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Electron-deficient linear tetranuclear ruthenium(I) carboxylate chains

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ABSTRACT

The reaction of carboxylic acids RCOOH (R = ^{t}Bu, Ph, Fc) with [$Ru_3(CO)_{12}$] in refluxing acetonitrile afforded dark purple/red solids. These reacted with phosphines in a 2:1 (Ru:P) ratio to form phosphine-substitued derivatives of the electron-deficient tetraruthenium chains, *viz.*, [$Ru_4(CO)_8(\mu\text{-OOCR})_4(PR'_3)_2$] (where R′ = Ph or OMe).

1. Introduction

The reaction of [$Ru_3(CO)_{12}$] (**1**) with carboxylic acids (**2**) have been reported to give polymeric, tetranuclear or dinuclear species made up of diruthenium [$Ru_2(CO)_4(\mu\text{-OOCR})_2$] units, depending on the identity of the acid and the reaction conditions used [1–16]. Polymeric complexes [$\{Ru_2(CO)_4(\mu\text{-OOCR})_2\}_\infty$] were first reported by Lewis et al. [12]. These comprised dinuclear [$Ru_2(CO)_4(\mu\text{-OOCR})_2$] sawhorse units linked together by two Ru—O bonds, between an Ru atom of one unit and an O atom of the carboxylato bridge of the other unit [5,7,8]. They dissolved reversibly in coordinating solvents (S), such as, acetonitrile, tetrahydrofuran or pyridine, to form dinuclear complexes. These were proposed to have the formulation [$Ru_2(CO)_4(\mu\text{-OOCR})_2(S)_2$], on the basis of their reactions with phosphines (PR'_3) to form the dinuclear derivatives [$Ru_2(CO)_4(\mu\text{-OOCR})_2(PR'_3)_2$] [4,12]; a single crystal X-ray structural determination on [$Ru_2(CO)_4(\mu\text{-OOCAd})_2(PPh_3)_2$] confirmed it to comprise a sawhorse diruthenium unit, with the two PPh_3 ligands occupying the axial positions [3].

Interestingly, reaction of the polymer with a phosphine in a 2:1 (Ru:P) ratio afforded the tetraruthenium species [$Ru_4(CO)_8(\mu\text{-OOCR})_4(PR_3)_2$]. These can be regarded as “dimer of dimers” with two dinuclear units linked via either Ru—O interactions, or an unsupported Ru—Ru bond (Fig. 1) [10,11]. Analogues with a carboxylic acid in place of the phosphines have also been isolated from some of the reactions of [$Ru_3(CO)_{12}$] with carboxylic acids [5–7,9]. Only two examples of the “dimer of dimers” containing an unsupported Ru—Ru bond have been reported, however, that with R = C_6H_3-3,5-$(CF_3)_2$ and CO ligands in the axial positions reported by the group of Petrukhina [6], and that with R = 1-adamantyl (Ad) and PPh_3 ligands in the axial positions reported by us [3]. These two tetraruthenium complexes are interesting because they are electron-deficient, with a total valence electron count of 64 compared to the 66 required by the EAN rule. We now believe that these “dimer of dimers” containing an unsupported Ru—Ru bond may not be at all uncommon; our findings on this point are reported here.

2. Results and discussion

We have examined the products of the reaction of **1** with four different carboxylic acids **2**, and their reactivity; some of the chemistry for R = Ad (**a**) and ^{t}Bu (**b**) have already been reported [3,2]. Our results are summarised in Scheme 1.

