

The synthesis and reactivity of some indenyl and bis-indenyl ruthenium carbonyl complexes

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Abstract

The reaction of $[\text{Ru}_3(\text{CO})_{12}]$ (**1**), with indene in refluxing xylene affords $[\{(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{CO})_2\}_2]$ (**2**), in high yield. An analogous reaction of **1** with 2-phenylindene affords the expected dinuclear complex $[\{(\eta^5\text{-C}_9\text{H}_6\text{Ph})\text{Ru}(\text{CO})_2\}_2]$ (**5**), and a heptaruthenium cluster $[(\text{C}_9\text{H}_4\text{Ph})\text{Ru}_7(\mu\text{-H})(\mu\text{-CO})_2(\text{CO})_{16}]$ (**6**). The indenyl ligand in compound **6** exhibits a novel bonding mode in which the benzenoid ring is $\mu_4, \eta^1: \eta^1: \eta^2: \eta^2$ bound to the cluster. Refluxing **1** with bis-indenyl methane affords the dinuclear complex $[\text{Ru}_2(\text{CO})_4\{\mu\text{-}(\eta^5\text{-C}_9\text{H}_6)_2\text{CH}_2\}]$ (**7**), which reacts with iodine via Ru–Ru bond cleavage to give $[\text{Ru}_2\text{I}_2(\text{CO})_4\{(\eta^5\text{-C}_9\text{H}_6)_2\text{CH}_2\}]$ (**8**).

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1. Introduction

Transition metal complexes containing the indenyl ligand have received much attention due to their enhanced reactivity and catalytic ability as compared to the cyclopentadienyl analogues [1]. For example, $[(\eta^5\text{-C}_9\text{H}_7)\text{RuCl}(\text{PPh}_3)_2]$ showed efficient catalytic activity and selectivity for the redox isomerisation of allyl and propargyl alcohols [2], dynamic kinetic resolution of racemic alcohols [3], and the cycloaddition of 1,6-heptadiyne with bicycloalkenes [4], when compared to its cyclopentadienyl analogue, $[\text{CpRuCl}(\text{PPh}_3)_2]$. Cyclopentadienyl complexes of ruthenium have been reported as an excellent catalyst for many organic reactions [5]. In contrast, catalytic studies involving indenyl ruthenium complexes are only emerging, but some reactions investigated have included olefin cyclopropanation [6], cycloaddition reactions [4,7], hydration reactions [8], dimerisation of terminal alkynes [9], and radical polymerization [10]. Most of the catalytic studies for indenyl ruthenium complexes are based on $[(\eta^5\text{-C}_9\text{H}_7)\text{RuCl}(\text{L})_2]$

(where L = monodentate phosphine), and $[(\eta^5\text{-C}_9\text{H}_7)\text{RuCl}(\text{COD})]$.

In this study, we would like to report on our studies into the reaction of indene and its derivatives such as bis-indenyl and phenylindene, with $[\text{Ru}_3(\text{CO})_{12}]$ (**1**), to find a convenient entry into the chemistry of indenyl and bis-indenyl ruthenium complexes.

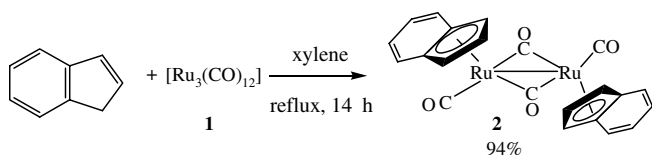
2. Results and discussion

2.1. Indenyl complexes

The reaction of indene with **1** in boiling heptane was reported to give $[\{(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{CO})_2\}_2]$ (**2**), in an unspecified yield [11]. Complex **2** was also reported to be obtainable in 9.4% yield (together with 9.6% of $[\text{Ru}_4(\text{CO})_7(\mu\text{-CO})_2(\eta^2, \eta^5, \eta^2\text{-C}_9\text{H}_7)(\eta^5\text{-C}_9\text{H}_9)]$) by refluxing in methylcyclohexane; the yield of **2** was increased to 65% in refluxing methyl isobutyl ketone [12]. We have found that changing the solvent to xylene afforded **2** in 94% yield (Scheme 1). Compound **2** has been completely characterized, including by a single crystal X-ray diffraction study; the ORTEP plot and selected bond parameters are given in Fig. 1.

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Scheme 1.

