

The synthesis and structural analyses of ruthenium carbonyl cluster complexes containing the bis-(trimethylsilyl)hexatriyne ligand

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Abstract

Two ruthenium carbonyl cluster complexes: $\text{Ru}_3(\text{CO})_{10}[\mu_3\text{-}\eta^2\text{-C}_2(\text{C}\equiv\text{CSiMe}_3)_2]$, **2** (6% yield) and $\text{Ru}_4(\text{CO})_{12}[\mu_4\text{-}\eta^2\text{-C}_2(\text{C}\equiv\text{CSiMe}_3)_2]$, **3** (36% yield) were obtained from the reaction of the 1,6-bis-(trimethylsilyl)-1,3,5-hexatriyne, **1** with $\text{Ru}(\text{CO})_5$ at 25°C. Both compounds were characterized by a single crystal X-ray diffraction analysis. In both cases the Ru cluster is located on the central alkyne unit of the triyne **1**. Compound **2** contains a Ru_3 triangle with the alkyne coordinated in the common $\mu_3\text{-}||$ mode. In compound **3** the alkyne is coordinated in a μ_4 -mode. The lengths of the coordinated alkyne C–C bonds are considerably longer than the uncoordinated alkyne C–C bond lengths. Compound **2** was also obtained in a better yield (60%) from the reaction of **1** with $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$. Compound **2** reacts with $\text{Ru}(\text{CO})_5$ to yield compound **3**, indicating that it is probably a precursor to **3** in the original reaction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Hexatriyne; Ruthenium; Cluster; Crystal structures

1. Introduction

In recent years there have been great advances in the synthesis of extended linear and cyclic conjugated polyynes [1–3]. Linear polyynes are stabilized by termination with tertiary silyl groups [2] and σ -bonded metal complexes [3]. Macrocyclic polyynes [4] stabilized through the formation of π -bonding coordination to transition metal complexes [5] are of great interest.

It has been shown that the condensation of metal containing groups onto the triple bond of alkynes can be an effective method for the synthesis of mixed metal cluster complexes [6]. We are interested in trying to use polyynes as focal points for the synthesis of large metal cluster complexes with novel structures. Herein are described the results of our studies of the reaction of $\text{Ru}(\text{CO})_5$ with 1,6-bis-(trimethylsilyl)-1,3,5-hexatriyne, **1**.

2. Results and discussion

Two ruthenium carbonyl cluster complexes: $\text{Ru}_3(\text{CO})_{10}[\mu_3\text{-}\eta^2\text{-C}_2(\text{C}\equiv\text{CSiMe}_3)_2]$, **2** in 6% yield and $\text{Ru}_4(\text{CO})_{12}[\mu_4\text{-}\eta^2\text{-C}_2(\text{C}\equiv\text{CSiMe}_3)_2]$, **3** in 36% yield were obtained from the reaction of the 1,6-bis-(trimethylsilyl)-1,3,5-hexatriyne, **1** with $\text{Ru}(\text{CO})_5$ at 25°C. Both compounds were characterized by a combination of IR, $^1\text{H-NMR}$ and single crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of **2** is shown in Fig. 1. Selected interatomic distances and angles are listed in Tables 1 and 2, respectively. The triyne is coordinated to a triangular cluster of three ruthenium atoms by the central C–C triple bond. The coordination exhibits the $\mu_3\text{-}||$ orientation on the cluster. The $\mu_3\text{-}||$ orientation is known to be much more common than the $\mu_3\text{-}\perp$ alternative [7]. The coordinated C–C triple bond C(3)–C(4) at 1.395(9) Å is much longer than the two uncoordinated C–C triple bonds, C(1)–C(2) = 1.193(8) Å and C(5)–C(6) = 1.199(8) Å. This elongation is typical of coordinated C–C triple

