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Key indicators

Single-crystal X-ray study
T = 183 K
Mean $\sigma(\text{C}-\text{C}) = 0.007 \text{ \AA}$
R factor = 0.039
wR factor = 0.107
Data-to-parameter ratio = 24.0

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

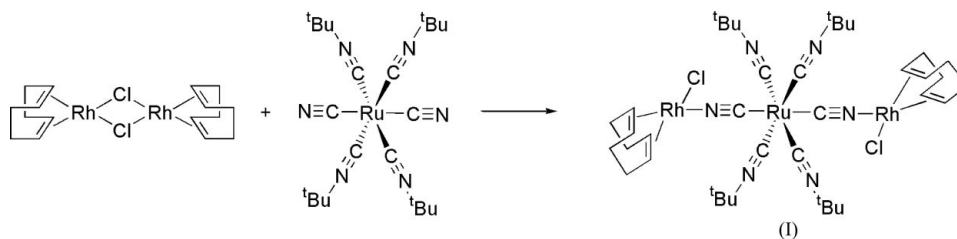
Tetrakis(*tert*-butyl isocyanide- $2\kappa\text{C}$)dichloro-
 $1\kappa\text{Cl}, 3\kappa\text{Cl}$ -di- μ -cyano- $1\kappa\text{N}:2\kappa\text{C}; 2\kappa\text{C}:3\kappa\text{N}$ -
bis[1,3(η^4)-cycloocta-1,5-diene]dirhodium(I)-
ruthenium(II)

The title compound, $[\text{Rh}_2\text{Ru}(\text{CN})_2\text{Cl}_2(\text{C}_8\text{H}_{12})_2(\text{C}_5\text{H}_9\text{N})_4]$, was obtained from the reaction of the chloro(1,5-cyclooctadiene)rhodium(I) dimer with *trans*-dicyanotetra(*tert*-butyl isocyanide)ruthenium(II) by cleavage of the chloro bridges in the dimeric rhodium starting complex. The molecular structure shows the Ru atom in a nearly ideal octahedral coordination geometry, whereas the Rh atoms are situated in square-planar ligand environments. The central ruthenium ion is located on a crystallographic twofold axis. The crystal structure is realized by infinite chains of the trinuclear complex units which are connected by $\text{C}-\text{H}\cdots\text{Cl}$ interactions. These chains are further linked by another $\text{C}-\text{H}\cdots\text{Cl}$ interaction to produce the observed three-dimensional structure.

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Comment

The title compound, (I), is the first structurally characterized example of a compound with an Rh and an Ru atom bridged by a cyanide ligand.



Recently, some of us published the facile synthesis of *cis*- and *trans*- $[\text{Ru}(\text{CN}^t\text{Bu})_4(\text{CN})_2]$ from $\text{Ru}_3(\text{CO})_{12}$ and *tert*-butyl isocyanide by the reductive cleavage of isocyanide ligands and the concomitant oxidation of the Ru atoms (Imhof & Dönnecke, 2003). In the meantime we were able to transfer this reaction principle to other transition metal carbonyls and we are actually investigating the potential of this cyano complex to produce cyanide-bridged coordination polymers with a controllable three-dimensional arrangement of the metal centers. Since the resulting coordination polymers often show very complex magnetic and electronic properties, we were looking for a way to produce trinuclear segments of the polymer chains in order to investigate the communication between the metal centers in these trinuclear complexes; we thus hope also to understand the properties of the polymers.

