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# Synthesis and structures of the silyl bridged bis(indenyl) diruthenium complexes and a novel indenyl nonanuclear ruthenium cluster $Ru_9(\mu_6\text{-}C)(CO)_{14}(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^2\text{-}C_9H_7)_2$

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**Abstract**

Thermal treatment of $C_9H_7SiMe_2C_9H_7$ and $C_9H_7Me_2SiOSiMe_2C_9H_7$ with $Ru_3(CO)_{12}$ in refluxing xylene gave the corresponding diruthenium complexes $(E)[(\eta^5\text{-}C_9H_6)Ru(CO)]_2(\mu\text{-}CO)_2$ [E = $Me_2Si$ (**1**), $Me_2SiOSiMe_2$ (**2**)]. A desilylation product $[(\eta^5\text{-}C_9H_7)Ru(CO)]_2(\mu\text{-}CO)_2$ (**3**) was also obtained in the latter case. Similar treatment of $C_9H_7Me_2SiSiMe_2C_9H_7$ with $Ru_3(CO)_{12}$ gave a novel indenyl nonanuclear ruthenium cluster $Ru_9(\mu_6\text{-}C)(CO)_{14}(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^2\text{-}C_9H_7)_2$ (**5**) with carbon-centered tricapped trigonal prism geometry, in addition to the diruthenium complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_9H_6)Ru(CO)]_2(\mu\text{-}CO)_2$ (**4**) and the desilylation product **3**. Complex **4** can undergo a thermal rearrangement to form the product $[(Me_2Si)(\eta^5\text{-}C_9H_6)Ru(CO)_2]_2$ (**6**). The molecular structures of **1**, **2**, **4**, **5**, and **6** were determined by X-ray diffraction.

*Keywords:* Ruthenium carbonyl; Indenyl; Metal—metal bond; Thermal rearrangement; Cluster

## 1. Introduction

Much attention has been focused on the synthesis and reactions of indenyl metal complexes due to their various metal—indenyl bonding modes [1] and enhanced reactivities both in catalysis [2] and in reactions [3], in comparison to their cyclopentadienyl analogues. The bridged bis(indenyl) metallocene complexes have been intensively studied as the stereospecific olefin polymerization catalysts [2]. However, in contrast to the extensive study of the bridged bis(cyclopentadienyl) dinuclear metal complexes [4], only a few of the bridged bis(indenyl) dinuclear metal complexes have been reported, mainly due to the poor reactivity of indenyl ligands [5]. As a part of an effort to explore the relationship between the bridging group with the structure (such as metal—metal bond length) and the reactivity in the bridged bis(cyclopentadienyl) or bis(indenyl) dinuclear metal complexes, here we report the synthesis and structures of the silyl bridged bis(indenyl) diruthenium complexes. A novel indenyl nonanuclear ruthenium cluster $(\mu_6\text{-}C)Ru_9(CO)_{14}(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^2\text{-}C_9H_7)_2$ with carbon-centered tricapped trigonal prism geometry is also obtained unexpectedly and fully characterized.

## 2. Results and discussion

### 2.1. Reaction of $C_9H_7EC_9H_7$ (E = $SiMe_2$, $Me_2SiOSiMe_2$, $Me_2SiSiMe_2$) with $Ru_3(CO)_{12}$

The cyclopentadienyl or indenyl diruthenium complexes were synthesized generally by the corresponding ligands with $Ru_3(CO)_{12}$ in refluxing heptane or other alkane with high boiling point [5,6]. However, when the reactions of the silyl bridged bis(indene) ligands with $Ru_3(CO)_{12}$ were done in refluxing heptane, decane, decalin, DME or even methyl isobutyl ketone [7], only the desilylation product $[C_9H_7Ru(CO)]_2(\mu\text{-}CO)_2$ was obtained. This problem has

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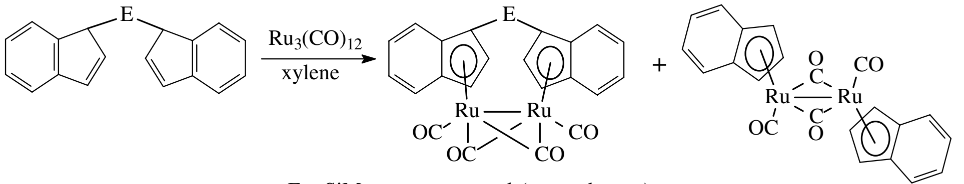
puzzled us a long time. Recently, we found that xylene as solvent for the reaction of silyl or germyl bridged biscyclopentadiene ligands with metal carbonyl can significantly depress the desilylation or degermylation reaction [8]. So xylene was chosen as solvent for the reactions of the silyl bridged bis(indenyl) ligands with $Ru_3(CO)_{12}$, and the expected products were obtained. When bis(1-indenyl) dimethylsilane $C_9H_7SiMe_2C_9H_7$ reacted with $Ru_3(CO)_{12}$ in refluxing xylene, the expected diruthenium product $(SiMe_2)[(\eta^5\text{-}C_9H_6)Ru(CO)]_2(\mu\text{-}CO)_2$ (**1**) was obtained in 21% yield (Scheme 1). The $^1H$ NMR spectrum of **1** shows three groups of peaks for the five-membered ring protons of the indenyl groups at 6.57(2H), 6.46(2H), 5.54(4H) ppm and three singlets for the Si—Me protons at 0.89, 0.80, 0.61 ppm (Table 1), indicating the existence of a mixture of *meso* and *racemic* isomers with a ratio of about 1:1. The two isomers can not be separated by TLC due to the almost equal $R_f$ values. But a single crystal of the *racemic* isomer of **1** was obtained by recrystallization and determined by X-ray diffraction.

Similarly, thermal treatment of 1,3-bis(1-indenyl) tetramethyldisiloxane $C_9H_7Me_2SiOSiMe_2C_9H_7$ with $Ru_3(CO)_{12}$ in refluxing xylene gave the expected diruthenium complex $(Me_2SiOSiMe_2)[(\eta^5\text{-}C_9H_6)Ru(CO)]_2(\mu\text{-}CO)_2$ (**2**) (15%) and a desilylation product $[(\eta^5\text{-}C_9H_7)Ru(CO)]_2(\mu\text{-}CO)_2$ (**3**) (8%) (Scheme 1). The $^1H$ NMR spectrum of **2** displayed two doublets for the five-membered ring protons of the indenyl groups at 6.46, 5.52 ppm, and two singlets for Si—Me protons at 0.53, 0.33 ppm, indicating the existence of a single isomer. The single crystal X-ray diffraction analysis showed that it is the *meso* isomer.

When 1,2-bis(1-indenyl) tetramethyldisilane $C_9H_7Me_2SiSiMe_2C_9H_7$ reacted with $Ru_3(CO)_{12}$ in refluxing xylene, a novel indenyl nonanuclear ruthenium cluster $Ru_9(\mu_6\text{-}C)(CO)_{14}(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^2\text{-}C_9H_7)_2$ (**5**) (3%) was obtained unexpectedly, in addition to the diruthenium complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_9H_6)Ru(CO)]_2(\mu\text{-}CO)_2$ (**4**) (8%) and the desilylation product **3** (8%) (Scheme 2).