The reaction of **1** and **2** in refluxing acetonitrile gave yellow solutions which, upon the removal of volatiles, gave either dark purple (**3a** and **3b**) or dark red (**3c** and **3d**) solids. These solids dissolved in various solvents to give orange-yellow solutions but reverted to their original colours upon removal of the solvent. Further characterisation of **3c** and **3d** other than by IR spectroscopy was hampered by their tendency to form an orange solid. For example, **3c** gradually turned orange when left in air and more readily so when heated (80 °C) under vacuum. The IR

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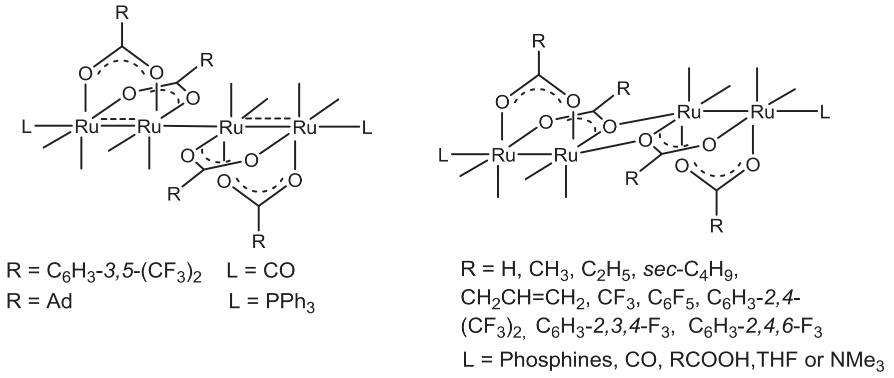
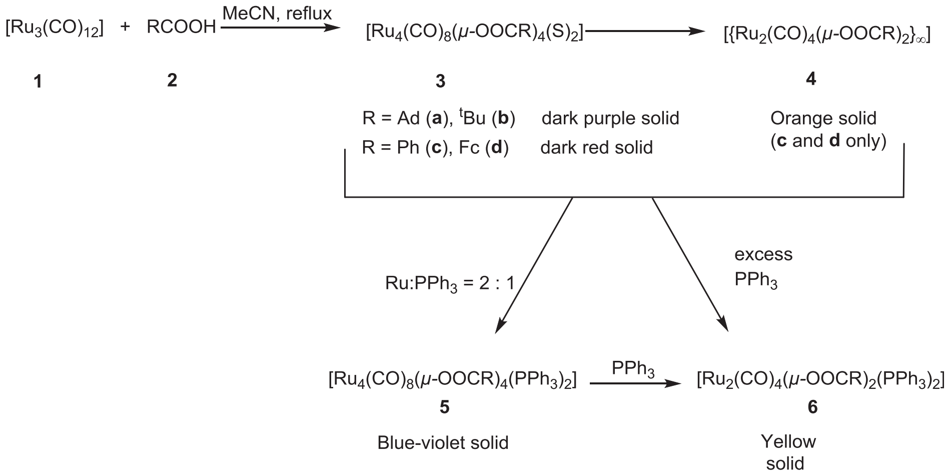


Fig. 1. Ru–Ru vs Ru–O interactions found in tetraruthenium chain complexes [1,3,5–7,9–11,13–16].



Scheme 1.

characteristics of the orange solid **4c** are similar to that for the previously reported benzoate polymer $[\{Ru_2(CO)_4(\mu\text{-OOCPh})_2\}_\infty]$ and hence, we believe that it is also polymeric [9]. A dichloromethane solution of **3d** similarly afforded an orange precipitate **4d** on standing. Although the IR spectrum is identical to that for dark red **3d**, we believe that **4d** is also a polymer. In contrast, both **3a** and **3b** remained purple upon heating in vacuum and showed no precipitation when left standing in a dichloromethane solution. Their mass spectra shows ions corresponding to both diruthenium and tetraruthenium fragments but not higher nuclearities such as a hexaruthenium.