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bonds [7] and is similar to that found for the complexes $\text{Ru}_3(\text{CO})_{10}(\mu_3\text{-}\eta^2\text{-C}_2\text{Me}_2)$, **4** $\text{C}-\text{C} = 1.359(7)$ Å [8] and the two diyne complexes $\text{Ru}_3(\text{CO})_{10}[\mu_3\text{-}\eta^2\text{-C}_2\text{Ph}(\text{C}\equiv\text{CPh})]$, **5** [9] and $\text{Ru}_3(\text{CO})_8(\text{dppm})[\mu_3\text{-}\eta^2\text{-C}_2\text{Ph}(\text{C}\equiv\text{CPh})]$, **6** [10] each of which contains one coordinated triple bond and one uncoordinated triple bond, $\text{C}-\text{C} = 1.395(6)$ Å and $\text{C}-\text{C} = 1.182(8)$ Å, and $\text{C}-\text{C} = 1.44(1)$ Å and $\text{C}-\text{C} = 1.20(1)$ Å, respectively. Compound **2** contains one bridging carbonyl ligand, $\nu = 1880$ cm^{-1} . Interestingly, the metal–metal bond with the bridging carbonyl ligand, $\text{Ru}(1)\text{--Ru}(3) = 2.8313(9)$ Å, is significantly longer than the other two metal–metal bonds, $\text{Ru}(1)\text{--Ru}(2) = 2.7402(8)$ Å and $\text{Ru}(2)\text{--Ru}(3) = 2.7297(8)$ Å. This could possibly be attributed to steric crowding, the metal atoms bridged by the carbonyl ligand each have five ligands, while $\text{Ru}(2)$ has only four, if the $\text{C}(3)\text{--C}(4)$ π -bond is considered as a single site. The metal–metal bond distances in **2** are not significantly different from those in compound **4**, $2.8304(7)$ Å [$2.8186(7)$ Å], $2.7271(7)$ Å [$2.7149(7)$ Å] and $2.7092(6)$ Å [$2.7213(6)$ Å] (values in brackets represent a second independent molecule, where the large value is also for the metal–metal bond containing the bridging carbonyl ligand. The SiMe_3 groups in **2** are equivalent spectroscopically, $^1\text{H-NMR}$, $\delta = 0.14$ ppm. There are only a few other examples of triangular trimetal clusters containing triyne ligands. These include the compounds $\text{M}_2\text{Fe}(\text{CO})_7\text{Cp}_2[\mu_3\text{-}\eta^2\text{-C}_2(\text{C}\equiv\text{CBu}^t)_2]$, $\text{M} = \text{Mo}$ and W [11], and the osmium homolog of **2** [12].

An ORTEP drawing of the molecular structure of **3** is shown in Fig. 2. Selected interatomic distances and angles are listed in Tables 3 and 4, respectively. As in **2**, the triyne is coordinated to the central $\text{C}-\text{C}$ triple bond of **1**, but is bonded to four ruthenium atoms. This $\mu_4\text{-C}-\text{C}$ bond is significantly longer than that in **2**,

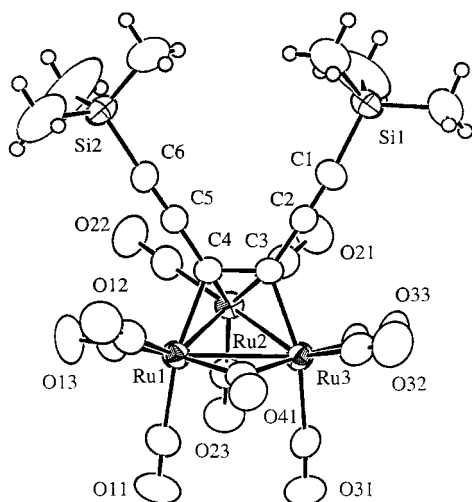


Fig. 1. An ORTEP diagram of $\text{Ru}_3(\text{CO})_{10}[\mu_3\text{-}\eta^2\text{-C}_2(\text{C}\equiv\text{CSiMe}_3)_2]$, **2** showing 40% probability thermal ellipsoids.