The $^1H$ NMR spectrum of **4** shows two groups of multiplets for the five-membered ring protons of the indenyl groups at 6.47–6.42 and 5.56–5.52 ppm, and four singlets for the Si—Me protons at 0.56, 0.54, 0.42, and 0.33 ppm, indicating the existence of a mixture of *meso* and *racemic* isomers with a ratio of about 1:1, which also cannot be separated by TLC due to the almost equal $R_f$ values. The IR spectra of **1** and **2**show two terminal and two bridging carbonyl absorption peaks at 1981, 1942, 1819, 1779, and 2002, 1946, 1819, 1771 $cm^{-1}$, respectively. But the IR spectrum of **4** shows four terminal and four bridging carbonyl absorption peaks at 1995, 1976, 1952, 1936, 1814, 1779, 1770, and 1755 $cm^{-1}$, further indicating the existence of a mixture of *meso* and *racemic* isomers. Complex **1** is also a mixture of *meso* and *racemic* isomers, but its IR spectrum shows only four peaks of carbonyl, which can attributed to

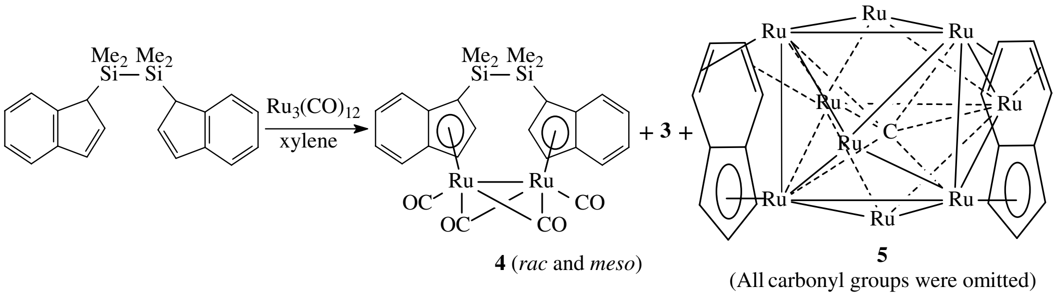


E = $SiMe_2$ **1** (*rac* and *meso*)
$SiMe_2OSiMe_2$ **2** (*meso*) **3**

Scheme 1.

Table 1
$^1H$ NMR data of complexes **1**–**6** (in $CDCl_3$, ppm)

| Complex | $C_6$-ring H of indenyl | $C_5$-ring H of indenyl | Si—Me |
|---|---|---|---|
| **1** | 7.60–7.25 (m, 8H) | 6.57 (d, *J* = 2.50 Hz, 2H)<br>6.46 (d, *J* = 2.50 Hz, 2H)<br>5.54 (m) (total 4H) | 0.89 (s), 0.80 (s), 0.61 (s)<br>(total 6H) |
| **2** | 7.31–7.09 (m, 8H) | 6.46 (d, *J* = 2.60 Hz, 2H)<br>5.52 (d, *J* = 2.60 Hz, 2H) | 0.53 (s, 6H), 0.33 (s, 6H) |
| **3** | 7.35–7.15 (m, 8H) | 5.63 (d, *J* = 2.60 Hz, 4H)<br>5.57 (t, *J* = 2.60 Hz, 2H) | |
| **4** | 7.55–7.05 (m, 8H) | 6.47–6.42 (m, 2H)<br>5.56–5.52 (m, 2H) | 0.56 (s, 3H), 0.54 (s, 3H)<br>0.42 (s, 3H), 0.33 (s, 3H) |
| **5** | 6.82 (m, 1H), 6.80 (m, 1H), 6.38 (m, 1H), 5.76 (t, 1H), 5.59 (d, *J* = 2.70 Hz, 1H), 5.31 (m, 1H), 5.06 (q, 2H), 4.58 (q, 2H), 4.35 (d, *J* = 3.04 Hz, 2H), 4.11 (m, 2H) | | |
| **6** | 7.53 (m, 4H)<br>7.16 (m, 4H) | 5.75–5.70 (m), 5.58 (m)<br>(total 4H) | 0.92 (s), 0.60 (s), 0.50 (s), 0.36 (s)<br>(total 12H) |

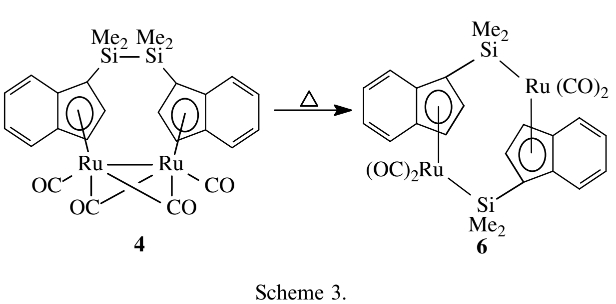


Scheme 2.

that the difference between the *meso* and *racemic* isomers of **1** in IR spectra is too small, and the absorption peaks are completely overlapped. In our previous work, the pure *meso* and *racemic* isomers of the tetramethyldisilylene bridged bis(tetrahydroindenyl) tetracarbonyl diiron complexes were isolated and showed completely same IR absorptions [5f].

The solubility of **5** in common organic solvents such as chloroform, acetone and DMSO is not very well. The $^1$H NMR signal of **5** only shows multiple groups of peaks at 6.82–4.11 ppm for the indenyl protons and no the signal of Ru—H, which precludes the possibility that the compound could be a hydride. The IR spectrum of **5** shows four terminal carbonyl and two bridging carbonyl absorption peaks at 1985, 1966, 1948, 1934, and 1807, 1779 cm$^{-1}$. To explore the formation of **5**, reaction of indene with $Ru_3(CO)_{12}$ in refluxing xylene was done. However, only the indenyl diruthenium complex $[C_9H_7Ru(CO)]_2(\mu\text{-}CO)_2$ was monitored by TLC and obtained. So the tetramethyldisilylene bridge with proper length and rigid may promote the formation of the novel indenyl nonanuclear cluster **5**.

Similar to the cyclopentadienyl analogues [6k,6l], the tetramethyldisilylene bridged bis(indenyl) diruthenium complex **4** can also undergo the thermal rearrangement to form the expecting rearrangement product $[(Me_2Si)(\eta^5\text{-}C_9H_6)Ru(CO)_2]_2$ (**6**) (Scheme 3). The $^1$H NMR spectrum of **6** shows multi groups of multiplets for the five-membered ring protons of the indenyl groups at 5.75–5.70 and 5.58 ppm, and four singlets for Si—Me protons at 0.92, 0.60, 0.50, and 0.36 ppm, indicating the existence of the *meso* and *racemic* isomers. Its IR spectrum shows only two terminal carbonyl absorptions at 2002 and 1954 cm$^{-1}$.



Scheme 3.

