

***trans*-Dicyanotetrakis(2-isocyano-2,4,4-trimethylpentane)ruthenium(II)**

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Key indicators

Single-crystal X-ray study
 T = 173 K
 Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
 R factor = 0.032
 wR factor = 0.072
 Data-to-parameter ratio = 22.7

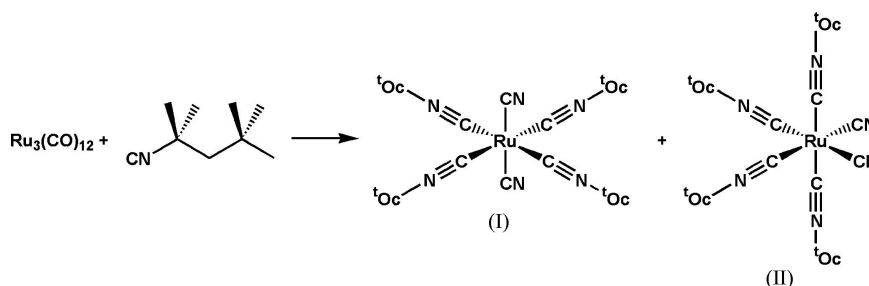
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the centrosymmetric title compound, $[\text{Ru}(\text{CN})_2(\text{C}_9\text{H}_{17}\text{N})_4]$, the central Ru atom is octahedrally coordinated by four isocyanide and two cyanide ligands in a *trans* configuration. The corresponding *cis* isomer, which is also produced in the reaction of $\text{Ru}_3(\text{CO})_{12}$ with isooctylisocyanide, is not configurationally stable and slowly isomerizes into the *trans* isomer in solution.

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Comment

The construction of coordination oligomers or polymers by the use of cyanide ligands as bridging ligands between two transition metal centers has found considerable interest during the last years due to the electronic, magnetic or even optical properties of the corresponding materials (recent examples: Lesouëzec *et al.*, 2004; Toma *et al.*, 2005; Berlinguette *et al.*, 2004; Chen *et al.*, 2005; Halbauer, Leibelng & Imhof, 2006). Recently we found that the reaction of $\text{Ru}_3(\text{CO})_{12}$ with isocyanides in the presence of carbon monoxide leads to the quantitative formation of the octahedral complexes $[\text{Ru}(\text{CN})_2(\text{RNC})_4]$ as a 1:1 mixture of their *cis*- and *trans*-isomers (Dönnecke *et al.*, 2003). This reaction concept may also be used for the reaction of $\text{Fe}_2(\text{CO})_9$ or $\text{Mn}_2(\text{CO})_{10}$, whereas very stable mononuclear transition metal carbonyls like $\text{Mo}(\text{CO})_6$ react *via* the substitution of CO ligands by isocyanide groups (Halbauer, Dönnecke *et al.*, 2006; Halbauer, Görls & Imhof, 2006; Imhof *et al.*, 2006).



The chemical scheme shows the formation of the title compound (I), together with the corresponding *cis*-isomer (II), from $\text{Ru}_3(\text{CO})_{12}$ and 2-isocyano-2,4,4-trimethylpentane. The formation of the *cis*-isomer is evident from column chromatography of the product mixture, nevertheless it is transformed into the *trans*-isomer (I) in solution. The formation of (I) and (II) is obviously a redox reaction in which Ru(0) is oxidized to Ru(II) and isocyanides are reductively cleaved. In our studies concerning this reaction sequence, it became obvious that only those isocyanides react which, by a formal bond cleavage into a cyanide anion and a carbenium

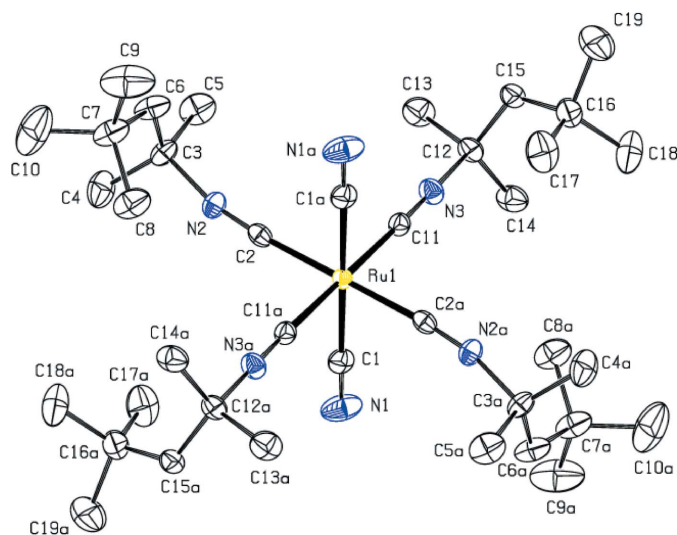


Figure 1

Molecular structure of *trans*-[Ru(CN)₂(C₈H₁₇N≡C)₄]. Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Symmetry code (a): $-x, -y, -z$.

ion, produce a tertiary carbenium ion, whereas isocyanides like cyclohexylisocyanide, isopropylisocyanide or aromatic isocyanides do not react. This also fits the observation of Schaal *et al.* (1985) that carbenium ions (formed from enolisable ketones in the presence of HBF₄) react with hexacyanometallates to produce hexakis-isocyanide complexes, which would be the 'reverse reaction' of what is shown in the chemical scheme.