Table 1

Selected intramolecular bond distances for **2**^a

Atom	Atom	Distance (Å)	Atom	Atom	Distance (Å)
Ru(1)	Ru(2)	2.7402(8)	Si(1)	C(53)	1.83(1)
Ru(1)	Ru(3)	2.8313(9)	Si(2)	C(6)	1.843(7)
Ru(1)	C(4)	2.104(6)	Si(2)	C(61)	1.75(1)
Ru(1)	C(41)	2.107(7)	Si(2)	C(62)	1.78(1)
Ru(2)	Ru(3)	2.7297(8)	Si(2)	C(63)	1.81(1)
Ru(2)	C(3)	2.256(6)	O	C(av)	1.130(8)
Ru(2)	C(4)	2.246(6)	O(41)	C(41)	1.151(7)
Ru(3)	C(3)	2.102(6)	C(1)	C(2)	1.193(8)
Ru(3)	C(41)	2.200(8)	C(2)	C(3)	1.435(9)
Si(1)	C(1)	1.842(7)	C(3)	C(4)	1.395(9)
Si(1)	C(51)	1.83(1)	C(4)	C(5)	1.416(9)
Si(1)	C(52)	1.83(1)	C(5)	C(6)	1.199(8)

^a Estimated standard deviations in the least significant figure are given in parentheses.

$\text{C}(3)\text{--C}(4)$ at $1.47(1)$ Å, while the two uncoordinated $\text{C}-\text{C}$ triple bonds, $\text{C}(1)\text{--C}(2) = 1.17(1)$ Å and $\text{C}(5)\text{--C}(6) = 1.18(1)$ Å are not changed significantly. These distances are similar to those observed for the complex $\text{Ru}_4(\text{CO})_{12}[\mu_4\text{-}\eta^2\text{-C}_2\text{Ph}(\text{C}\equiv\text{CPh})_2]$, **7** which contains one μ_4 -coordinated $\text{C}-\text{C}$ triple bond at $1.46(1)$ Å and one uncoordinated $\text{C}-\text{C}$ triple bond at $1.19(1)$ Å [13]. As expected, the SiMe_3 groups in **3** are spectroscopically equivalent; $^1\text{H-NMR}$, $\delta = 0.15$ ppm.

We found that **2** could be obtained in a better yield (60%) by using the activated triruthenium reagent $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ [14]. Assuming that **2** was a probable precursor to **3**, we attempted to convert **2** into **3** by reaction with $\text{Ru}(\text{CO})_5$. This procedure was moderately successful and provided **3** in 43% yield. A summary of the results of this study are shown in Scheme 1.

Most μ_4 -alkyne tetraruthenium cluster complexes have been obtained from reactions $\text{Ru}_3(\text{CO})_{12}$ or $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ with that alkyne [13,15]. Low et al. have recently also obtained compound **3** from the reaction of **1** with $\text{Ru}_3(\text{CO})_{12}$ in hexane solution at reflux [12].

3. Experimental

3.1. General data

Reagent grade solvents were distilled freshly and stored over 4-Å molecular sieves. The reaction was performed under a nitrogen atmosphere. Infrared spectra were recorded on a Nicolet 5DXBO FTIR spectrophotometer. $^1\text{H-NMR}$ spectra were recorded on Varian Mercury spectrometers at 400 MHz. $\text{Ru}_3(\text{CO})_{12}$ was purchased from Strem Chemicals, Inc. and was used without further purification. $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ was prepared according to the published procedure [14]. The 1,6-bis(trimethylsilyl)-1,3,5-hexatriyne, **1** was