It had been assumed earlier that the complexes **3a** and **3b** were polymeric [3,2]. The ^{1}H NMR spectrum of **3b**, however, exhibits a resonance at 1.25 ppm, which can be assigned to a bound pivalic acid similar to that reported for the diruthenium species $[Ru_2(CO)_4(\mu\text{-OOC}^tBu)_2(^tBuCOOH)_2]$ [9]; weak IR bands at ~1600–1700 cm^{-1} can also be attributed to the carbonyl stretches of the bound pivalic acid group. Complex **3b** thus probably has the formulation $[Ru_4(CO)_8(\mu\text{-OOC}^tBu)_4(^tBuCOOH)_2]$. The mass spectrum of an acetonitrile solution, on the other hand, shows fragments corresponding to substitution of the acid ligands by acetonitrile. We therefore believe that all the solids **3** are tetraruthenium species with the formulation $[Ru_4(CO)_8(\mu\text{-OOCR})_4(S)_2]$; the intense purple/red colours are due to the presence of an unsupported, electron-deficient Ru–Ru bond, and they are weakly coordinated in the axial positions by a solvent molecule (like acetonitrile or dichloromethane [17]), or a carboxylic acid. They are probably mixtures of solvent- and acid-coordinated species, depending on the synthetic methodology and the work-up procedure.

That **3a** and **3b** are more stable in the tetranuclear form may possibly be due to steric crowding; it has been reported that pivalate complexes resist polymerization because of steric crowding at the α position of the acid [9]. A longer Ru–Ru chain is also presumed to be less favoured as that will require even more electron-deficiency. Interestingly, for R = C_6H_3-3,5-$(CF_3)_2$, it has been reported that both a tetranuclear species containing an unsupported Ru–Ru bond, and a polymeric species containing Ru–O interactions, could be formed [6]. Taken together, we believe that these suggest that polymeric **4** containing Ru–O linkages is the more favoured form but a sterically bulky R group can disfavor this.

The reaction of polymeric **4** with phosphines has been described as a depolymerization reaction, in which the diruthenium species was first formed, whatever the Ru:P ratio [10,11]. Irrespective of the true nature of **3** and **4**, we have observed that both undergo a similar depolymerization reaction with PPh_3, except that when the Ru:P ratio was 2:1, the linear tetranuclear chains $[Ru_4(CO)_8(\mu\text{-OOCR})_4(PPh_3)_2]$ (**5**) were obtained as dark blue/violet solids beside the diruthenium species $[Ru_2(CO)_4(\mu\text{-OOC}^tBu)_2(PPh_3)_2]$ (**6**). With an excess of the phosphine, only **6** was formed. The $P(OMe)_3$ analogue $[Ru_4(CO)_8(\mu\text{-OOC}^tBu)_4\{P(OMe)_3\}_2]$ (**5b′**) has also been similarly synthesised from **3b**. We have observed (by spot TLC) that **6** was first formed, and over a longer reaction time, the tetraruthenium species **5** resulted, with a concomitant decrease in the amount of **6**.

The electronic spectra of solid **5b-d** all showed a strong absorption maximum at 540–590 nm. As in the complexes **3**, dissolution in a number of organic solvents gave orange/yellow solutions which reverted to their original colour upon solvent removal. This was reflected in the electronic spectrum of **5d**, for example, in which peaks at 338 nm and 590 nm were replaced by a new peak at 353 nm in dichloromethane. We attribute this to reversible formation of a dinuclear solvent adduct $[Ru_2(CO)_4(\mu\text{-}OOCR)_2(PPh_3)\ (S)]$. This is in agreement with our previous computational studies in which we have shown that the LUMO in complex **5a** was located primarily at the unsupported Ru–Ru bond and hence this bond was susceptible to nucleophilic attack [3]. As expected, the reaction of **5b** with $P(OMe)_3$ afforded the asymmetrically-substituted dinuclear species $[Ru_2(CO)_4(\mu\text{-}OOC^{t}Bu)_2(PPh_3)\ (P(OMe)_3)]$ (**7**), which was found to exist in equilibrium with the symmetrically-substituted homologues **6b** and **6b**′ (Scheme 2); the equilibrium was established within a day, and the equilibrium constant has been estimated (on the basis of NMR integration ratios) to be ~4.6. This observation is also consistent with ligands in the axial positions being significantly less tightly bound than those in radial positions.