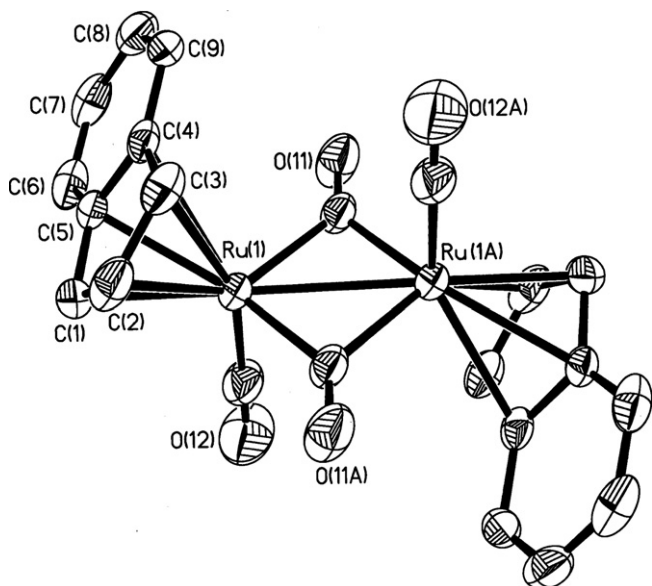


Fig. 1. ORTEP plot (thermal ellipsoids are drawn at 50% probability; all hydrogen atoms omitted) and selected bond parameters for **2**. C*–Ru(1) = 1.952(4); Ru(1)–Ru(1A) = 2.7412(5); Ru(1)–C(1) = 2.207(4); Ru(1)–C(2) = 2.262(4); Ru(1)–C(3) = 2.279(4); Ru(1)–C(4) = 2.398(3); Ru(1)–C(5) = 2.326(3); Ru(1)–C(11) = 2.049(4); Ru(1)–C(11A) = 1.992(4); Ru(1A)–C(11) = 1.992(4); Ru(1)–C(12) = 1.854(4); C(11)–O(11) = 1.167(4); C(12)–O(12) = 1.142(5); Ru(1)–C(11)–O(11) = 135.0(3); Ru(1A)–C(11)–O(11) = 139.6(3); Ru(1)–C(12)–O(12) = 179.4(4); Ru(1)–C(11)–Ru(1A) = 85.42(14); C(2)–Ru(1)–C(3) = 35.59(16); C(1)–Ru(1)–C(3) = 60.81(16). C* = centroid of the five-membered ring – C(1), C(2), C(3), C(4) and C(5). Slip-fold parameters: [13] slip distortion (Δ) = 0.119(4) Å; hinge angle (HA) = 7.09°; fold angle (FA) = 8.51°.

The crystal structure of **2**, including its bond parameters, is very similar to that of the cyclopentadienyl analogue [$\{\text{CpRu}(\text{CO})_2\}_2$] [14]. The molecular structure consists of two ruthenium atoms at a single bond distance [2.7412(5) Å], each carrying one terminal and one bridging carbonyl ligands, and the indenyl groups are arranged trans to one another and ligate each metal in an η^5 -fashion. The bridging carbonyl groups and the ruthenium atoms are coplanar.

In the description of η^5 -indenyl complexes, it is useful to examine the degree of distortion from η^5 to η^3 coordination; the latter being equivalent to an allyl-ene bonding description of the C₅-ring. As described by Taylor and Marder, the degree of distortion can be discussed in terms of the slip-fold distortion parameters: slip distortion (Δ), hinge angle (HA), and fold angle (FA) [13]. The Ru–C distances to the ring junction carbons (C(4,5)) in **2** (average = 2.362(3) Å) are longer than the Ru–C(1,3) distances

(average = 2.249(4) Å), and the distortion values of the slip-fold parameters are: slip distortion (Δ) = 0.119(4) Å, hinge angle = 7.09° and fold angle = 8.51°. These values fall within the range for small distortion from a η^5 bonding mode [13].

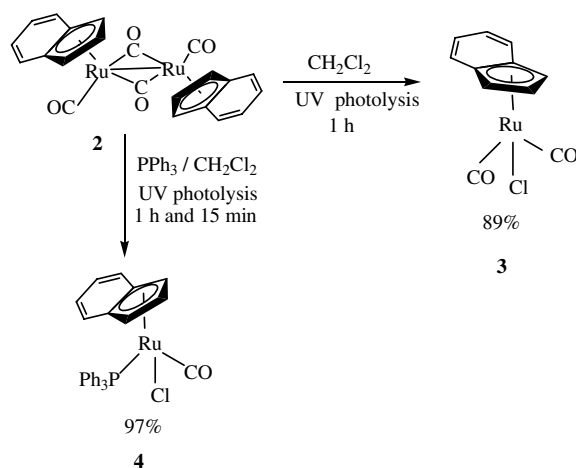
UV photolysis of a dichloromethane solution of **2** afforded [$(\eta^5\text{-C}_9\text{H}_7)\text{RuCl}(\text{CO})_2$] (**3**) in 89% yield (Scheme 2); compound **3** can also be prepared by stirring **2** with CCl_4 . Compound **3** was tested as a catalyst for the dimerisation of phenylacetylene in toluene; heating a toluene solution of phenylacetylene containing 1 mol% of **3** for 17 h gave mostly unreacted phenylacetylene; 2-phenyl naphthalene was obtained in 4% isolated yield.

UV photolysis of **2** with PPh_3 gave [$(\eta^5\text{-C}_9\text{H}_7)\text{RuCl}(\text{CO})(\text{PPh}_3)$] (**4**) (Scheme 2); it has earlier been obtained by stirring [$(\eta^5\text{-C}_9\text{H}_7)\text{RuCl}(\text{PPh}_3)_2$] with KOH and wet chloroform for 40 h in 2-propanol (89% yield) [15]. The ^1H NMR spectrum for **4** showed different chemical shifts for the H¹ and H³ protons of the indenyl ligand, which has been attributed to asymmetry at the Ru centre [16].

We have completely characterized **4**, including by a single crystal X-ray diffraction study; the ORTEP plot and selected bond parameters are given in Fig. 2. As in **2**, the indenyl ligand in **4** exhibits small distortion from a η^5 bonding mode; the Ru–C distances to the ring junction carbons (C(8,9)) (average = 2.363(4) Å) are longer than the Ru–C(1,3) distances (average = 2.2045(4) Å), and the slip-fold parameters are: slip distortion = 0.159(4) Å, hinge angle = 7.52° and fold angle = 10.32°.

2.2. Phenylindenyl ruthenium complexes

Interestingly, the reaction of **1** with 1-phenylindene in refluxing heptane afforded the expected dinuclear compound [$\{(\eta^5\text{-C}_9\text{H}_6\text{Ph})\text{Ru}(\text{CO})_2\}_2$] (**5**), in 17% yield, and a smaller amount of the novel cluster **6**, together with many unidentified products (Scheme 3). Both **5** and **6** have been completely characterized, including by single crystal X-ray diffraction studies; their ORTEP plots, together with



Scheme 2.