Table 2
Selected intramolecular bond angles for **2**^a

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
Ru(2)	Ru(1)	Ru(3)	58.65(2)	Ru(2)	C(3)	Ru(3)	77.5(2)
Ru(2)	Ru(1)	C(4)	53.3(2)	Ru(2)	C(3)	C(2)	122.0(4)
Ru(2)	Ru(1)	C(41)	107.8(2)	Ru(2)	C(3)	C(4)	71.5(4)
Ru(3)	Ru(1)	C(4)	69.9(2)	Ru(3)	C(3)	C(2)	127.0(5)
Ru(3)	Ru(1)	C(41)	50.3(2)	Ru(3)	C(3)	C(4)	109.8(4)
Ru(1)	Ru(2)	Ru(3)	62.34(2)	C(2)	C(3)	C(4)	123.0(6)
Ru(1)	Ru(2)	C(3)	70.1(2)	Ru(1)	C(4)	Ru(2)	78.0(2)
Ru(1)	Ru(2)	C(4)	48.7(2)	Ru(1)	C(4)	C(3)	110.2(4)
Ru(3)	Ru(2)	C(3)	48.7(1)	Ru(1)	C(4)	C(5)	125.7(5)
Ru(3)	Ru(2)	C(4)	70.2(2)	Ru(2)	C(4)	C(3)	72.4(4)
C(3)	Ru(2)	C(4)	36.1(2)	Ru(2)	C(4)	C(5)	121.3(4)
Ru(1)	Ru(3)	Ru(2)	59.01(2)	C(3)	C(4)	C(5)	123.9(6)
Ru(1)	Ru(3)	C(3)	70.1(2)	C(4)	C(5)	C(6)	177.8(7)
Ru(1)	Ru(3)	C(41)	47.5(2)	Si(2)	C(6)	C(5)	175.8(6)
Ru(2)	Ru(3)	C(3)	53.8(2)	Ru	C	O(av)	177.0(8)
Ru(2)	Ru(3)	C(41)	105.4(2)	Ru(1)	C(41)	Ru(3)	82.2(3)
C(3)	Ru(3)	C(41)	88.6(2)	Ru(1)	C(41)	0(41)	141.7(6)
Si(1)	C(1)	C(2)	174.3(7)	Ru(3)	C(41)	0(41)	136.0(6)
C(1)	C(2)	C(3)	178.0(7)				

^a Estimated standard deviations in the least significant figure are given in parentheses.

prepared according to the published procedure [16]. Product separation was performed by TLC in air on Analtech 0.25 mm silica gel 60 Å F₂₅₄ glass plates and silica gel 70–230 mesh from Aldrich. The elemental analysis was performed by Oneida Research Services, Whitesboro, NY.

3.1.1. Reaction of **1** with Ru(CO)₅

Ru(CO)₅ was prepared and used in situ by our previously reported procedure [17] by using a 100 mg amount of Ru₃(CO)₁₂ (0.156 mmol) dissolved in 120 ml hexane in a 250 ml three-necked flask equipped with a reflux condenser and by irradiating (UV, medium pressure mercury lamp at 1000 W) in the presence of CO until the IR spectrum showed no Ru₃(CO)₁₂ remaining. After irradiation the flask was cooled to 0°C, and

evacuated and refilled with nitrogen several times to remove the excess CO. A quantity of 1,6-bis(trimethylsilyl)-1,3,5-hexatriyne (9.0 mg, 0.041 mmol) was then added, and the solution was stirred for 20 h. The temperature was allowed to increase to 25°C after mixing. A red solution was obtained. The volume was reduced to about 20 ml by rotary evaporation. The products were then separated by column chromatography on silica gel using hexane solvent. This yielded 55.7 mg of Ru₃(CO)₁₂ from the first yellow band; 14.2 mg of red Ru₄(CO)₁₂[μ₄-η²-C₂(C≡CSiMe₃)₂], **3** (36% yield based on triyne) from the second band, 2.1 mg of orange Ru₃(CO)₁₀[μ₃-η²-C₂(C≡CSiMe₃)₂], **2** (6% yield) from the third band. Analytical and spectral data for **2**: IR (νCO) cm⁻¹, in hexane): 2100(m), 2069(vs),

Table 3
Selected intramolecular bond distances for **3**^a

Atom	Atom	Distance (Å)	Atom	Atom	Distance (Å)
Ru(1)	Ru(3)	2.722(1)	Si(1)	C(52)	1.86(1)
Ru(1)	Ru(4)	2.757(1)	Si(1)	C(53)	1.86(2)
Ru(1)	C(3)	2.24(1)	Si(2)	C(6)	1.83(1)
Ru(1)	C(4)	2.22(1)	Si(2)	C(61)	1.81(2)
Ru(2)	Ru(3)	2.764(1)	Si(2)	C(62)	1.78(2)
Ru(2)	Ru(4)	2.723(1)	Si(2)	C(63)	1.79(3)
Ru(2)	C(3)	2.23(1)	O	C(av)	1.13(1)
Ru(2)	C(4)	2.21(1)	C(1)	C(2)	1.17(1)
Ru(3)	Ru(4)	2.835(1)	C(2)	C(3)	1.45(1)
Ru(3)	C(3)	2.15(1)	C(3)	C(4)	1.47(1)
Ru(4)	C(4)	2.12(1)	C(4)	C(5)	1.48(1)
Si(1)	C(1)	1.84(1)	C(5)	C(6)	1.18(1)
Si(1)	C(51)	1.83(2)			

^a Estimated standard deviations in the least significant figure are given in parentheses.