The reaction of $[\text{Rh}(\text{cod})\text{Cl}]_2$ with *trans*- $[\text{Ru}(\text{CN}^t\text{Bu})_4(\text{CN})_2]$ in dry dichloromethane leads to the almost quantitative formation of (I). The cleavage of chloro bridges by Lewis bases is a commonly known process (Cotton *et al.*, 1999). With

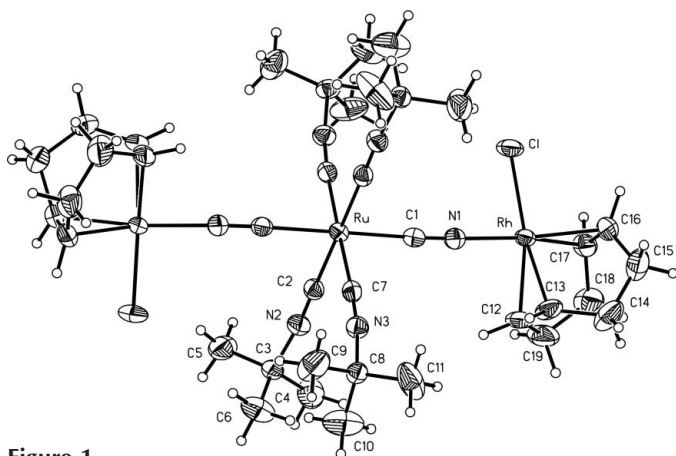


Figure 1
Molecular structure of $\{\mu\text{-trans}[\text{Ru}(\text{BuNC})_4(\text{CN})_2][\text{Rh}(\text{cod})\text{Cl}]_2\}$. Displacement ellipsoids are drawn at the 40% probability level. Unlabeled atoms are related to labeled atoms by the symmetry code $(-x, y, \frac{1}{2} - z)$.

this reaction it becomes evident that cyano ligands that are already coordinated to a transition metal are still basic enough to induce the cleavage of chloro bridges.

The molecular structure of (I) is presented in Fig. 1; the most important bond lengths and angles are given in Table 1. The central Ru ion is situated on a crystallographic twofold axis, resulting in a nearly perfect octahedral coordination geometry formed by the four isocyanide ligands and the two cyano groups. The cyanide groups act as bridging ligands between the Ru and Rh centers. Owing to the symmetry of the molecule the chloro(cod)rhodium subunits exhibit a *trans* configuration relative to each other. The Rh atoms show a square-planar ligand environment built up of the N atom of the bridging cyanide, the chloro ligand and the centers of the olefinic double bonds (C12=C13 and C16=C17). The deviations from this plane are well below 0.1 Å.

A Cambridge Structural Database (Version 5.26 of November 2004; Allen, 2002) search found 15 structurally characterized compounds in which rhodium ions are coordinated by cyanide bridging two transition metals and in which the rhodium centers are connected to the N atom of the bridging ligand. The compounds may be divided into two basic groups concerning the arrangement of the metal atoms. There are cyclic structures consisting of four metals with all metal ions being connected by bridging cyanide groups. These compounds have been described for Rh atoms only (Kalb *et al.*, 1982; Klausmeyer *et al.*, 1998) or for combinations of rhodium with platinum (Fornies *et al.*, 2004). In addition, there has been a report concerning a metalcycle of Rh atoms bridged by only two cyanide groups, which therefore exhibits two metal–metal bonds (Martinez *et al.*, 1991). Three-dimensional arrangements of rhodium ions bridged by cyanide ligands have been described in terms of a cuboidal structure (Klausmeyer *et al.*, 1998) and as an oligomer with seven rhodium centers, which is best described as a cube with one missing corner (Contakes *et al.*, 1998). All other structures

reported so far are linear coordination complexes, being either discrete dinuclear (Atkinson *et al.*, 1993; Bezrukova *et al.*, 1993) or trinuclear (Deeming *et al.*, 1988; Atkinson *et al.*, 1993) compounds. There have also been reports of coordination polymers, which were synthesized from rhodium carboxylates and hexacyanoferrate(II) (Kim *et al.*, 2001), hexacyanocobaltate(III) (Lu *et al.*, 1996) or $[(\eta^5\text{-C}_5\text{H}_5)\text{Ir}(\text{CO})_3]$ (Contakes *et al.*, 2000). The title compound is the first structurally characterized compound with an Rh and an Ru atom bridged by a cyanide ligand.