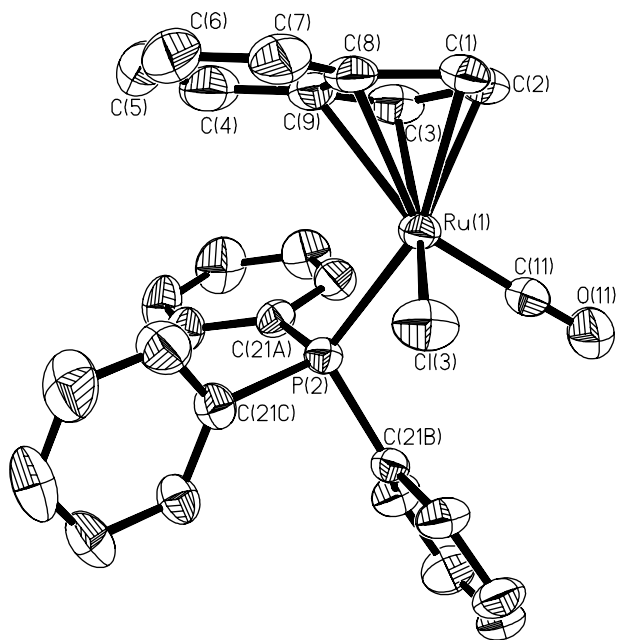


Fig. 2. ORTEP plot (thermal ellipsoids are drawn at 50% probability; all hydrogen atoms omitted) and selected bond parameters for **4**. $C^*-Ru(1) = 1.917(4)$; $Ru(1)-C(1) = 2.224(4)$; $Ru(1)-C(2) = 2.189(4)$; $Ru(1)-C(3) = 2.185(5)$; $Ru(1)-C(8) = 2.357(4)$; $Ru(1)-C(9) = 2.369(4)$; $Ru(1)-Cl(3) = 2.4110(11)$; $Ru(1)-P(2) = 2.3323(9)$; $P(2)-C(21A) = 1.821(4)$; $P(2)-C(21B) = 1.830(4)$; $P(2)-C(21C) = 1.832(4)$; $C(11)-Ru(1)-Cl(3) = 94.05(13)$; $C(11)-Ru(1)-P(2) = 87.25(12)$; $P(2)-Ru(1)-Cl(3) = 90.56(4)$; $C(21A)-P(2)-Ru(1) = 113.40(13)$; $C(21B)-P(2)-Ru(1) = 114.49(12)$; $C(21C)-P(2)-Ru(1) = 117.21(13)$. Slip-fold parameters: $\Delta = 0.159(4)$ Å; HA = 7.52° ; FA = 10.32° .

selected bond parameters, are shown in Figs. 3 and 4, respectively.

The IR spectrum of **5** shows a pattern which is very similar to that reported for $[Ru_2(CO)_4\{\mu-(\eta^5-C_9H_6)_2CH_2-CH_2\}]$ [22], indicating the presence of both the *cis* and *trans* isomers. Dinuclear η^5 -dienylruthenium and iron complexes are known to exist as mixtures of *cis* and *trans* isomers in solution [11,23]. However, it is mostly the *trans* isomers that crystallize out in the solid state [14,17]. As a rare

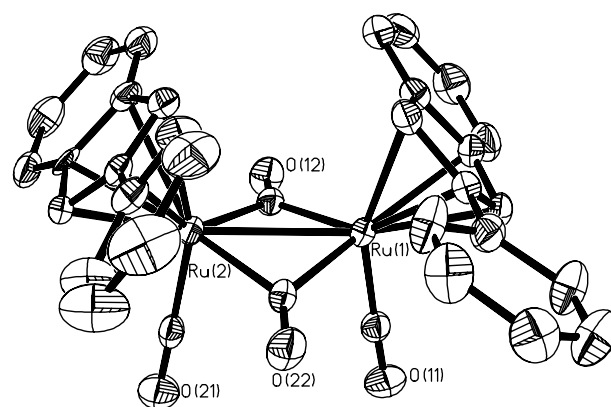
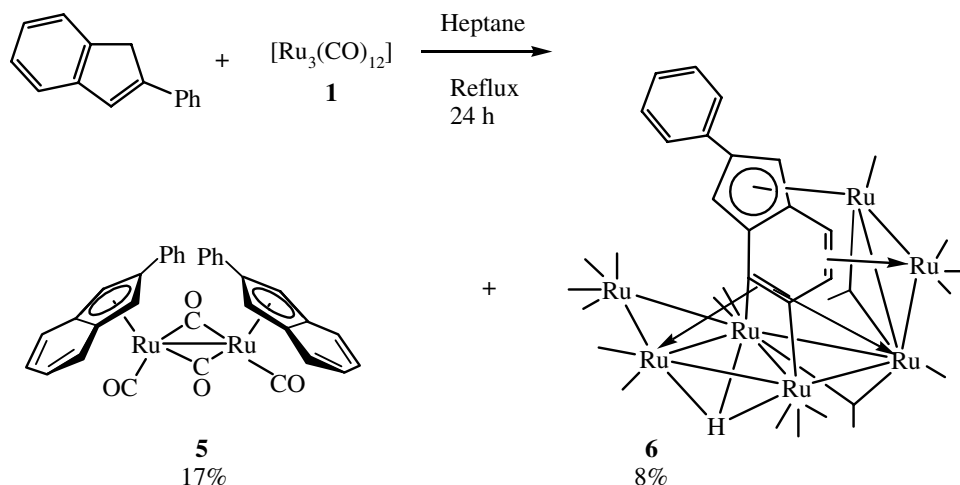