Crystallographic discussion

All the chains **5** have been characterised by single crystal X-ray crystallographic studies; that for **5a** has been reported earlier [3]. The crystal structure of **6b** has also been determined. The ORTEP plot of **5b** illustrating its molecular structure is given in Fig. 2, while that for **6b**, together with selected bond parameters, is given in Fig. 3. Two different isomorphs were obtained for **5b**′; red monoclinic crystals and red/green dichroic orthorhombic crystals. Essential bond parameters for the tetraruthenium chains **5**, together with a common atomic numbering scheme, are tabulated in Table 1. The molecules of **5b**, **5b′(monoclinic)**, **5c** and **5d** possess crystallographic inversion symmetry about the unsupported Ru2–Ru2′ bond. As has already been observed for **5a**, the central Ru–Ru bond is significantly longer than the outer Ru–Ru bonds, consistent with bond orders of 1.0 and 1.5, respectively. There is also apparent asymmetry in the Ru–CO bond lengths; > 1.85 Å for Ru1–CO and <1.85 Å for Ru2–CO. Interestingly, the ν_{CO} pattern of the IR spectrum of crystalline **5c** is different from that of the powdered form obtained from, say, initial synthesis. Both gave the same solution-phase IR spectrum, however (Figs. S9 and S10). Presumably, several conformers are present in the non-crystalline form, which may account for the broadening and extra peaks observed in the spectrum. A similar broadening was also observed in the spectrum of **5d** but not that of **5b**.

3. Concluding remarks

In this work, we have shown that the reaction of $[Ru_3(CO)_{12}]$ with various carboxylic acids appear to afford initially either tetraruthenium $[Ru_4(CO)_8(\mu\text{-}OOCR)_4(S)_2]$ or polymeric $[\{Ru_2(CO)_4(\mu\text{-}OOCR)_2\}_\infty]$ complexes, depending on the nature of the acid. Irrespective of the exact nature of the product, however, they reacted with phosphines in a 2:1 (Ru:P) ratio to afford electronically deficient, linear tetranuclear chains $[Ru_4(CO)_8(\mu\text{-}OOCR)_4(PPh_3)_2]$. This thus represents a general synthetic strategy to this unusual class of chain complexes.

4. Experimental

4.1. General procedure

All reactions were performed under an argon atmosphere using standard Schlenk techniques. All reagents were from commercial sources and used as supplied without further purification. Reaction mixtures were separated by preparative thin-layer chromatography (TLC) on 20 cm × 20 cm plates precoated with silica gel $K60F_{254}$, purchased from Merck. Infrared spectra were recorded on a Bruker Alpha FT-IR spectrometer. ESI spectra were recorded on a Waters UPLC-Q-TOF mass spectrometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker BBFO400 spectrometer. ^1H chemical shifts were referenced to the residual proton resonances of the respective deuterated solvents, and ^{31}P chemical shifts were referenced to 85% H_3PO_4 as an external standard. Elemental analyses were performed by the microanalytical laboratory at the Nanyang Technological University. Uv–vis spectra were recorded on a Varian Cary 100 spectrometer. The syntheses and characterization data for the pivalate analogue is presented here, while those for the benzoate and ferrocenecarboxylate analogues are available in the supporting information.

4.2. Reaction of 1 and 2b

Cluster **1** (210.9 mg, 0.330 mmol) and **2b** (202.7 mg, 1.984 mmol) were refluxed in CH_3CN (50 mL) for 18 h under an argon atmosphere. After removal of the solvent, the residue was taken up in DCM and the resulting orange solution filtered through silica gel. The filtrate was evaporated to dryness to afford **3b** as a dark purple solid.