The crystal structure of the title compound is shown in Fig. 2; the shortest intermolecular contacts are presented in Table 2. Infinite chains of the trinuclear complex units are built up by C–H···Cl hydrogen bonds (Desiraju & Steiner, 1999) between the chloro ligands and an H atom of one of the isocyanide ligands of a neighboring molecule and *vice versa*. These infinite chains are interconnected in a three-dimensional arrangement by additional C–H···Cl contacts, which have been omitted from Fig. 2 for the sake of clarity (Table 2).

Experimental

$[\text{Rh}(\text{cod})\text{Cl}]_2$ (3.2 mg, 0.007 mmol) in dry dichloromethane was added to a solution of *trans*- $[\text{Ru}(\text{BuNC})_4(\text{CN})_2]$ hydrate (6.6 mg, 0.013 mmol) in dichloromethane. After stirring for 15 min, the solvent was removed *in vacuo*, producing a yellow powder of the title compound. Recrystallization from dichloromethane yielded yellow prismatic crystals suitable for this X-ray diffraction study. IR (KBr, cm^{-1}): $\nu(\text{CH}_3)$ 2980 (*s*), 2934 (*m*), $\nu(\text{CN})$ 2224 (*m*), $\nu(\text{NC})$ 2169 (*vs*), 2174 (*s*), 2118 (*m*), $\delta(\text{CH})$ 1457 (*m*), $\delta(\text{CMe}_3)$ 1399 (*w*), 1372 (*s*); MS (micro-ESI in dichloromethane/methanol) [*m/z*, (%): 943 (32) $\{[\text{Ru}(\text{BuNC})_4(\text{CN})_2]\text{Rh}_2(\text{cod})_2\text{Cl}\}^+$, 697 (100) $\{[\text{Ru}(\text{BuNC})_4(\text{CN})_2]\text{Rh}(\text{cod})\}^+$.

Crystal data

$[\text{Rh}_2\text{Ru}(\text{CN})_2\text{Cl}_2(\text{C}_8\text{H}_{12})_2(\text{C}_5\text{H}_9\text{N})_4]$	$D_x = 1.389 \text{ Mg m}^{-3}$
$M_r = 978.71$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 4052 reflections
$a = 21.7982$ (5) Å	$\theta = 3.3\text{--}27.5^\circ$
$b = 11.3347$ (4) Å	$\mu = 1.16 \text{ mm}^{-1}$
$c = 21.4881$ (8) Å	$T = 183$ (2) K
$\beta = 118.189$ (2)°	Prism, yellow
$V = 4679.5$ (3) Å ³	$0.03 \times 0.03 \times 0.02 \text{ mm}$
$Z = 4$	

Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.041$
φ and ω scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: none	$h = -28 \rightarrow 28$
16239 measured reflections	$k = -13 \rightarrow 14$
5332 independent reflections	$l = -25 \rightarrow 27$
4052 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2 + 3.4513P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.107$	$(\Delta/\sigma)_{\text{max}} = 0.008$
$S = 1.03$	$\Delta\rho_{\text{max}} = 1.17 \text{ e \AA}^{-3}$
5332 reflections	$\Delta\rho_{\text{min}} = -0.68 \text{ e \AA}^{-3}$
222 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Rh—N1	2.043 (3)	Ru—C2	2.005 (4)
Rh—C12	2.093 (4)	Ru—C1	2.044 (4)
Rh—C16	2.105 (4)	N1—C1	1.139 (5)
Rh—C13	2.106 (4)	N2—C2	1.138 (4)
Rh—C17	2.125 (3)	N3—C7	1.148 (4)
Rh—Cl	2.3651 (9)	C12—C13	1.389 (7)
Ru—C7	2.004 (4)	C16—C17	1.386 (6)
N1—Rh—C12	89.62 (16)	C7—Ru—C2 ⁱ	178.92 (14)
N1—Rh—C16	157.77 (16)	C7 ⁱ —Ru—C2 ⁱ	85.22 (14)
C12—Rh—C16	98.82 (18)	C2—Ru—C2 ⁱ	95.5 (2)
N1—Rh—C13	91.42 (14)	C7—Ru—C1	92.40 (13)
C12—Rh—C13	38.64 (19)	C7 ⁱ —Ru—C1	90.24 (13)
C16—Rh—C13	82.80 (16)	C2—Ru—C1	90.60 (14)
N1—Rh—C17	163.92 (15)	C2 ⁱ —Ru—C1	86.80 (14)
C12—Rh—C17	82.55 (16)	C7—Ru—C1 ⁱ	90.23 (13)
C16—Rh—C17	38.25 (17)	C7 ⁱ —Ru—C1 ⁱ	92.39 (13)
C13—Rh—C17	91.18 (16)	C2—Ru—C1 ⁱ	86.81 (14)
N1—Rh—Cl	89.58 (9)	C2 ⁱ —Ru—C1 ⁱ	90.60 (14)
C12—Rh—Cl	154.69 (15)	C1—Ru—C1 ⁱ	176.1 (2)
C16—Rh—Cl	91.29 (12)	C1—N1—Rh	175.8 (3)
C13—Rh—Cl	166.66 (16)	C2—N2—C3	172.4 (4)
C17—Rh—Cl	91.53 (11)	C7—N3—C8	173.0 (3)
C7—Ru—C7 ⁱ	94.1 (2)	N1—C1—Ru	175.3 (3)
C7—Ru—C2	85.22 (14)	N2—C2—Ru	172.9 (3)
C7 ⁱ —Ru—C2	178.92 (14)	N3—C7—Ru	175.5 (3)