Fig. 3. ORTEP plot (thermal ellipsoids are drawn at 50% probability; all hydrogen atoms omitted) and selected bond parameters for **5**. $Ru(1)-Ru(2) = 2.7333(7)$; $C^*-Ru(1) = 1.945(6)$; $C^*-Ru(2) = 1.953(6)$; $Ru(1)-C(11) = 1.859(7)$; $Ru(1)-C(12) = 2.045(6)$; $Ru(1)-C(22) = 2.034(6)$; $Ru(2)-C(21) = 1.859(6)$; $Ru(2)-C(12) = 2.027(6)$; $Ru(2)-C(22) = 2.038(6)$; $C(21)-O(21) = 1.141(7)$; $C(22)-O(22) = 1.156(7)$; $Ru(1)-C(12)-Ru(2) = 84.3(2)$; $Ru(1)-C(22)-Ru(2) = 84.3(2)$; Slip-fold parameters: [13] $\Delta = 0.180(6)$ Å; HA = 7.13° ; FA = 6.96° for IndRu(1) and $\Delta = 0.182(6)$ Å; HA = 6.96° ; FA = 6.24° for IndRu(2).

example, both the *cis* and *trans* isomeric structures of $[CpFe(CO)_2]_2$ have been reported [18]. Thus, the molecular structure of **5** reported here, in which the indenyl groups are arranged *cis* to one another, is the first reported example of a structurally characterized *cis* isomer for ruthenium. The slip-fold distortion values fall in the range of small distortion from a η^5 bonding mode [15]. The smaller FA value compared to the corresponding HA value indicates that the benzenoid ring of the phenylindenyl ligand is bent towards the ruthenium centre, and is unusual for η^5 -indenyl complexes.

The valence electron count for the heptaruthenium cluster **6** is 104, if the benzenoid ring is regarded as a 6-electron donor, which makes it electron-deficient with 10 metal-metal bonds. However, the bonding of the benzenoid with the $Ru(3)Ru(4)Ru(5)Ru(6)$ butterfly metal core may best be regarded as similar to that found in similar tetranuclear



Scheme 3.

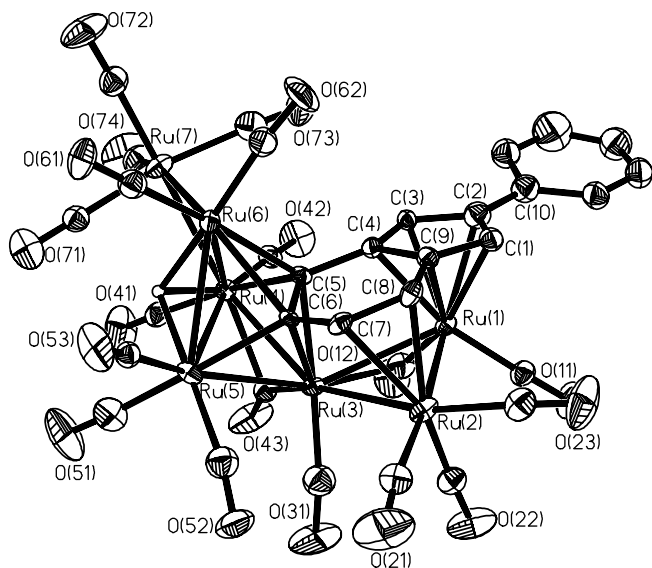


Fig. 4. ORTEP plot (thermal ellipsoids are drawn at 50% probability; all organic hydrogen atoms omitted) and selected bond parameters for **6**. Ru(1)–Ru(2) = 2.759(2); Ru(1)–Ru(3) = 2.876(2); Ru(2)–Ru(3) = 2.838(2); Ru(3)–Ru(4) = 2.756(2); Ru(3)–Ru(5) = 2.762(2); Ru(4)–Ru(6) = 2.780(2); Ru(4)–Ru(7) = 2.796(2); Ru(4)–Ru(5) = 2.952(2); Ru(5)–Ru(6) = 2.854(2); Ru(6)–Ru(7) = 2.721(2); Ru(1)–C(1) = 2.219(19); Ru(1)–C(2) = 2.26(2); Ru(1)–C(3) = 2.251(17); Ru(1)–C(4) = 2.218(18); Ru(1)–C(9) = 2.214(18); Ru(2)–C(7) = 2.392(17); Ru(2)–C(8) = 2.304(19); Ru(3)–C(5) = 2.237(17); Ru(3)–C(6) = 2.215(16); Ru(4)–C(5) = 2.146(17); Ru(5)–C(6) = 2.140(16); Ru(6)–C(5) = 2.200(18); Ru(6)–C(6) = 2.349(17); C(4)–C(5) = 1.477(2); C(5)–C(6) = 1.446(2); C(6)–C(7) = 1.430(2); C(7)–C(8) = 1.395(3); C(8)–C(9) = 1.447(3); C(9)–C(4) = 1.468(2).

butterfly clusters and hence is not electron-deficient [19]. To the best of our knowledge, this is the first example of such a bonding mode exhibited by the indenyl ligand. The Ru–Ru contacts span a large range, from 2.756(2) to 2.952(2) Å. The shortest metal–metal bond (Ru(3)–Ru(4)) is bridged by a carbonyl ligand and the longest metal–metal bond (Ru(4)–Ru(5)) is bridged by the C₆ ring of the indenyl ligand. The hydride ligand appears to be capping the Ru(4)–Ru(5)–Ru(6) face, as indicated by a potential energy calculation [20]; this is also corroborated by a singlet resonance at –18.7 ppm in the ¹H NMR spectrum [21].