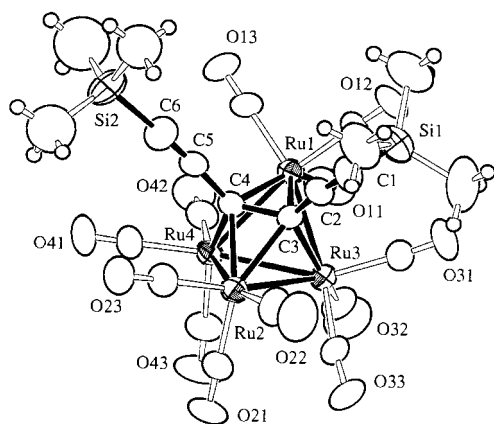


Fig. 2. An ORTEP diagram of Ru₄(CO)₁₂[μ₄-η²-C₂(C≡CSiMe₃)₂], **3** showing 40% probability thermal ellipsoids.

Table 4
Selected intramolecular bond angles for **3**^a

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
Ru(3)	Ru(1)	Ru(4)	62.33(3)	C(1)	C(2)	C(3)	172(1)
Ru(3)	Ru(1)	C(3)	50.3(3)	Ru(1)	C(3)	Ru(2)	123.1(5)
Ru(3)	Ru(1)	C(4)	72.2(3)	Ru(1)	C(3)	Ru(3)	76.5(3)
Ru(4)	Ru(1)	C(3)	72.2(3)	Ru(1)	C(3)	C(2)	117.5(7)
Ru(4)	Ru(1)	C(4)	49.0(3)	Ru(1)	C(3)	C(4)	70.1(5)
C(3)	Ru(1)	C(4)	38.6(3)	Ru(2)	C(3)	Ru(3)	78.2(3)
Ru(3)	Ru(2)	Ru(4)	62.22(3)	Ru(2)	C(3)	C(2)	118.3(7)
Ru(3)	Ru(2)	C(3)	49.7(3)	Ru(2)	C(3)	C(4)	70.0(5)
Ru(3)	Ru(2)	C(4)	71.5(3)	Ru(3)	C(3)	C(2)	127.8(8)
Ru(4)	Ru(2)	C(3)	73.0(3)	Ru(3)	C(3)	C(4)	106.9(7)
Ru(4)	Ru(2)	C(4)	49.5(3)	C(2)	C(3)	C(4)	125(1)
C(3)	Ru(2)	C(4)	38.7(3)	Ru(1)	C(4)	Ru(2)	124.8(5)
Ru(1)	Ru(3)	Ru(2)	91.53(4)	Ru(1)	C(4)	Ru(4)	78.8(3)
Ru(1)	Ru(3)	Ru(4)	59.43(3)	Ru(1)	C(4)	C(3)	71.3(5)
Ru(1)	Ru(3)	C(3)	53.2(3)	Ru(1)	C(4)	C(5)	117.1(7)
Ru(2)	Ru(3)	Ru(4)	58.17(3)	Ru(2)	C(4)	Ru(4)	77.8(3)
Ru(2)	Ru(3)	C(3)	52.2(3)	Ru(2)	C(4)	C(3)	71.3(6)
Ru(4)	Ru(3)	C(3)	71.7(3)	Ru(2)	C(4)	C(5)	117.3(7)
Ru(1)	Ru(4)	Ru(2)	91.69(4)	Ru(4)	C(4)	C(3)	110.3(7)
Ru(1)	Ru(4)	Ru(3)	58.24(3)	Ru(4)	C(4)	C(5)	125.5(7)
Ru(1)	Ru(4)	C(4)	52.3(3)	C(3)	C(4)	C(5)	124.2(9)
Ru(2)	Ru(4)	Ru(3)	59.61(3)	C(4)	C(5)	C(6)	176(1)
Ru(2)	Ru(4)	C(4)	52.6(3)	Si(2)	C(6)	C(5)	177(1)
Ru(3)	Ru(4)	C(4)	71.2(3)	Ru	C	O(av)	177(1)
Si(1)	C(1)	C(2)	177(1)				

^a Estimated standard deviations in the least significant figure are given in parentheses.