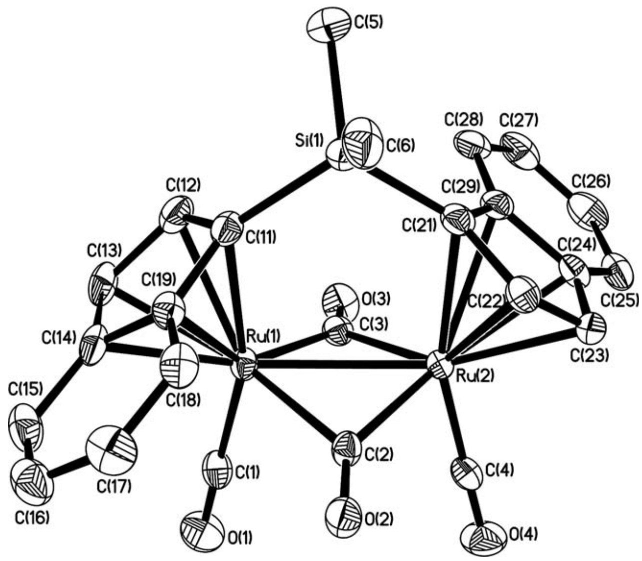


Fig. 1. ORTEP diagram of $(SiMe_2)[(\eta^5\text{-}C_9H_6)Ru(CO)]_2(\mu\text{-}CO)_2$ (**1**). Thermal ellipsoids are shown at the 30% level.

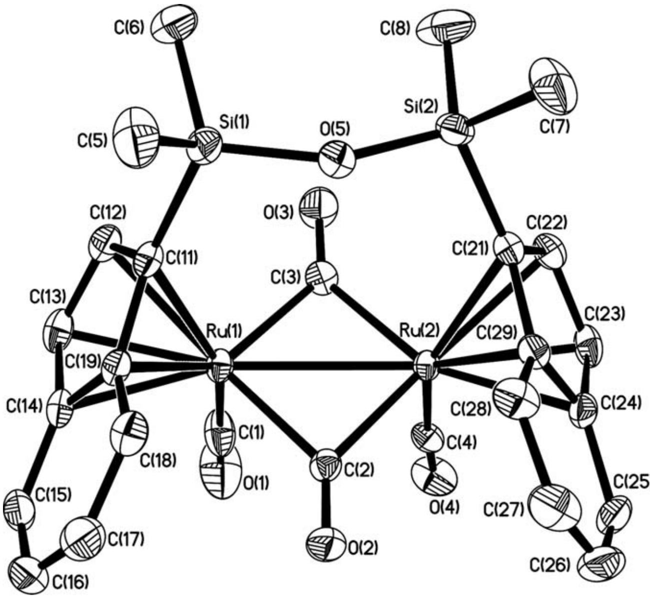


Fig. 2. ORTEP diagram of $(Me_2SiOSiMe_2)[(\eta^5\text{-}C_9H_6)Ru(CO)]_2(\mu\text{-}CO)_2$ (**2**). Thermal ellipsoids are shown at the 30% level.

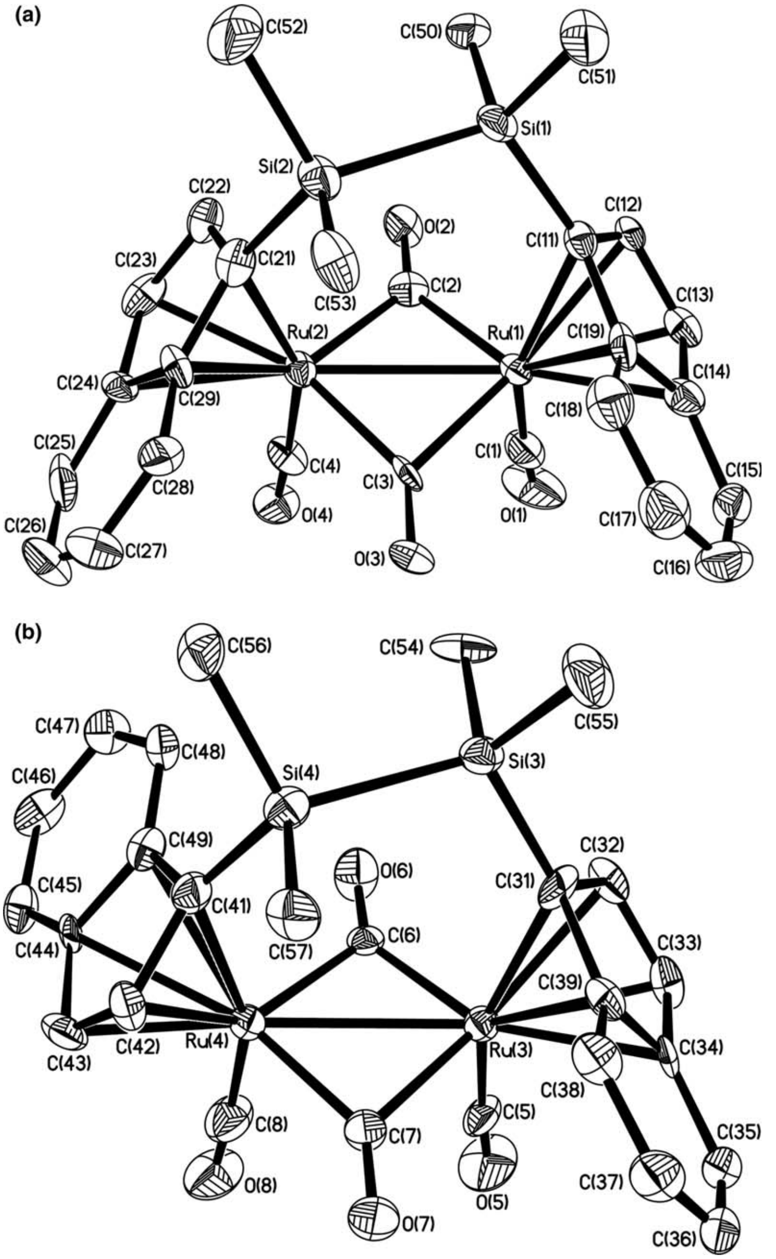


Fig. 3. ORTEP diagram of $(Me_2SiSiMe_2)[(\eta^5\text{-} C_9H_6)Ru(CO)]_2(\mu\text{-}CO)_2$ (**4**). Thermal ellipsoids are shown at the 30% level. The top drawing shows the unit of the *meso* isomer **4m**. The bottom drawing depicts the unit of the *racemic* isomer **4r**.

### 2.2. Molecular structures

The molecular structures of **1**, **2**, **4**, **6**, and **5**, are shown in Figs. 1–5, respectively.