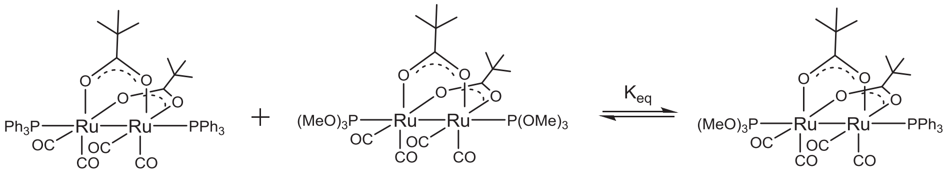
Yield = 222.5 mg (87%).

IR (DCM): ν_{CO} 2042 (vs), 1990 (m), 1960 (vs), 1924 (w); ν_{COO} 1742 (vw), 1670 (w), 1606 (vw), 1558 (m), 1485 (w), 1422 (w) cm^{-1}. IR (KBr): ν_{CO} 2034 (vs), 1999 (m), 1979 (vs), 1947 (s); ν_{COO} 1547 (m), 1484 (m), 1421 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.14 (s, ^{t}BuCOO, 36H), δ 1.25 (s, ^{t}BuCOOH, 18H) ppm.

ESI-MS$^+$ *m*/*z* (MeCN): 1015.80 $[Ru_4(CO)_8(\mu\text{-}OOCC_4H_9)_3+2MeCN]^+$, 972.78 $[Ru_4(CO)_8(\mu\text{-}OOCC_4H_9)_3+MeCN]^+$, 933.76 $[Ru_4(CO)_8(\mu\text{-}OOCC_4H_9)_3]^+$, 497.90 $[Ru_2(CO)_4(\mu\text{-}OOCC_4H_9)+2MeCN]^+$, 456.87 $[Ru_2(CO)_4(OOCC_4H_9)+MeCN]^+$. Elemental Analysis (%) calcd for $C_{38}H_{56}O_{20}Ru_4.CH_2Cl_2$: C 35.43, H 4.42; found: C 35.36, H 4.71.

4.3. Synthesis of $[Ru_2(CO)_4(\mu\text{-}OOC^tBu)_2(PPh_3)_2]$, 6b

Complex **3b** (15.9 mg, 0.0307 mmol) and PPh_3 (18.6 mg, 0.0709 mmol) were stirred in DCM for 15 min. Separation of the crude product by TLC, with DCM: Hex = 1:2 as eluent, gave a yellow



6b **6b'** **7**

Scheme 2.

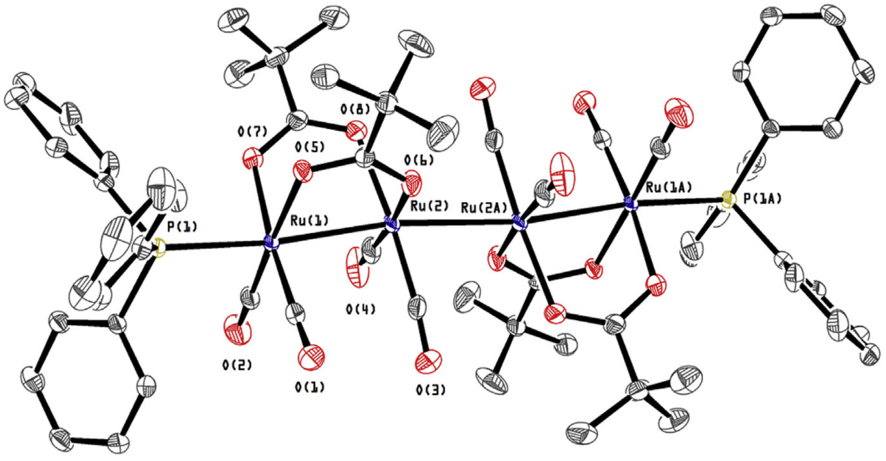


Fig. 2. ORTEP plot of $Ru_4(CO)_8(\mu\text{-}OOC^tBu)_4(PPh_3)_2$ (5b). Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