2062(vs), 2037(s), 2017(m), 1880(w); ¹H-NMR (δ in CDCl₃): 0.14(s, 18H). Anal. Calc. (found) for **2**: C, 33.25(32.96); H, 2.15(2.26). For **3**: IR (ν CO) cm⁻¹, in hexane): 2076 (vs), 2050 (s), 2045 (vs), 2021(s), 1978(w); ¹H-NMR (δ in CDCl₃): 0.15(s, 18H). Anal. Calcd (found) for **3**: C, 30.28 (30.06); H, 1.93 (1.89).

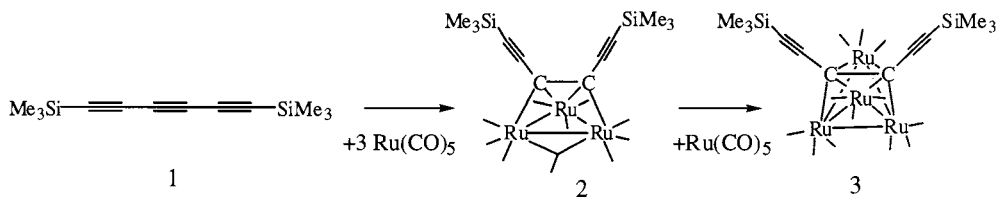
3.1.2. Reaction of **1** with Ru₃(CO)₁₀(NCMe)₂

An 11.5 mg amount (0.017 mmol) of Ru₃(CO)₁₀(NCMe)₂ was dissolved in 15 ml THF in a 25 ml three neck r. b. flask. A 3.8-mg quantity of **1** (0.017 mmol) was then added to the Ru₃(CO)₁₀(NCMe)₂ solution. The reaction mixture was stirred for 30 min at 25°C, and then the solvent was removed in vacuo. The residue was then redissolved in CH₂Cl₂ and transferred to TLC plates and eluted using hexane solvent. Three bands were eluted. The first band (yellow) was

Ru₃(CO)₁₂. The second band yielded 1.1 mg of **3**, 7%. The third band yielded 8.2 mg of **2**, 60%.

3.1.3. Synthesis of **3** from **2** plus Ru(CO)₅

Ru(CO)₅ was prepared by our previously reported procedure [17] and used in situ by using a 15.0 mg amount (0.023 mmol) of Ru₃(CO)₁₂ dissolved in 15 ml hexane in a 25 ml three-necked flask equipped with a reflux condenser and irradiating (UV, medium pressure mercury lamp at 360 watt) in the presence of a CO purge until IR spectra showed no Ru₃(CO)₁₂ remaining. After irradiation the flask was cooled to 0°C, and evacuated and refilled with nitrogen several times to remove the excess CO. 8.0 mg of **2** was then added, and the solution was stirred for 20 hr. The temperature was allowed to increase to 25°C during this time, and a red solution formed. The solvent was removed in vacuo,



Scheme 1.

and the residue was then redissolved in CH_2Cl_2 , transferred to TLC plates and eluted using hexane solvent. Two bands were eluted. The first band (yellow) was $\text{Ru}_3(\text{CO})_{12}$. The second band (red) yielded 4.1 mg of **3**, 43% yield.

3.2. Crystallographic analysis

Orange crystals of **2** suitable for diffraction analysis were grown by slow evaporation of the solvent at -15°C from 4:1 hexane/ CH_2Cl_2 solvent mixture. Dark red crystals of **3** were grown by slow evaporation of the solvent at 25°C from solutions 1:1 benzene/octane solvent mixture. The crystals used for the diffraction measurements were mounted in thin-walled glass capillaries. The diffraction measurements were made on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo-K α radiation at 20°C . The crystallographic unit cells were determined and refined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 5. All data processing was performed on a Silicon-Graphics INDIGO² Workstation by using the TEXSAN structure solving program library obtained