2.3. Bis(indenyl) complexes

The reaction of **1** with 1,2-bis(3-indenyl) methane in refluxing xylene afforded **7** in 54% yield (Scheme 4); the

analogous reaction in refluxing heptane afforded a complex mixture.

The IR spectrum (ν_{CO}) of **7** shows a pattern which is very similar to those for the related compounds [Ru₂(CO)₄{ μ -(η^5 -C₉H₆)₂CH₂CH₂}] [22], [Ru₂(CO)₄{ μ -(η^5 -C₅H₄)₂CH₂CH₂}] [23], and [Ru₂(CO)₄{ μ -(η^5 -C₉H₆)₂CHCH₃}] [24], all of which have the η^5 rings constrained in a mutually cis configuration. The ¹H NMR spectrum of **7** exhibits a pair of doublets at 5.48 ppm and 6.24 ppm, due to the ring protons. These shifts are similar to those reported for related indenyl ruthenium compounds [25], and are diagnostic of η^5 coordination of each indenyl ligand. Compound **7** has also been characterized by a single crystal X-ray diffraction study. There are two crystallographically distinct molecules; the ORTEP plot of one molecule is given in Fig. 5, together with selected bond parameters for both molecules. The distortion value of the slip-fold parameters for **7** falls in the range of small distortion from a η^5 bonding mode [13].

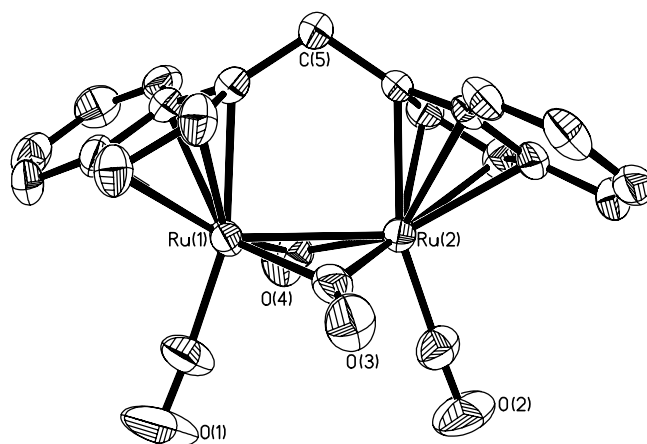
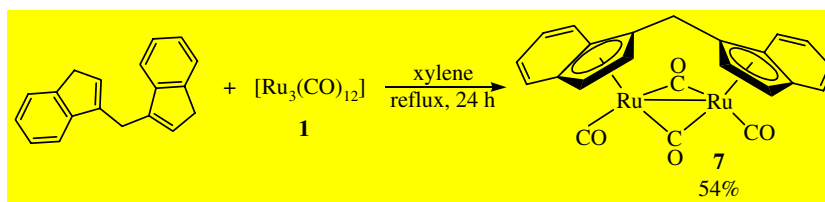


Fig. 5. ORTEP plot of complex **7** molecule A (thermal ellipsoids are drawn at 50% probability; all hydrogen atoms omitted), and selected bond parameters. Molecule A: C*–Ru(1) = 1.934 Å; C*–Ru(2) = 1.930 Å; Ru(1)–Ru(2) = 2.6697(6) Å; Δ (Ru(1)) = 0.091(5) Å; HA (Ru(1)) = 6.20°; FA (Ru(1)) = 7.73°; Δ (Ru(2)) = 0.097(5) Å; HA (Ru(2)) = 5.58°; FA (Ru(2)) = 7.31°; C(1)–O(1) = 1.145(7) Å; C(1)–O(2) = 1.128(7) Å; C(1)–O(3) = 1.184(6) Å; C(1)–O(4) = 1.168(6) Å; C(11)–C(5) = 1.507(7) Å; C(1)–Ru(1)–Ru(2) = 108.4(2)°; C(2)–Ru(2)–Ru(1) = 109.7(2)°; C(11)–C(5)–C(21) = 114.4(4)°. Molecule B: C*–Ru(1) = 1.934 Å; C*–Ru(2) = 1.931 Å; Ru(1)–Ru(2) = 2.6744(6) Å; Δ (Ru(1)) = 0.104(5) Å; HA (Ru(1)) = 6.01°; FA (Ru(1)) = 7.80°; Δ (Ru(2)) = 0.090(5) Å; HA (Ru(2)) = 5.35°; FA (Ru(2)) = 5.87°; C(1)–O(1) = 1.132(6) Å; C(1)–O(2) = 1.137(6) Å; C(1)–O(3) = 1.181(6) Å; C(1)–O(4) = 1.169(6) Å; C(11)–C(5) = 1.510(8) Å; C(1)–Ru(1)–Ru(2) = 108.61(17)°; C(2)–Ru(2)–Ru(1) = 109.60(17)°; C(11)–C(5)–C(21) = 114.6(4)°.



Scheme 4.

Compound **7** displayed the same reactivity as $[\text{Ru}_2(\text{CO})_4\{\mu-(\eta^5\text{-C}_5\text{H}_4)_2\text{CH}_2\}]$ and $[\text{CpRu}(\text{CO})_2]_2$ towards halogens. Thus, ruthenium–ruthenium bond cleavage occurred rapidly on treatment with iodine giving $[\text{Ru}_2\text{I}_2(\text{CO})_4\{(\eta^5\text{-C}_9\text{H}_6)_2\text{CH}_2\}]$ (**8**). The IR spectrum (ν_{CO}) of **8** shows two bands at 2046s and 1992vs cm^{-1} , similar to that reported for $[\text{Ru}_2\text{I}_2(\text{CO})_4\{(\eta^5\text{-C}_5\text{H}_4)_2\text{CH}_2\}]$ [26].