Complexes **1**, **2**, and **4** are silyl bridged bis(indenyl) diruthenium complexes. As shown in Figs. 1–3, **1** is a *racemic* isomer, while **2** is a *meso* isomer, but in **4**, the *meso* isomer **4m** and *racemic* isomer **4r** are cocrystallized with the ratio of 1:1. The Ru—Ru bond distances are 2.7149(12), 2.755(2), 2.772(2), and 2.7858(12) Å for complexes **1**, **4m**, **4r**, and **2**, respectively, increasing with the increasing of the bridging atoms. The values are similar to that in the common bridged and nonbridged indenyl analogue [5e,6i,6k,9]. The dihedral angles between the two five-membered ring planes of indenyl groups are 75.8° and 66.5° for complexes **1** and **2**, respectively, decreasing with the bridge lengthening. However, the dihedral angles for **4m** and **4r** are 77.0° and 78.7°, even larger than that for the short dimethylsilylene bridged analogue **1**, probably due to the larger repulsion between the indenyl ligands with the four crowded methyl groups at the two bridging silicon atoms. The torsion angles CEN—Ru—Ru—CEN (CEN denotes the center of the five-membered ring of indenyl group) are 12.7°, 0.4°, 4.0°, and 10.0° for complexes **1**, **2**, **4m**, and **4r**, respectively. The significant distortions of the geometry can be attributed to the large intramolecular non-bonded interactions in the short dimethylsilylene bridged complex **1** and the crowded tetramethyldisilylene

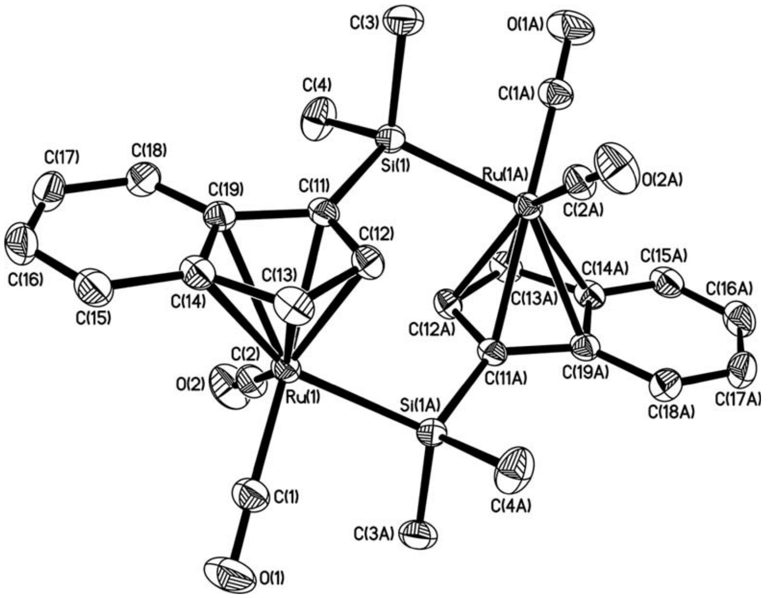


Fig. 4. ORTEP diagram of $[(Me_2Si)(\eta^5\text{-}C_9H_6)Ru(CO)_2]_2$ (**6**). Thermal ellipsoids are shown at the 30% level.

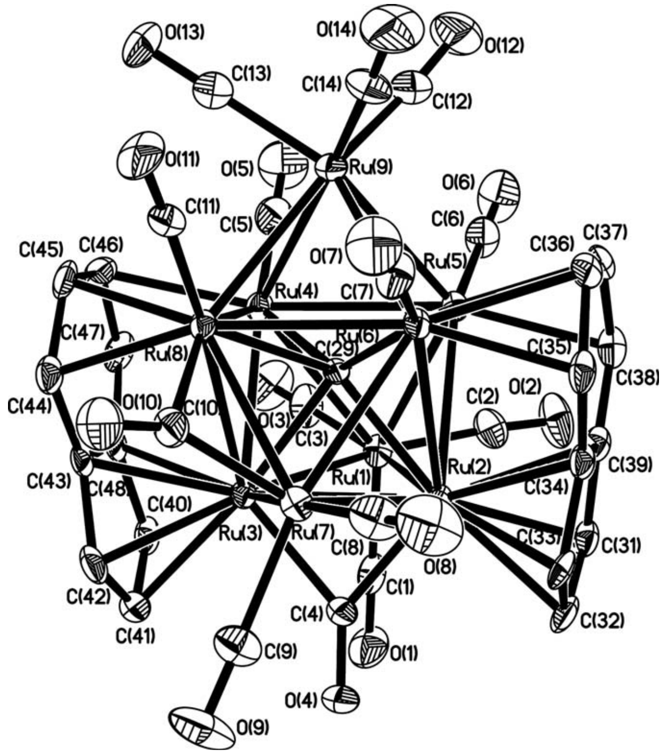


Fig. 5. ORTEP diagram of $Ru_9(\mu_6\text{-}C)(CO)_{14}(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^2\text{-}C_9H_7)_2$ (**5**). Thermal ellipsoids are shown at the 30% level.

bridged complex **4**, especially in the *racemic* isomers. The small fold angles between the five-membered ring plane and the six-membered ring plane of an indenyl group for complexes **1**, **2**, **4m**, and **4r** (0.3°, 2.5°; 2.5°, 3.3°; 3.0°, 3.0°; 4.3°, 4.9°) indicate that the indenyl groups are planar on the whole but slightly pucker outward. In **4m** and **4r**, the six-membered rings Ru(2)—Ru(1)—C(11)—Si(1)—Si(2)—C(21) and Ru(4)—Ru(3)—C(31)—Si(3)—Si(4)—C(41) constituting the molecular frameworks adopt a twist–boat conformation. The Si—Si distances [2.342(7), 2.344(7) Å] are longer than those of the corresponding cyclopentadienyl analogue $(Me_2SiSiMe_2)[C_5H_4Ru(CO)]_2(\mu\text{-}CO)_2$ [2.316(9) Å] [6k], possibly owing to the enlarged intramolecular nonbonded interaction.

Like many related analogues [6k,6l,10,11], complex **6** has $C_i$ symmetry. The two silicon atoms [Si(1), Si(1A)] and the two bridgehead carbon atoms of the indenyl rings [C(11), C(11A)] are coplanar, and the two ruthenium atoms lie on different sides of the plane with deviation of 0.8089 Å. The six-membered ring Ru(1)—Si(1 A)—C(11 A)—Ru(1A)—Si(1)—C(11) constituting the molecular skeleton adopts a standard chair conformation. The small fold angle between the five-membered ring plane and the six-membered ring plane of the indenyl group (2.8°) indicates that the indenyl groups are planar on the whole. The Ru—Si distance is 2.3768(10) Å, much shorter than that of the cyclopentadienyl analogues $[Me_2Si(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ [2.4074(9) Å] [6k], $[Me_2Si(\eta^5\text{-}C_5Me_4)Ru(CO)_2]_2$ (2.424(1) Å) [6l], and those in acyclic analogues (2.452(3)–2.507(8) Å) [12]. The Ru—CEN distance (1.933 Å) is also significantly shorter than that of the diruthenium substances **4m** and **4r** (1.949, 1.956; 1.956, 1.971 Å). The structural stability (stable molecular skeleton and short bond lengths) of the rearrangement product is believed to be one of the driving forces of the thermal rearrangement reaction.