Table 5
Crystallographic data for compounds **2** and **3**

Compound	2	3
Formula	$\text{Ru}_3\text{Si}_2\text{O}_{10}\text{C}_{22}\text{H}_1$	$\text{Ru}_4\text{Si}_2\text{O}_{12}\text{C}_{24}\text{H}_1$
Formula weight	801.76	958.85
Crystal system	Monoclinic	Orthorhombic
<i>a</i> (Å)	15.432(2)	23.338(5)
<i>b</i> (Å)	13.334(2)	14.838(2)
<i>c</i> (Å)	15.759(2)	10.045(2)
β (°)	106.06(1)	90.0
<i>V</i> (Å ³)	3116.0(7)	3478(1)
Space group	<i>P</i> 2 ₁ / <i>n</i> (Number 14)	<i>P</i> na2 ₁ (Number 33)
Z value	4	4
ρ_{calc} (g/cm ³)	1.71	1.83
μ (Mo-K α) (cm ⁻¹)	15.57	18.24
2 θ_{max} (°)	46	46
Number observed (<i>I</i> > 3 σ)	2796	2870
Number of variables	335	365
Goodness-of-fit (GOF) ^a	1.38	1.75
Max shift in final cycle	0.00	0.01
Residuals: <i>R</i> , <i>R</i> _w	0.031; 0.029	0.033; 0.039
Abs. cor.	Difabs	Difabs
Transmission coefficient, max/min	1.00/0.56	1.00/0.64
Largest peak in final differential map (e ⁻ /Å ³)	0.34	0.50

$$^a R = \frac{\sum_{hkl} (|F_{\text{obs}}| - |F_{\text{calc}}|) / \sum_{hkl} |F_{\text{obs}}|}{\sum_{hkl} |F_{\text{calc}}| / \sum_{hkl} |F_{\text{obs}}|^{1/2}}, \quad w = 1/\sigma^2(F_{\text{obs}}); \quad R_w = \frac{[\sum_{hkl} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2]^{1/2}}{[\sum_{hkl} w(|F_{\text{obs}}|)^2]^{1/2}}, \quad \text{GOF} = \frac{[\sum_{hkl} w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / (n_{\text{data}} - n_{\text{vari}})]^{1/2}}{[\sum_{hkl} w(|F_{\text{obs}}|)^2]^{1/2}}$$

from the Molecular Structure Corp., The Woodlands, TX. Neutral atom scattering factors were calculated by the standard procedures [18a]. Anomalous dispersion corrections were applied to all non-hydrogen atoms [18b]. Lorentz/polarization (Lp) corrections were applied to the data. Full matrix least-squares refinements minimized the function: $\sum_{hkl} w(|F_{\text{o}}| - |F_{\text{c}}|)^2$, where $w = 1/\sigma^2(F)$, $\sigma(F) = \sigma(F_{\text{o}}^2)/2F_{\text{o}}$ and $\sigma(F_{\text{o}}^2) = [\sigma(I_{\text{raw}})^2 + (0.02I_{\text{net}})^2]^{1/2}/\text{Lp}$.

4. Supplementary materials

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 102550 for compound **2** and CCDC No. 102551 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: +44-1223-336033, or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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References