The molecular structure of (I) is depicted in Fig.1. Ru1 is situated at a crystallographic center of inversion, leading to an almost perfect octahedral coordination geometry. The metal-carbon bonds of the cyanide ligands are slightly longer than the corresponding bonds of ruthenium to the C atoms of the isocyanide groups. Although the isoctyl substituents are very bulky, the C–N–C bond angles C2–N2–C3 and C11–N3–C12 deviate only slightly from linearity. Nevertheless, in contrast to all the X-ray diffraction experiments on related compounds undertaken by our group so far, the structure of (I) is the only one without any solvent molecules in the unit cell. The crystal structure of (I) is therefore established by rather weak C–H...N interactions of the isocyanides towards the cyanide ligands of neighboring molecules (C6–H6A...N1 2.605 Å, C15–H15A...N1 2.493 Å).

Experimental

A 89 mg sample of Ru₃(CO)₁₂ (0.139 mmol) was placed into a stainless steel autoclave together with 0.59 ml 2-isocyno-2,4,4-trimethylpentane (3.34 mmol) and 3.5 ml anhydrous toluene. The autoclave was pressurized with 10 bar of carbon monoxide and heated to 413 K overnight. After cooling the autoclave, releasing the pressure and evaporating the solvent *in vacuo*, an oily yellow residue was obtained. Chromatographic workup yielded two fractions, both showing identical mass spectra. Using acetone as the solvent resulted

in the elution of the first fraction (*R_f* value in TLC 0.84); the second fraction was obtained using a mixture of acetone and ethanol (3:1) as the eluent (*R_f* value in TLC 0.24). Crystallization of the first fraction from mixtures of chloroform and light petroleum (b.p. 313–333 K) in a 2:1 ratio produced crystals of the title compound. No crystalline material of the second fraction was obtained. TLC experiments after two weeks showed that the second fraction [*cis*-isomer (II)] had been isomerized to the *trans*-isomer (I) (*R_f* value now 0.82). MS and spectroscopic data of (I): IR (KBr, 293 K) [cm⁻¹]: 2216 (*w*, CN), 2166 (*vs*, RNC), 2119 (*m*, RNC); MS (Micro-ESI in methanol/acetone): 1441 [Ru(CN)₂(O₂CNC)₄]₂Na⁺, 1419 [Ru(CN)₂(O₂CNC)₄]₂H⁺, 732 [[Ru(CN)₂(O₂CNC)₄]₂Na⁺, 710 [Ru(CN)₂(O₂CNC)₄]₂H⁺, 620 [Ru(CN)₂(O₂CNC)₃(CNH)]Na⁺, 598 [Ru(CN)₂(O₂CNC)₃(CNH)]H⁺, 508 [Ru(CN)₂(O₂CNC)₂(CNH)₂]₂Na⁺, 486 [Ru(CN)₂(O₂CNC)₂(CNH)₂]₂H⁺, 396 [Ru(CN)₂(O₂CNC)(CNH)₃]₂Na⁺, 374 [Ru(CN)₂(O₂CNC)(CNH)₃]₂H⁺, 284 [Ru(CN)₂(CNH)₄]₂Na⁺, 262 [Ru(CN)₂(CNH)₄]₂H⁺; ¹H-NMR (*d*₆-acetone, 293 K) [p.p.m.]: 1.1 (*s*, 9 H, CH₃), 1.6 (*s*, 6 H, CH₃), 1.7 (*s*, 2 H, CH₂); ¹³C-NMR (*d*₆-acetone, 293 K) [p.p.m.]: 31.6 (CH₃), 32.2 (CH₃), 54.3 (CH₂), 60.5 (C), 130.6 (CN), 146.3 (RNC).

Crystal data

[Ru(CN) ₂ (C ₈ H ₁₇ N) ₄]	<i>Z</i> = 2
<i>M_r</i> = 710.06	<i>D_x</i> = 1.097 Mg m ⁻³
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 10.3752 (2) Å	<i>μ</i> = 0.39 mm ⁻¹
<i>b</i> = 13.6464 (5) Å	<i>T</i> = 173 (2) K
<i>c</i> = 15.3603 (5) Å	Block, colorless
<i>β</i> = 98.800 (2)°	0.12 × 0.10 × 0.07 mm
<i>V</i> = 2149.17 (11) Å ³	

Data collection

Nonius KappaCCD diffractometer	4878 independent reflections
<i>φ</i> and <i>ω</i> scans	3547 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: none	<i>R_{int}</i> = 0.035
8584 measured reflections	<i>θ_{max}</i> = 27.5°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 0.0187P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.072$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.02	$\Delta\rho_{max} = 0.25 \text{ e \AA}^{-3}$
4878 reflections	$\Delta\rho_{min} = -0.46 \text{ e \AA}^{-3}$
215 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Ru1–C2	1.9958 (19)	C2–N2	1.151 (2)
Ru1–C11	1.998 (2)	N2–C3	1.464 (2)
Ru1–C1	2.0658 (19)	C11–N3	1.150 (2)
C1–N1	1.141 (2)	N3–C12	1.462 (2)
C2–Ru1–C11	87.79 (7)	N2–C2–Ru1	173.99 (16)
C2–Ru1–C1	93.64 (7)	C2–N2–C3	165.96 (19)
C11–Ru1–C1	91.20 (7)	N3–C11–Ru1	178.05 (15)
N1–C1–Ru1	177.74 (17)	C11–N3–C12	178.61 (19)

All H atoms were placed in idealized positions (C–H = 0.98 Å) and were refined as riding, with $U_{iso}(H) = 1.5U_{eq}(C)$.

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997); data reduction: DENZO; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); 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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