3. Conclusion

A high yield synthetic route to dimer **2** has been developed which allows further exploration of the chemistry and catalytic activity of indenyl ruthenium carbonyl complexes. Photolysis of **2** in dichloromethane solution gives **3** while carbonyl substitution to afford **4** occurs with PPh_3 . The analogous reaction with phenylindene, however, affords the dinuclear species **5** only in low yield, as well as a novel heptaruthenium cluster **6**, in which the benzenoid ring of the indenyl ligand behaves like a benzyne. The symmetric methylene-bridged dinuclear complex **7** has also been synthesized, and its reaction with iodine leads to cleavage of the ruthenium–ruthenium bond.

4. Experimental

4.1. General procedures

All reactions were performed under argon using Schlenk techniques. Solvents were purified, dried, distilled, and stored under nitrogen prior to use, except for xylene which was used as supplied. Routine NMR spectra were recorded on a Bruker ACF300, DPX 300, or AV300 NMR spectrometer as CDCl_3 solutions unless otherwise stated. ^1H chemical shifts reported were referenced against the residual proton signals of the solvents. Mass spectra were obtained on a Finnigan MAT95XL-T spectrometer in a 3NBA matrix (FAB), or a Macromass VG7035 at 70 eV (EI). All elemental analyses were performed by the micro-analytical laboratory at NUS. UV photolyses were carried out with a Hanovia 450 watt UV lamp with a nominal λ_{max} of 254 nm. 1,2-Bis(3-indenyl)methane was prepared according to the literature method [27]. The cluster $\text{Ru}_3(\text{CO})_{12}$ (**1**) was purchased from Oxkem Ltd. and used as supplied. All other reagents are commercially available and used without further purification.

4.2. Synthesis of $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{CO})_2]_2$ (**2**)

A xylene solution (20 ml) of indene (0.7 ml, 6.00 mmol) and **1** (200 mg, 0.313 mmol) was refluxed under argon for 14 h. The solvent was then removed under reduced pressure and the residue obtained was dissolved in the minimum amount of dichloromethane and chromatographed on a silica gel column. Elution with hexane/ CH_2Cl_2 (1/1, v/v) gave **2** as an orange yellow band. Yield = 241 mg, 94% with respect to ruthenium.

Orange yellow solid. $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{CO})_2]_2$ (**2**). IR (CH_2Cl_2): ν_{CO} 2000vs, 1959vs, 1784vs cm^{-1} . ^1H NMR (δ , CDCl_3): 5.57 (t, 1H, H^2), 5.63 (d, 2H, $\text{H}^{1,3}$), 7.2–7.32 (m, 4H, H^{4-7}). FAB-MS: 546 $[\text{M}]^{2+}$. Anal. Calc. for $\text{C}_{22}\text{H}_{14}\text{O}_4\text{Ru}_2$: C, 48.53; H, 2.59. Found: C, 48.83; H, 2.53%.

4.3. Synthesis of $[(\eta^5\text{-C}_9\text{H}_7)\text{RuCl}(\text{CO})_2]$ (**3**)

A CCl_4 solution of **2** (50 mg, 91.91 μmol) was stirred at room temperature for 48 h. The solvent was then removed under reduced pressure and the residue obtained was chromatographed on a silica gel column. Elution with 100% CH_2Cl_2 afforded **3** as a pale yellow band. Yield = 51 mg, 90% with respect to ruthenium.

Compound **3** can also be prepared by UV photolysis of a dichloromethane solution of **2** (50 mg, 91.91 μmol) for 1 h. The solvent was then removed under reduced pressure and the residue obtained was chromatographed on a silica gel column. Elution with 100% CH_2Cl_2 afforded **3**. Yield = 50.5 mg, 89% with respect to ruthenium. Yellow solid. $[(\eta^5\text{-C}_9\text{H}_7)\text{RuCl}(\text{CO})_2]$ (**3**). IR (CH_2Cl_2): ν_{CO} 2052vs, 1995vs cm^{-1} . ^1H NMR (δ , CDCl_3): 5.59 (d, 2H, $\text{H}^{1,3}$), 5.75 (t, 1H, H^2), 7.45–7.56 (m, 4H, H^{4-7}). FAB-MS: 308 (M^+). Anal. Calc. for $\text{C}_{11}\text{H}_7\text{ClO}_2\text{Ru}$: C, 42.94; H, 2.29. Found: C, 42.65; H, 2.44%.

4.4. Synthesis of $[(\eta^5\text{-C}_9\text{H}_7)\text{RuCl}(\text{CO})(\text{PPh}_3)]$ (**4**)

A 10 ml dichloromethane solution of **2** (20 mg, 36.8 μmol) and PPh_3 (9.7 mg, 37.0 μmol) was photolysed under UV for 1 h and 15 min. The solvent was then removed under reduced pressure and the residue obtained was extracted with dichloromethane and chromatographed on silica gel column. Elution with 100% CH_2Cl_2 afforded a dark orange band of **4**. Yield = 38.5 mg, 97% with respect to ruthenium.