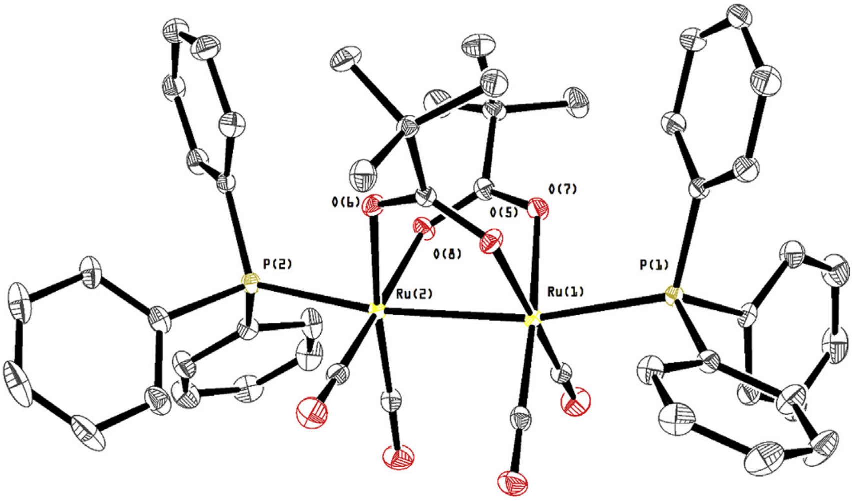


Fig. 3. ORTEP plot of $Ru_2(CO)_4(\mu\text{-}OOC^tBu)_2(PPh_3)_2$ (6b). Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)-Ru(2) = 2.6978(2), Ru(2)-P(2) = 2.4373(5), Ru(1)-P(1) = 2.4284(5), Ru(1)-O(5) = 2.1157(13), Ru(1)-O(7) = 2.1295(13), Ru(2)-O(6) = 2.1532(13), Ru(2)-O(8) = 2.1286(13); Ru(1)-Ru(2)-P(2) = 169.475(13), Ru(2)-Ru(1)-P(1) = 167.572(13), Ru(2)-Ru(1)-O(5) = 83.09(4), Ru(2)-Ru(1)-O(7) = 81.51(4), Ru(1)-Ru(2)-O(6) = 82.10(4), Ru(1)-Ru(2)-O(8) = 83.72(4), O(7)-Ru(1)-O(5) = 84.38(5), O(6)-Ru(2)-O(8) = 83.77(5).

solid upon removal of solvent. NMR and IR spectral values were comparable with the literature [18].

Yield = 21.8 mg (68%).

IR (DCM): ν_{CO} 2022 (vs), 1978 (m), 1949 (s), 1918 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.79 (s, ^{t}Bu, 18H), 7.37–7.63 (m, Ph, 30H) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 13.6 ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 13.4 ppm. ESI-MS$^+$ *m/z*: 1041.09 M$^+$, 1064.47 [M+Na]$^+$, 1013.10 [M–CO]$^+$. Elemental Analysis (%) calcd for $C_{50}H_{48}O_8P_2Ru_2$: C 57.69, H 4.65; found: C 57.93, H 4.95.

4.4. Synthesis of [$Ru_4(CO)_8(\mu\text{-}OOC^tBu)_4(PPh_3)_2$], 5b

Complex **3b** (17.4 mg, 0.0474 mmol) and PPh_3 (4.4 mg, 0.0237 mmol) [Ratio of Ru: PPh_3 = 2:1] was stirred in DCM for 18 h. After removal of the solvent, the residue was separated by TLC with DCM as eluent. Two products were isolated; a yellow solid identified as [$Ru_2(CO)_4(\mu\text{-}OOC^tBu)_2(PPh_3)_2$] (**6b**, 6.2 mg, 13%) and a dark violet solid identified as[$Ru_4(CO)_8(\mu\text{-}OOC^tBu)_4(PPh_3)_2$] (**5b**, 23.6 mg, 64%). The dark violet solid was crystallized by slow evaporation of a diethyl ether solution at 4 °C, which gave dichroic red/green crystals of diffraction quality.