Complex **5** is a novel nonanuclear ruthenium cluster. In an unit cell there are two independent molecules, which have similar structural parameters, and one of them is shown in Fig. 5. The simplified structure are also shown in Fig. 6 for clarity with omitting of the carbonyl groups. The metal atom framework for the nonanuclear ruthenium

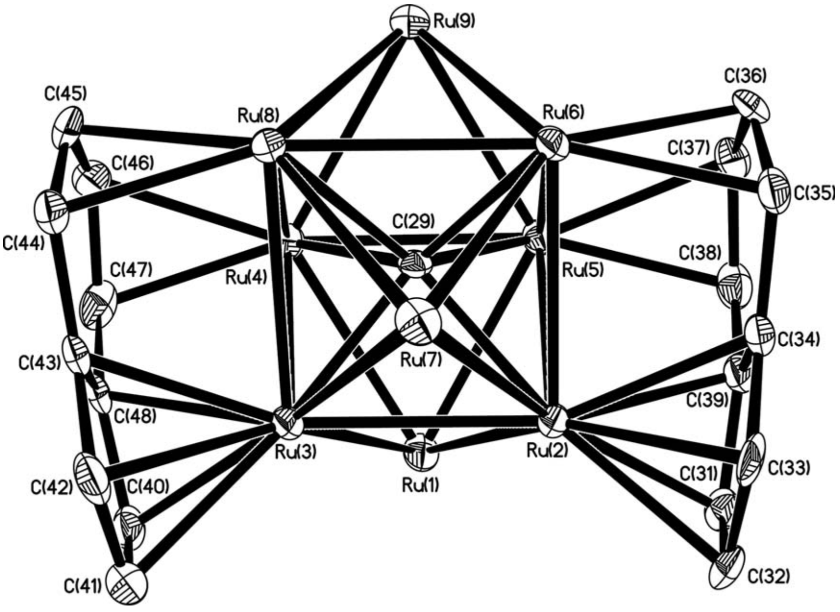


Fig. 6. Simplified ORTEP diagram of $Ru_9(\mu_6\text{-}C)(CO)_{14}(\mu_3\text{-}\eta^5{:}\eta^2{:}\eta^2\text{-}C_9H_7)_2$ (**5**) with omitting of the carbonyl groups.

cluster is a tricapped trigonal prism [13], encapsulating a carbide atom. The six ruthenium atoms Ru(2), Ru(5), Ru(6), Ru(3), Ru(4), and Ru(8) [or Ru(11), Ru(14), Ru(15), Ru(12), Ru(13), and Ru(17)] form a slightly distorted trigonal prism, of which each square face is further capped by an additional ruthenium atom [Ru(1), Ru(7), and Ru(9); or Ru(10), Ru(16), and Ru(18)]. The dihedral angle between the two triangular faces is 2.3° (or 2.2°). The edges and heights of the trigonal prism are in the range of 2.7520–2.8429 Å and 2.6683–2.7773 Å, respectively, while the distances between the capping ruthenium atom and the prism are in the range of 2.7327–2.8167 Å. All the Ru—Ru distances are shorter than that in $Ru_6C(CO)_{17}$ (2.826–2.998 Å) with octahedral geometry [14], $Ru_4(CO)_9(\eta^5,\eta^2,\eta^2\text{-}C_9H_7)(\eta^5\text{-}C_9H_9)]$ (2.765–2.972 Å) [7], and $Ru_3(CO)_{12}$ (2.854(1) Å) [15]. The Ru—C ($\mu_6$-C) distances are very different. The Ru(2)—C(29) [2.173(8) Å] and Ru(8)—C(29) [2.165(8) Å] distances are significantly longer than the others [2.076–2.119 Å] in a molecule, while the Ru(11)—C(30) [2.162(9) Å] distance is significantly longer than the others [2.075–2.134 Å] in another molecule. There is a number of clusters with tricapped trigonal prism geometry [16], but only a few of them with a bare atom in the cage [17]. Complex **5**, to our knowledge, is the first carbon-centered tricapped trigonal prismatic metal cluster.

High nuclearity ($M_n$, $n \geqslant 7$) metal clusters are of interest as intermediates in the transition from molecular to metallic behavior [18]. High nuclearity ruthenium clusters are still comparatively rare [19]. There are some reports on the ruthenium clusters containing seven [20,21], eight [22], 10 [23], and 11 [24] ruthenium atoms. But only one nonanuclear ruthenium cluster $[H_3Ru_9(CO)_{20}(\mu_7\text{-}P)(P^tBu)_3]$ [21] was reported. So complex **5** is the second example of nonanuclear ruthenium cluster. Compounds containing $Ru_6(\mu_6\text{-}C)$ moiety have been studied extensively [14,23,25,26]. The six ruthenium atoms of all these compounds form an octahedron which encapsulates a carbide atom. And complex **5** is also the first ruthenium cluster with $Ru_6(\mu_6\text{-}C)$ moiety as a triangular prism geometry, although there are some reports on the carbon-centered triangular prismatic tungsten clusters [27].

In complex **5**, the three ruthenium atoms in each triangular face of the trigonal prism coordinated with an indenyl ligands in facial bonding mode: one ruthenium is in $\eta^5$ mode, the other two are in $\eta^2$ mode, each interacting with a different segment of the indenyl ligand. There are also only a few of examples with this bonding mode observed in the ruthenium and osmium clusters [7,28]. The $\eta^5$-indenyl coordinated Ru(2) and Ru(3) [or Ru(11) and Ru(12)] share a bridging carbonyl, which makes the Ru(2)—Ru(3) [2.6683(12) Å] or Ru(11)—Ru(12) bond [2.6721(12) Å] much shorter than the other Ru—Ru bonds (2.7327–2.8429 Å) of the cluster and those in many cyclopentadienyl and indenyl diruthenium complexes (2.70–2.74 Å) [5e,9,6i]. The $\eta^2$-indenyl coordinated ruthenium atoms are coordinated each with a terminal carbonyl and Ru(8) or Ru(17) also shares a bridging carbonyl with a capped atom Ru(7) or Ru(16), which is further coordinated with two terminal carbonyls. The other two capped atoms Ru(1) and Ru(9) [or Ru(10) and Ru(18)] are coordinated each with three terminal carbonyls. The dihedral angle between the two five-membered ring planes of indenyl groups is 21.0° (or 19.6°). The fold angles between the five-membered ring plane and the six-membered ring plane of the indenyl groups are 7.6° and 7.6° (or 6.8° and 7.2°), larger than that for the complexes **1**, **2**, **4m** and **4r** (0.3–4.9°), indicating the poor coplanarity of the indenyl groups and the good hapticity of the indenyl ligands. The six-membered ring of $\eta^5$-coordinated indenyl groups generally exhibits a butadiene-like property [5b,29], which could be hydrogenated and result in the more stable tetrahydroindenyl complexes [5c,5d,30] or even undergo the Diels–Alder reaction with benzyne [31]. The structural parameters of complexes **1**, **2**, **4m**, **4r**, and **6** also support this viewpoint. The two C—C bond distances of the six-membered rings of the indenyl groups are significantly shorter and close to the double bond length (1.34–1.35 Å). However, after $\eta^2$-coordination with ruthenium in **5**, the C—C bond distances [C(35)—C(36) 1.434(15) Å, C(37)—C(38) 1.412 (13) Å, C(44)—C(45) 1.404(15) Å, C(46)—C(47) 1.412(13) Å; C(53)—C(54) 1.395(14) Å, C(55)—C(56) 1.399(14) Å, C(62)—C(63) 1.392(14) Å, C(64)—C(65) 1.408(14) Å] are significantly enlarged and close to the adjacent C—C bonds [1.426–1.477 Å], indicating that the $\eta^2$-coordination with metal weakens the C—C bond.