Orange yellow solid. $[(\eta^5\text{-C}_9\text{H}_7)\text{RuCl}(\text{CO})(\text{PPh}_3)]$ (**4**). IR (CH_2Cl_2): ν_{CO} 1953vs cm^{-1} . ^1H NMR (δ , C_6D_6): 3.66 (s, 1H, H^3), 4.96 (t, $J = 2.46$ Hz, H^2), 5.37 (s, 1H, H^1), 6.53–7.52 (m, 19H, Ph and H^{4-7}). ^{31}P NMR (δ , C_6D_6): 46.37(s). FAB-MS: 542 $[\text{M}]^+$. Literature values: [15] IR (CH_2Cl_2): ν_{CO} 1954vs cm^{-1} . ^1H NMR (δ , C_6D_6): 3.72 (s, 1H, H^3), 5.03 (t, $J = 2.54$ Hz, H^2), 5.45 (s, 1H, H^1), 6.59–7.60 (m, 19H). ^{31}P NMR (δ , C_6D_6): 48.88(s). FAB-MS: 542 $[\text{M}]^+$.

4.5. Reaction of **3** with phenylacetylene

Phenylacetylene (143 μL , 1.30 mmol) and **3** (4 mg, 13.051 μmol) were heated in toluene (4 ml) at 110 $^\circ\text{C}$ for 17 h. The solvent was then removed under reduced pressure and the residue obtained was dissolved in the minimum amount of dichloromethane and chromatographed on silica gel TLC plates. Elution with 100% hexane gave 2-phenyl naphthalene as a pale yellow band ($R_f = 0.85$). Yield = 5.8 mg, 4.4% wrt phenylacetylene. ^1H NMR (δ ,

CDCl₃): 7.34–7.40 (m, 1H), 7.46–7.52 (m, 4H), 7.72–7.77 (m, 3H), 7.88–7.93 (m, 3H) [28]. EI-MS: 204 [M]⁺.

4.6. Reaction of **1** and phenylindene

A heptane solution (10 ml) of 2-phenylindene (30 mg, 0.156 mmol) and **1** (40 mg, 0.625 mmol) was refluxed under argon for 24 h. The solvent was then removed under reduced pressure and the residue obtained was extracted with dichloromethane and chromatographed on a silica gel column. Elution with 100% hexane gave the unreacted ligand (24 mg, 80%) followed by **1** (26 mg, 65%).

Elution with hexane/CH₂Cl₂ (1/1, v/v) afforded a mixture of **5**, **6** and six other unidentified products. Compounds **5** and **6** were further purified by chromatography on silica gel TLC plates with hexane/CH₂Cl₂ (1/1, v/v) as eluant.

Band 4 (*R_f* = 0.42), brown solid. [(C₉H₄Ph)Ru₇(μ-H)(μ-CO)₂(CO)₁₆] (**6**). Yield = 1 mg, 8% with respect to consumed ruthenium. IR (CH₂Cl₂): ν_{CO} 2106w, 2081vs, 2062s, 2032vs, 2014w, 2000vw, 1941w cm⁻¹. ¹H NMR (δ, CDCl₃): 4.88 (s, 2H, H^{1,3}), 7.34–7.65 (m, 7H, Ph and H^{6,7}), –18.74 (s, 1H, RuHRu). FAB-MS: 1289 [M–4CO]⁺.

Band 5 (*R_f* = 0.49), yellow solid. [(η⁵-C₉H₆Ph)Ru(CO)₂]₂ (**5**). Yield = 4 mg, 17% with respect to consumed ruthenium. IR (CH₂Cl₂): ν_{CO} 2000vs, 1960vs, 1794vs cm⁻¹. ¹H NMR (δ, CDCl₃): 5.93 (s, 2H, H^{1,3}), 7.39–7.22 (m, 9H,

Ph and H^{4–7}). FAB-MS: 697 [M]⁺. Anal. Calc. for C₂₃H₁₄O₄Ru₂ · 1/2CH₂Cl₂: C, 47.12; H, 2.52. Found: C, 47.51; H, 2.68%.

4.7. Synthesis of [Ru₂(CO)₄{μ-(η⁵-C₉H₆)₂CH₂}] (**7**)

A xylene solution (20 ml) of 1,2-bis(3-indenyl)methane (0.38g, 1.557 mmol) and **1** (250 mg, 0.391 mmol) was refluxed under argon for 24 h. The solvent was then removed under reduced pressure and the residue obtained was extracted with dichloromethane and chromatographed on silica gel TLC plates. Elution with hexane/CH₂Cl₂ (1/1, v/v) gave three bands.

Band 1 (*R_f* = 0.88), very pale yellow, unreacted ligand. Yield = 100 mg, 26%.

Band 2 (*R_f* = 0.75), yellow, unreacted **1**. Yield = 80 mg, 32%.

Band 3 (*R_f* = 0.19), orange yellow solid. [Ru₂(CO)₄{μ-(η⁵-C₉H₆)₂CH₂}] (**7**). Yield = 120 mg, 54% wrt reacted **1**. IR (CH₂Cl₂): ν_{CO} 1998vs, 1961m, 1785vs cm⁻¹. ¹H NMR (δ, CDCl₃): 3.70 (s, 2H, CH₂), 5.48 (d, 2H, H^{2/3}), 6.24 (d, 2H, H^{3/2}), 7.29–7.32 (m, 4H, H^{4–7}), 7.50–7.61 (m, 4H, H^{4–7}). FAB-MS: 558 [M]²⁺. Anal. Calc. for C₂₃H₁₄O₄Ru₂ · 1/2CH₂Cl₂: C, 47.12; H, 2.52. Found: C, 47.52; H, 2.57%. The presence of dichloromethane in the analytical sample was confirmed by ¹H NMR spectroscopy.