Symmetry code: (i) $-x, y, -z + \frac{1}{2}$

Table 2
Hydrogen-bond geometry (Å, °).

D—H...A	H...A	D...A	D—H...A
C9—H9B...Cl ⁱⁱ	2.73	3.652 (5)	156
C5—H5C...Cl ⁱⁱⁱ	2.84	3.736 (5)	153
C11—H11C...Cl ⁱⁱ	2.93	3.800 (5)	149

Symmetry codes: (ii) $x, -y + 1, z + \frac{1}{2}$; (iii) $x, -y, z + \frac{1}{2}$

All H atoms were placed in idealized positions (C—H = 0.98–1.00 Å) and were refined with $U_{\text{iso}}(\text{H})$ values of 1.2 or 1.5 times $U_{\text{eq}}(\text{C})$. The highest electron density peak is located at 0.1648, 0.5413, 0.4723.

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997); data reduction: DENZO; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Siemens, 1990); software used to prepare material for publication: SHELXL97.

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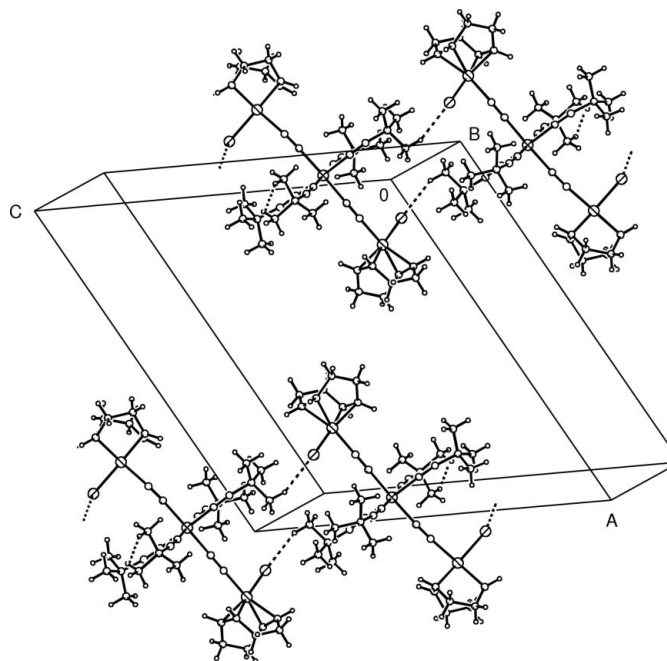


Figure 2
Packing diagram of $\{\mu\text{-trans}[\text{Ru}(\text{BuNC})_4(\text{CN})_2][\text{Rh}(\text{cod})\text{Cl}]_2\}$. Dashed lines indicate hydrogen bonds.

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