## 3. Conclusion

The silyl bridged bis(indenyl) diruthenium complexes can be synthesized by the reaction of the corresponding silyl bridged bis(indene) ligands with $Ru_3(CO)_{12}$ in refluxing xylene. The tetramethyldisilylene bridged bis(indenyl) diruthenium complex **4** can undergo a thermal rearrangement to form complex **6**. A novel indenyl nonanuclear ruthenium cluster $Ru_9(\mu_6\text{-}C)(CO)_{14}(\mu_3\text{-}\eta^5\text{:}\eta^2\text{:}\eta^2\text{-}C_9H_7)_2$ with carbon-centered tricapped trigonal prism geometry is also obtained unexpectedly and characterized by X-ray diffraction.

## 4. Experimental details

### 4.1. General procedures and starting materials

Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. All solvents were distilled from appropriate drying agents under argon before use. $^1H$ NMR spectra were recorded on a BRUKER AC-P200, while IR spectra were recorded as KBr disks on a Bruker Equinox 22 spectrometer. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. $C_9H_7SiMe_2C_9H_7$ [32] $C_9H_7Me_2SiOSiMe_2C_9H_7$ and $C_9H_7Me_2SiSiMe_2C_9H_7$ [33] were prepared according to the literature methods.

### 4.2. Reaction of $C_9H_7SiMe_2C_9H_7$ with $Ru_3(CO)_{12}$

A solution of 0.301 g (0.471 mmol) of $Ru_3(CO)_{12}$ and 0.213 g (0.740 mmol) of $C_9H_7SiMe_2C_9H_7$ in 30 mL of xylene was refluxed for 16 h. The solvent was removed under reduced pressure, and the residue was placed in an $Al_2O_3$ column. Elution with $CH_2Cl_2$/petroleum ether (1:3) developed a red band, which was collected and, after concentration, afforded 0.090 g (2%) of **1** as red crystals. M.p. 237 °C (dec). Anal. Calc. for $C_{24}H_{18}O_4Ru_2Si$: C, 47.99; H, 3.02. Found: C, 48.02; H, 3.17%. IR ($\nu_{CO}$, $cm^{-1}$): 1980(s), 1943(s), 1821(m), 1778(s).

### 4.3. Reaction of $C_9H_7Me_2SiOSiMe_2C_9H_7$ with $Ru_3(CO)_{12}$

Using similar procedure as described above, $C_9H_7Me_2SiOSiMe_2C_9H_7$ reacted with $Ru_3(CO)_{12}$ gave complexes **2** and **3** in 15% and 8% yields, respectively. **2**: m.p. 245 °C (dec). Anal. Calc. for $C_{26}H_{24}O_5Ru_2Si_2$: C, 46.28; H, 3.58. Found: C, 46.17; H, 3.55%. IR ($\nu_{CO}$, $cm^{-1}$): 2002(s), 1946(s), 1819(m), 1771(s). **3** [6c,34]: m.p. 245 °C (dec). IR ($\nu_{CO}$, $cm^{-1}$): 1937(s), 1910(m), 1773(s), 1744(m).

### 4.4. Reaction of $C_9H_7Me_2SiSiMe_2C_9H_7$ with $Ru_3(CO)_{12}$

Using similar procedure as described above, $C_9H_7Me_2SiSiMe_2C_9H_7$ was reacted with $Ru_3(CO)_{12}$ in refluxing xylene for 12 h, after chromatography and eluted with $CH_2Cl_2$/petroleum ether, complexes **3** and **4** were obtained both in 8% yield. Further elution with acetone gave complex **5** in 3% yield. For **4**: m.p. 194 °C (dec). Anal. Calc. for $C_{26}H_{24}O_4Ru_2Si_2$: C, 47.40; H, 3.67. Found: C, 47.89; H, 3.49%. IR ($\nu_{CO}$, $cm^{-1}$): 1995(s), 1976(s), 1952(m), 1936(m), 1814(m), 1779(s), 1770(s), 1755(m). For **5**: m.p. >300 °C. Anal. Calc. for $C_{33}H_{14}O_{14}Ru_9$: C, 25.67; H, 0.91. Found: C, 25.50; H, 0.95%. IR ($\nu_{CO}$, $cm^{-1}$): 1985(s, br), 1966(s, br), 1948(s, sh), 1934(s, sh), 1807(s), 1779(m, sh).

### 4.5. Rearrangement reaction of **4**

The solution of **4** (0.040 g) in xylene (20 mL) was heated under reflux for 36 h and seriously decomposition of the substance was observed. The solvent was removed under reduced pressure, and the residue was placed in an $Al_2O_3$ column. Elution with the $CH_2Cl_2$/petroleum ether gave 0.006 g (15 %) of **6** as yellow crystals. M.p. 251 °C (dec). Anal. Calc. for $C_{26}H_{24}O_4Ru_2Si_2$: C, 47.40; H, 3.67. Found: C, 48.33; H, 3.55%. IR ($\nu_{CO}$, $cm^{-1}$): 2002 (s), 1954(s).

### 4.6. Crystallographic studies

Single crystals of complexes **1**, **2**, **4**, **5**, and **6** suitable for X-ray diffraction were obtained from hexane/$CH_2Cl_2$ solution. Data collection was performed on a BRUKER SMART 1000, using graphite-monochromated Mo Kα radiation ($\omega - 2\theta$ scans, $\lambda = 0.71073$ Å). Semiempirical absorption corrections were applied using the SADABS program [35]. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were using the SHELXTL-97 program system. The crystal data and summary of X-ray data collection are presented in Table 3. Selected bond lengths and angles are listed in Table 2.

