometer	Enraf–Nonius CAD-4
Scan speed, deg min^{-1}	5.0–0.50
Scan width	$0.66 + 0.35 \tan \theta$
2θ scan limits, deg	0–50
Scan method	$\omega - 2\theta$
Standard reflections	3
Unique data	4637
Unique, $F_o \geqslant 3\sigma F_o$	3793
R, %	0.026
R_w [b], ($w = 1.0$), %	0.031
Number of parameters	290
GOF	2.072
$\Delta(\rho)$max, e Å^{-3}	1.50

[a] Non-standard from $P2_1/c$. Equivalent position (x, y, z), $(\bar{x}, \bar{y}, \bar{z})$, $(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$, $(\frac{1}{2}-x, 2+y, \frac{1}{2}-z)$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w[F_o]^2]^{1/2}$. [c] GOF $= [\Sigma w(|F_o| - |F_c|)^2/(\text{no. obs} - \text{no. var})]^{1/2}$

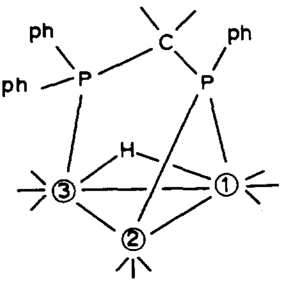
rived from the traced contamination water in the solvent THF. The H-bridged Ru(1)–Ru(3) bond is on average 0.14 Å longer than the other two Ru–Ru bonds. It has been demonstrated that such elongations are characteristic of bridging hydride ligands. [2–5]

The P atom and one N atom of the ligand $P(NEt_2)_2$ bond to the Ru_3 core and form a five-membered cage-like skeleton. The bond lengths: Ru(3)–N(2) = 2.241(4), Ru(1)–P = 2.308(1), Ru(2)–P = 2.285(1), N(2)–P = 1.787(4) Å; bond angles: Ru(3)–N(2)–P = 87.8(1)°, Ru(1)–P–Ru(2) = 75.67(4)°, Ru(1)–P–N(2) = 107.4(1)°, Ru(2)–P–N(2) = 109.7(1)°, and along the μ_3,N(2),P atoms, there is a symmetric plane for the five-membered skeleton.

The three-atom μ_3-bridges which bind to the triangular metal core are a common feature of many compounds involving oxygen- or nitrogen-containing ligands. The stabilization by bridging in clusters is comparable with the chelation effect in mononuclear compounds [6]. Thus the complex $HOs_3(CO)_9[NC_5H_4(NH)]$ [2] is stable and this cluster shows a three-atom NCN μ_3-bridge which binds to the Os_3 core to form a six-membered Os_3NCN cage-like skeleton as follows:



The cluster HRu$_3$(μ_3,η^2-PphCH$_2$Pph$_2$)(CO)$_9$ with a μ_2,3e-donating P atom has been made by Lugan et al. [3]. The crystal structure (**a**) shows that the P atom is unsymmetrically bridging to the two Ru atoms, the distance difference is 0.026 Å and reveals that the donated electron density is concentrated toward the Ru(2) atom (without bridging H) for the sake of equilibrium of electron density around each Ru atom. It is noted that the Ru(1) already has some extra electron density from the bridging H but Ru(2) has not. The crystal structure of our title compound is **1**(**a**) mode because the H-bridged Ru(1)–Ru(3) bond is longer than the other two Ru–Ru bonds. This structure shows a distance difference of 0.023 Å between the P atom and the two Ru atoms. These two **a**-mode crystal molecules do not simply obey the 18-electron rule for their three Ru atoms and their bridging H and bridging P are not fully symmetric. The HRu$_3$(μ_3,η^2-PphCH$_2$Pph$_2$)(CO)$_9$ has been found to contain an isomer **b** in solution as detected by ^{31}P NMR and ^{1}H NMR spec-



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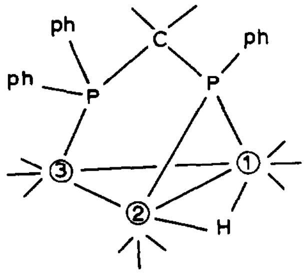

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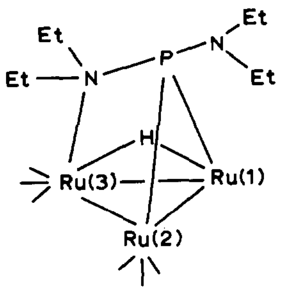
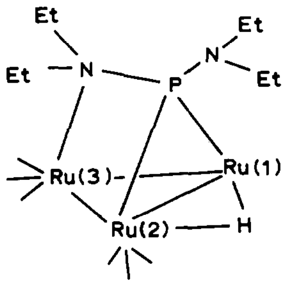


1a

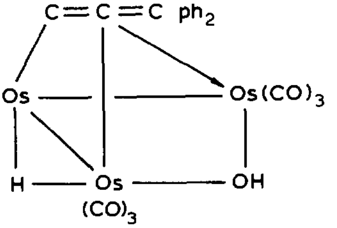


1b

troscopy. The positions of the H bridge in **a** and **b** are different and the **b** isomer does obey the 18-electron rule for all three Ru atoms.

The ^{1}H NMR spectrum of a solution of **1** shows two sets of bridging-H resonances (δ: -12.8 singlet, -15.5 doublet). Thus the **1b** isomer exists in solution.

The crystal molecular structure of $HRu_3(\mu_3,\eta^2\text{-}C_7H_4NS_2)(CO)_9$ with a μ_3,η^2-ligand involving a two-electron donating N atom has been determined by Jeannin et al. [4]. This cluster comprises a three-atom SCN bridge bonded to the Ru_3 core to form a six-membered Ru_3SCN cage-like skeleton. The $HRu_3(\mu_3,\eta^2\text{-}PphCH_2Pph_2)(CO)_9$ likewise comprises a three-atom PCP bridge bonded to the Ru_3 core to form a six-membered Ru_3PCP cage-like structure. The title compound is unique in the sense that it is composed of a two-atom PN bridge bonded to the Ru_3 core to form a five-membered Ru_3PN cage-like skeleton. This structure resembles that of $HOs_3(OH)(\mu_3,CCCph_2)(CO)_9$ [7] as made by Aime et al., which is composed of a Os_3CC five-membered cage-like skeleton but whose ligand is a four-electron donor and the Os_3 is an open triangle:



There is a Ru_3 carbonyl cluster $Ru_3[P(NMe_2)_3]_2(CO)_9$ in which the alkyl amino-phosphine molecules, as simple π-acid donors, have replaced the CO ligands [8], and only the P atoms of the ligand, as two-electron donors are coordinated to the metal core. The PR_2 ligand is generally a μ,η^1 three-electron donor which bridges the two metal atoms via the P atom in most of the metal carbonyl clusters. Compound **1** has a phosphido- and amine-containing ligand $P(NEt_2)_2$, as a μ_3,η^2 five electron donor, which is unique since its hard atom N is a donor-coordinating atom. The five membered cage-like structure probably stabilizes the cluster formed and enables the hard N atom to become an electron donor.

Supplementary material. Atomic thermal ellipsoid views of all non-hydrogen atoms of **1**; tables of interatomic distances and angles, final temperature factors, and a list of observed and calculated structure factors for **1** (19 pages) are available from Mr. Liu Qiwang.

Acknowledgement

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