Table 1
Crystal and refinement data for **2**, **4–7**

Compound	2	4	5	6	7
Empirical formula	C ₂₂ H ₁₄ O ₄ Ru ₂	C ₂₈ H ₂₂ ClO _{1.25} PRu	C ₃₅ H ₂₄ Cl ₂ O ₄ Ru ₂	C ₃₄ H ₁₂ Cl ₂ O ₁₈ Ru ₇	C ₄₇ H ₃₀ Cl ₂ O ₈ Ru ₄
Formula weight	544.47	545.95	781.58	1486.83	1197.89
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
Unit cell dimensions					
<i>a</i> (Å)	9.1811(5)	9.3163(6)	13.422(2)	8.9051(12)	11.2826(6)
<i>b</i> (Å)	13.1477(7)	10.3414(7)	10.2211(17)	21.294(3)	12.9353(7)
<i>c</i> (Å)	8.1203(5)	12.5301(8)	22.240(4)	22.204(3)	15.0553(8)
α (°)	90	87.648(2)	90	90	86.7220(10)
β (°)	112.178(2)	82.999(2)	101.910(5)	100.841(3)	82.2890(10)
γ (°)	90	82.796(2)	90	90	75.7240(10)
Volume (Å ³)	907.68(9)	1188.33(13)	2985.5(9)	4135.3(9)	2109.5(2)
<i>Z</i>	2	2	4	4	2
<i>D</i> _{calc} (Mg/m ³)	1.992	1.526	1.739	2.388	1.886
Absorption coefficient (mm ⁻¹)	1.690	0.859	1.230	2.691	1.587
<i>F</i> (000)	532	552	1552	2808	1172
Crystal size (mm)	0.28 × 0.18 × 0.06	0.20 × 0.14 × 0.06	0.18 × 0.10 × 0.03	0.09 × 0.08 × 0.06	0.21 × 0.16 × 0.06
θ Range for data collection (°)	2.40–26.37	2.22–28.28	2.20–26.37	2.10–26.37	2.10–30.02
Reflections collected	7578	12615	26433	57379	32433
Independent reflections (<i>R</i> _{int})	1856 (0.0280)	5792 (0.0401)	6097 (0.0724)	8443 (0.1119)	10409 (0.0645)
Maximum and minimum transmission	0.9054 and 0.6490	0.9503 and 0.8470	0.9640 and 0.8089	0.8552 and 0.7937	0.9108 and 0.7317
Data/restraints/parameters	1856/0/155	5792/0/381	6097/0/484	8443/207/557	10409/6/547
Goodness-of-fit on <i>F</i> ²	1.053	1.077	1.156	1.429	0.537
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0311, <i>wR</i> ₂ = 0.0759	<i>R</i> ₁ = 0.0553, <i>wR</i> ₂ = 0.1204	<i>R</i> ₁ = 0.0613, <i>wR</i> ₂ = 0.1168	<i>R</i> ₁ = 0.1289, <i>wR</i> ₂ = 0.2465	<i>R</i> ₁ = 0.0469, <i>wR</i> ₂ = 0.0979
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0357, <i>wR</i> ₂ = 0.0783	<i>R</i> ₁ = 0.0705, <i>wR</i> ₂ = 0.1285	<i>R</i> ₁ = 0.0807, <i>wR</i> ₂ = 0.1253	<i>R</i> ₁ = 0.1398, <i>wR</i> ₂ = 0.2515	<i>R</i> ₁ = 0.0788, <i>wR</i> ₂ = 0.1077
Largest difference in peak and hole (e Å ⁻³)	1.072 and –0.301	1.302 and –0.383	1.224 and –0.782	2.310 and –1.625	1.191 and –0.698

4.8. Reaction of 7 with I₂

A mixture of complex **7** (6.1 mg, 10.9 μmol) and iodine (10 mg, 39.5 μmol) in chloroform was stirred at room temperature for 5 min. The solvent was then removed under reduced pressure and the residue obtained was dissolved in the minimum amount of dichloromethane and chromatographed on a silica gel column. Elution with hexane/CH₂Cl₂ (1/1, v/v) gave **8**. Yield = 8 mg, 90% with respect to ruthenium.

Orange-red solid. [Ru₂I₂(CO)₄{(η⁵-C₉H₆)₂CH₂}] (**8**). IR (CH₂Cl₂): ν_{CO} 1992vs, 2046vs cm⁻¹. ¹H NMR (δ, CDCl₃): 4.46 (s, 2H, CH₂), 5.60–5.64 (m, 4H, H^{2,3}), 7.41–7.83 (m, 4H, H⁴⁻⁷), 7.50–7.61 (m, 4H, H⁴⁻⁷). FAB-MS: 784 [M–CO]⁺. Anal. Calc. for C₂₃H₁₄O₄Ru₂·1/2CH₂Cl₂: C, 34.09; H, 1.74. Found: C, 33.68; H, 1.57%.

4.9. Crystal structure determinations

Crystals were grown from dichloromethane/hexane solutions and mounted on quartz fibres. X-ray data were collected on a Bruker AXS APEX system, using Mo Kα radiation, at 223 K with the SMART suite of programs [29]. Data were processed and corrected for Lorentz and polarisation effects with SAINT [30], and for absorption effects with SADABS [31]. Structural solution and refinement were carried out with the SHELXTL suite of programs [32]. Crystal and refinement data are summarised in Table 1. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. Organic hydrogen atoms were placed in calculated positions and refined with a riding model. For compound **4**, there was a residue which was modelled (with only the O atom) as a water solvent molecule with partial occupancy (occ = 0.25).

5. Supplementary material

CCDC 651230, 651231, 651232, 651233 and 651234 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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