Table 2
Selected bond distances (Å) and angles (°)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *Compound* ***1*** | | | | | | | |
| Ru(1)—Ru(2) | 2.7149(12) | Ru(1)—C(11) | 2.287(6) | Ru(2)—C(21) | 2.281(6) | Si(1)—C(11) | 1.879(6) |
| Si(1)—C(21) | 1.882(7) | C(14)—C(15) | 1.428(9) | C(14)—C(19) | 1.436(8) | C(15)—C(16) | 1.368(10) |
| C(16)—C(17) | 1.412(10) | C(17)—C(18) | 1.328(9) | C(18)—C(19) | 1.418(8) | C(24)—C(25) | 1.403(9) |
| C(24)—C(29) | 1.447(9) | C(25)—C(26) | 1.367(9) | C(26)—C(27) | 1.387(10) | C(27)—C(28) | 1.364(10) |
| C(28)—C(29) | 1.411(8) | | | | | | |
| C(11)—Ru(1)—Ru(2) | 94.54(15) | C(21)—Ru(2)—Ru(1) | 94.02(15) | C(11)—Si(1)—C(21) | 109.3(3) | | |
| Si(1)—C(11)—Ru(1) | 120.5(3) | Si(1)—C(21)—Ru(2) | 121.0(3) | | | | |
| *Compound* ***2*** | | | | | | | |
| Ru(1)—Ru(2) | 2.7858(12) | Ru(1)—C(11) | 2.338(5) | Ru(2)—C(21) | 2.332(4) | Si(2)—O(5) | 1.628(4) |
| Si(2)—C(21) | 1.859(5) | Si(1)—O(5) | 1.625(4) | Si(1)—C(11) | 1.866(5) | C(14)—C(15) | 1.413(7) |
| C(14)—C(19) | 1.431(6) | C(19)—C(18) | 1.409(6) | C(18)—C(17) | 1.363(7) | C(17)—C(16) | 1.388(8) |
| C(16)—C(15) | 1.355(7) | C(24)—C(25) | 1.414(7) | C(24)—C(29) | 1.426(7) | C(29)—C(28) | 1.414(7) |
| C(28)—C(27) | 1.373(8) | C(27)—C(26) | 1.387(9) | C(26)—C(25) | 1.350(9) | | |
| C(11)—Ru(1)—Ru(2) | 112.21(11) | C(21)—Ru(2)—Ru(1) | 113.52(11) | O(5)—Si(2)—C(21) | 108.94(19) | | |
| O(5)—Si(1)—C(11) | 111.24(19) | Si(1)—O(5)—Si(2) | 148.0(2) | Si(1)—C(11)—Ru(1) | 133.1(2) | | |
| Si(2)—C(21)—Ru(2) | 130.1(2) | | | | | | |
| *Compound* ***4*** | | | | | | | |
| Ru(1)—Ru(2) | 2.755(2) | Ru(1)—C(11) | 2.301(16) | Ru(2)—C(21) | 2.337(16) | Ru(3)—C(31) | 2.308(17) |
| Ru(3)—Ru(4) | 2.772(2) | Ru(4)—C(41) | 2.317(18) | Si(1)—C(11) | 1.870(17) | Si(1)—Si(2) | 2.342(7) |
| Si(2)—C(21) | 1.873(18) | Si(3)—C(31) | 1.854(18) | Si(3)—Si(4) | 2.344(7) | Si(4)—C(41) | 1.862(18) |
| C(14)—C(15) | 1.44(2) | C(15)—C(16) | 1.33(3) | C(16)—C(17) | 1.40(3) | C(17)—C(18) | 1.34(3) |
| C(16)—C(17) | 1.37(3) | C(14)—C(19) | 1.43(2) | C(24)—C(25) | 1.40(2) | C(25)—C(26) | 1.34(3) |
| C(26)—C(27) | 1.39(3) | C(27)—C(28) | 1.33(3) | C(28)—C(29) | 1.43(2) | C(24)—C(29) | 1.44(2) |
| C(34)—C(35) | 1.40(2) | C(35)—C(36) | 1.37(3) | C(36)—C(37) | 1.43(3) | C(37)—C(38) | 1.36(2) |
| C(38)—C(39) | 1.43(2) | C(34)—C(39) | 1.44(2) | C(44)—C(45) | 1.40(2) | C(45)—C(46) | 1.35(2) |
| C(46)—C(47) | 1.41(3) | C(47)—C(48) | 1.39(2) | C(48)—C(49) | 1.40(2) | C(44)—C(49) | 1.46(2) |
| C(11)—Ru(1)—Ru(2) | 106.6(4) | C(21)—Ru(2)—Ru(1) | 108.3(5) | C(31)—Ru(3)—Ru(4) | 106.9(4) | | |
| C(41)—Ru(4)—Ru(3) | 106.5(4) | C(11)—Si(1)—Si(2) | 114.8(6) | C(21)—Si(2)—Si(1) | 113.0(6) | | |
| C(31)—Si(3)—Si(4) | 112.3(6) | C(41)—Si(4)—Si(3) | 114.0(6) | Si(1)—C(11)–Ru(1) | 126.7(8) | | |
| Si(2)—C(21)—Ru(2) | 129.2(9) | Si(3)—C(31)—Ru(3) | 129.2(8) | Si(4)—C(41)—Ru(4) | 130.4(9) | | |
| *Compound* ***6*** | | | | | | | |
| Ru(1)—Si(1A) | 2.3768(11) | Ru(1)—C(11) | 2.255(3) | Si(1)—C(11) | 1.884(3) | Si(1)—Ru(1A) | 2.3768(10) |
| C(14)—C(15) | 1.409(4) | C(14)—C(19) | 1.430(4) | C(15)—C(16) | 1.351(5) | C(16)—C(17) | 1.396(6) |
| C(17)—C(18) | 1.368(5) | C(18)—C(19) | 1.418(5) | | | | |
| C(11)—Ru(1)—Si(1A) | 101.81(8) | C(11)—Si(1)—Ru(1A) | 112.06(10) | Si(1)—C(11)—Ru(1) | 130.94(15) | | |
| *Compound* ***5*** | | | | | | | |
| Ru(1)—Ru(2) | 2.7787(13) | Ru(1)—Ru(3) | 2.7897(12) | Ru(1)—Ru(4) | 2.7796(13) | Ru(1)—Ru(5) | 2.7327(12) |
| Ru(2)—Ru(3) | 2.6683(12) | Ru(2)—Ru(5) | 2.8140(12) | Ru(2)—Ru(6) | 2.8004(12) | Ru(2)—Ru(7) | 2.8167(12) |
| Ru(2)—C(29) | 2.173(8) | Ru(2)—C(31) | 2.241(9) | Ru(2)—C(32) | 2.239(9) | Ru(2)—C(33) | 2.224(9) |
| Ru(2)—C(34) | 2.231(9) | Ru(2)—C(39) | 2.239(10) | Ru(3)—Ru(4) | 2.7982(12) | Ru(3)—Ru(7) | 2.7954(12) |
| Ru(3)—Ru(8) | 2.8173(12) | Ru(3)—C(29) | 2.119(8) | Ru(3)—C(40) | 2.241(9) | Ru(3)—C(41) | 2.244(10) |
| Ru(3)—C(42) | 2.237(10) | Ru(3)—C(43) | 2.214(9) | Ru(3)—C(48) | 2.242(9) | Ru(4)—Ru(5) | 2.7557(13) |
| Ru(4)—Ru(8) | 2.8429(13) | Ru(4)—Ru(9) | 2.7835(12) | Ru(4)—C(29) | 2.098(9) | Ru(4)—C(46) | 2.242(10) |
| Ru(4)—C(47) | 2.189(10) | Ru(5)—Ru(6) | 2.7520(12) | Ru(5)—Ru(9) | 2.7825(13) | Ru(5)—C(29) | 2.084(9) |
| Ru(5)—C(37) | 2.274(9) | Ru(5)—C(38) | 2.205(10) | Ru(6)—Ru(7) | 2.7599(13) | Ru(6)—Ru(8) | 2.7773(12) |
| Ru(6)—Ru(9) | 2.7451(13) | Ru(6)—C(29) | 2.076(8) | Ru(6)—C(35) | 2.194(9) | Ru(6)—C(36) | 2.260(10) |
| Ru(7)—Ru(8) | 2.7592(13) | Ru(8)—Ru(9) | 2.8104(13) | Ru(8)—C(29) | 2.165(8) | Ru(8)—C(44) | 2.192(10) |
| Ru(8)—C(45) | 2.293(10) | C(34)—C(35) | 1.441(12) | C(35)—C(36) | 1.434(15) | C(36)—C(37) | 1.467(14) |
| C(37)—C(38) | 1.412(13) | C(38)—C(39) | 1.433(15) | C(34)—C(39) | 1.474(14) | C(43)—C(44) | 1.445(13) |
| C(44)—C(45) | 1.404(15) | C(45)—C(46) | 1.442(16) | C(46)—C(47) | 1.412(13) | C(47)—C(48) | 1.427(14) |
| C(43)—C(48) | 1.477(14) | Ru(10)—Ru(11) | 2.7845(13) | Ru(10)—Ru(12) | 2.7846(12) | Ru(10)—Ru(13) | 2.7645(13) |
| Ru(10)—Ru(14) | 2.7555(13) | Ru(11)—Ru(12) | 2.6721(12) | Ru(11)—Ru(14) | 2.8169(13) | Ru(11)—Ru(15) | 2.8075(13) |
| Ru(11)—Ru(16) | 2.8008(12) | Ru(11)—C(30) | 2.162(9) | Ru(11)—C(49) | 2.246(10) | Ru(11)—C(50) | 2.249(10) |
| Ru(11)—C(51) | 2.248(10) | Ru(11)—C(52) | 2.240(9) | Ru(11)—C(57) | 2.253(9) | Ru(12)—Ru(13) | 2.8003(12) |
| Ru(12)—Ru(16) | 2.7893(13) | Ru(12)—Ru(17) | 2.7997(12) | Ru(12)—C(30) | 2.116(8) | Ru(12)—C(58) | 2.253(10) |
| Ru(12)—C(59) | 2.265(10) | Ru(12)—C(60) | 2.240(9) | Ru(12)—C(61) | 2.212(9) | Ru(12)—C(66) | 2.227(10) |
| Ru(13)—Ru(14) | 2.7616(12) | Ru(13)—Ru(17) | 2.8245(12) | Ru(13)—Ru(18) | 2.7884(13) | Ru(13)—C(30) | 2.123(8) |
| Ru(13)—C(64) | 2.270(9) | Ru(13)—C(65) | 2.213(9) | Ru(14)—Ru(15) | 2.7639(12) | Ru(14)—Ru(18) | 2.7670(13) |
| Ru(14)—C(30) | 2.099(7) | Ru(14)—C(55) | 2.292(9) | Ru(14)—C(56) | 2.199(10) | Ru(15)—Ru(16) | 2.7373(13) |
| Ru(15)—Ru(17) | 2.7669(12) | Ru(15)—Ru(18) | 2.7502(13) | Ru(15)—C(30) | 2.075(8) | Ru(15)—C(53) | 2.219(10) |