- [1] (a) L. Brandsma, Preparative Acetylenic Chemistry, Ch. 10, 2nd Edition, Elsevier, Amsterdam, 1988. (b) A.M. Boldi, J. Anthony, C. Knobler, F. Diederich, Angew. Chem. Int. Ed. Engl. 31 (1992) 1240. (c) R.R. Tykwinski, F. Diederich, Liebigs Ann. Recueil (1997) 649. (d) U.H.F. Bunz, Synlett (1997) 1117.
- [2] (a) Y. Rubin, S.S. Lin, C. Knobler, J. Anthony, A.M. Boldi, F. Diederich, J. Am. Chem. Soc. 113 (1991) 6943. (b) R. Eastmond, D.R.M. Walton, Tetrahedron 28 (1972) 4591. (c) R. Eastmond, T.R. Johnson, D.R.M. Walton, Tetrahedron 28 (1972) 4601. (d) T.R. Johnson, D.R.M. Walton, Tetrahedron 28 (1972) 5221.
- [3] (a) J.A. Gladysz, T.A. Bartik, Angew. Chem. int Ed. Engl. 35 (1996) 414. (b) W. Weng, T.A. Bartik, J.A. Gladysz, Angew. Chem. int Ed. Engl. 33 (1994) 2199. (c) M. Brady, W. Weng, J.A. Gladysz, J. Chem. Soc. Chem. Commun. (1994) 2655. (d) W. Weng, T.A. Bartik, M. Brady, B. Bartik, J.A. Ramsden, A.M. Arif, J.A. Gladysz, J. Am. Chem. Soc. 117 (1995) 11922. (e) F. Coat, C. Lapinte, Organometallics 15 (1996) 477. (f) N. Le Narvor, L. Toupet, C. Lapinte, J. Chem. Am. Soc. 117 (1995) 7129. (g) N. Le Narvor, C. Lapinte, J. Chem. Soc. Chem. Commun. (1993) 357. (h) U.H.F. Bunz, Angew. Chem. int Ed. Engl. 35 (1996) 969.
- [4] (a) R. Gleiter, M. Merger, in: P.J. Stang, F. Diederich (Eds.), Modern Acetylene Chemistry, VCH, Weinheim, 1995, p. 285. (b) L.T. Scott, M.J. Cooney, in: P.J. Stang, F. Diederich (Eds.), Modern Acetylene Chemistry, VCH, Weinheim, 1995, p. 321. (c) F. Diederich, in: P.J. Stang, F. Diederich (Eds.), Modern Acetylene Chemistry, VCH, Weinheim, 1995, p. 442. (d) F. Diederich, Y. Rubin, Angew. Chem. int. Ed. Engl. 31 (1992) 1101. (e) M. Altman, J. Friedrich, F. Beer, R. Reuter, V.

- Enkelmann, U.H. F. Bunz, *J. Am. Chem. Soc.* 119 (1997) 1472.
(f) R. Gleiter, M. Merger *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2427.
- [5] Y. Rubin, M. Kahr, C. Knobler, F. Diederich, C.L. Wilkins, *J. Am. Chem. Soc.* 112 (1990) 4966.
- [6] G. Jaouen, A. Marinetti, B. Mentzen, R. Mutin, J.-Y. Saillard, B.G. Sayer, M.J. McGlinchey, *Organometallics* 1 (1982) 753.
- [7] S. Deabate, R. Giordano, E. Sappa, *J. Cluster Sci.* 8 (1997) 407.
- [8] S. Rivomanana, G. Lavigne, N. Lugan, J.-J. Bonnet, *Organometallics* 10 (1991) 2285.
- [9] M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, *Aus. J. Chem.* 49 (1996) 155.
- [10] M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 536–7 (1997) 93.
- [11] S.J. Etches, I.J. Hart, F.G.A. Stone, *J. Chem. Soc. Dalton Trans.* (1989) 2281.
- [12] (a) P.J. Low, G.D. Enright, A.J. Carty, *J. Organomet. Chem.* 565 (1998) 279. (b) P.J. Low, K.A. Udachin, G.D. Enright, A.J. Carty, *J. Organomet. Chem.* (1999) this issue.
- [13] M.I. Bruce, N.N. Zaitseva, B.W. Skelton, A.H. White, *Inorg. Chim. Acta* 250 (1996) 129.
- [14] S. Drake, R. Khattar, *Organomet. Syn.* 4 (1988) 234.
- [15] (a) B.F.G. Johnson, J. Lewis, B.E. Reichert, K.T. Schorpp, G.M. Sheldrick, *J. Chem. Soc. Dalton Trans.* (1977) 1417. (b) P.F. Jackson, B.F.G. Johnson, J. Lewis, P.R. Raithby, G.J. Will, M. McPartlin, W.J.H. Nelson, *J. Chem. Soc. Chem. Commun.* (1980) 1190. (c) J. Wang, M. Sabat, L.J. Lyons, D.F. Shriver, *Inorg. Chem.* 30 (1991) 382.
- [16] Y. Rubin, S.S. Lin, C.B. Knobler, J. Anthony, A.M. Boldi, F. Diederich, *J. Am. Chem. Soc.* 113 (1991) 6943.
- [17] R.D. Adams, T.S. Barnard, J.E. Cortopassi, W. Wu, Z. Li, *Inorg. Synth.* (1998) 280.
- [18] (a) *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, 1975, pp. 99–101, Table 2.2B. (b) *Ibid.* pp 149–150, Table 2.3.1.