Table 2 (*continued*)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *Compound* **5** | | | | | | | |
| Ru(15)—C(54) | 2.280(9) | Ru(16)—Ru(17) | 2.7681(13) | Ru(17)—Ru(18) | 2.7880(13) | Ru(17)—C(30) | 2.134(8) |
| Ru(17)—C(62) | 2.182(9) | Ru(17)—C(63) | 2.265(11) | C(52)—C(53) | 1.435(14) | C(53)—C(54) | 1.395(14) |
| C(54)—C(55) | 1.426(14) | C(55)—C(56) | 1.399(14) | C(56)—C(57) | 1.433(14) | C(52)—C(57) | 1.469(14) |
| C(61)—C(62) | 1.450(14) | C(62)—C(63) | 1.392(14) | C(63)—C(64) | 1.448(14) | C(64)—C(65) | 1.408(14) |
| C(65)—C(66) | 1.466(14) | C(61)—C(66) | 1.471(14) | | | | |

Table 3
Crystal data and summary of X-ray data collection for **1**, **2**, and **4**–**6**

| | **1** | **2** | **4** | **6** | **5** |
|---|---|---|---|---|---|
| Empirical formula | $C_{25}H_{20}Cl_2O_4Ru_2Si$ | $C_{26}H_{24}O_5Ru_2Si_2$ | $C_{26}H_{24}O_4Ru_2Si_2$ | $C_{26}H_{24}O_4Ru_2Si_2$ | $C_{68}H_{32}Cl_4O_{28}Ru_{18}$ |
| Formula weight | 685.54 | 674.77 | 658.77 | 658.77 | 3258.00 |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 16.178(7) | 9.431(4) | 9.549(2) | 7.682(3) | 10.994(3) |
| $b$ (Å) | 7.645(3) | 10.087(4) | 57.377(13) | 9.504(3) | 15.248(5) |
| $c$ (Å) | 20.373(8) | 15.355(6) | 10.750(3) | 10.435(4) | 22.957(7) |
| $\alpha$ (°) | | 72.936(6) | | 62.979(5) | 87.626(5) |
| $\beta$ (°) | 90.320(7) | 72.340(7) | 119.089(4) | 69.193(5) | 87.626(5) |
| $\gamma$ (°) | | 72.004(6) | | 78.075(6) | 87.642(5) |
| $V$ (Å$^3$) | 2519.9(17) | 1291.4(9) | 5147(2) | 633.5(4) | 3841(2) |
| $Z$ | 4 | 2 | 8 | 1 | 2 |
| $D_{calc}$ (g/cm$^3$) | 1.807 | 1.735 | 1.700 | 1.727 | 2.817 |
| $\mu$ (mm$^{-1}$) | 1.488 | 1.297 | 1.297 | 1.317 | 3.642 |
| $F$(000) | 1352 | 672 | 2624 | 328 | 3048 |
| Crystal size (mm) | 0.22 × 0.18 × 0.16 | 0.24 × 0.18 × 0.16 | 0.16 × 0.14 × 0.10 | 0.14 × 0.10 × 0.08 | 0.24 × 0.08 × 0.06 |
| Max. 2$\theta$ (°) | 52.80 | 52.88 | 50.00 | 52.84 | 52.82 |
| Reflections collected | 9184 | 7374 | 26,803 | 3689 | 22,052 |
| Independent reflections | 5096 | 5241 | 9073 | 2571 | 15,453 |
| $R_{int}$ | 0.0428 | 0.0297 | 0.1198 | 0.0188 | 0.0332 |
| No. of parameters | 310 | 321 | 621 | 156 | 1063 |
| Goodness-of-fit on $F^2$ | 1.099 | 1.020 | 1.255 | 1.044 | 1.062 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0463, 0.0953 | 0.0387, 0.0807 | 0.1173, 0.1873 | 0.0276, 0.0621 | 0.0453, 0.0926 |
| $R_1$, $wR_2$ (all data) | 0.0742, 0.1042 | 0.0671, 0.0902 | 0.1817, 0.2093 | 0.0358, 0.0652 | 0.0793, 0.1143 |

## 5. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 298888–298892 for compounds **1**, **2**, and **4**–**6**, respectively. Copies of this information may be obtained free of charge The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk of www: http://www.ccdc.cam.ac.uk).

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