IR (DCM): ν_{CO} 2036 (vs), 1985 (m), 1963 (s), 1917 (w) cm^{-1}. IR (KBr): ν_{CO} 2028 (vs), 1988 (m), 1967 (s), 1930 (w) cm^{-1}. ^1H NMR (C_6D_6): δ 1.13 (s, ^{t}Bu, 36H), 7.02–7.05 (m, Ph, 18H), 7.63–7.68 (m, Ph, 12H) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 8.6 ppm. ESI-MS$^+$ *m/z*: 1558.00 M$^+$, 1455.95 [M-^{t}BuCOO]$^+$, 594.96 [M-$Ru_2(CO)_4(\mu\text{-}OOC^tBu)_2(PPh_3)$-^{t}BuCOO]$^+$. Elemental Analysis (%) calcd for $C_{64}H_{66}O_{16}P_2Ru_4$: C 49.36, H 4.27; found: C 49.60, H 4.26. UV–vis (300–900 nm, solid, λ_{max}): 586, 350 nm.

4.5. Synthesis of [$Ru_2(CO)_4(\mu\text{-}OOC^tBu)_2\{P(OMe)_3\}_2$], 6b′

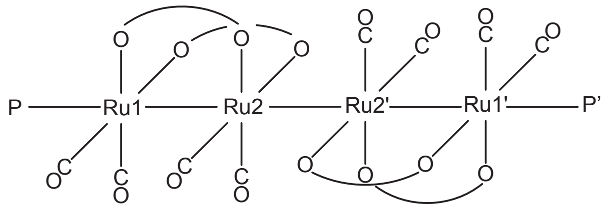
Complex **3b** (12.3 mg, 0.0238 mmol) and $P(OMe)_3$ (5.6 μL, 0.0476 mmol) were stirred in DCM for 4 h. Separation of the crude product by TLC, with DCM: Hex = 3:1 as eluent, gave a yellow solid upon removal of solvent.

Yield = 6.9 mg (38%).

4.6. Synthesis of [$Ru_4(CO)_8(\mu\text{-}OOC^tBu)_4\{P(OMe)_3\}_2$], 5b′

Complex **3b** (33.8 mg, 0.0654 mmol) and $P(OMe)_3$ (3.75 μL, 0.0318 mmol) [Ratio of Ru:P = 2:1] were stirred in DCM for 16 h.

Table 1
Bond lengths (Å) and angles (°) in **5**.



Bond parameter	5a [3]	5b	5b′ (monoclinic)	5b′ (orthorhombic)[a]	5c	5d
Ru1–Ru2	2.6851(5)	2.6796(2)	2.6761(3)	2.6756(3) 2.6732(3)	2.6724(5)	2.6985(4)
Ru2–Ru2′	2.8754(7)	2.8663(4)	2.8721(5)	2.8954(3)	2.8874(7)	2.8549(5)
Ru–P	2.3945(9)	2.3967(6)	2.3050(9)	2.2967(8) 2.3012(8)	2.3781(13)	2.3915(9)
Ru1–O	2.110(3); 2.138(3)	2.1158(16); 2.1288(15)	2.123(3); 2.134(3)	2.114(2); 2.125(2) 2.123(2); 2.137(2)	2.120(3); 2.129(3)	2.115(2); 2.136(2)
Ru2–O	2.076(3); 2.089(3)	2.0910(16); 2.0939(17)	2.101(3); 2.107(2)	2.105(2); 2.116(2) 2.105(2); 2.110(2)	2.103(3); 2.134(3)	2.066(2); 2.101(2)
Ru1–CO	1.851(4); 1.855(4)	1.855(2); 1.857(2)	1.864(4); 1.856(4)	1.857(3); 1.868(3) 1.862(3); 1.858(3)	1.855(5); 1.863(5)	1.854(4); 1.859(3)
Ru2–CO	1.821(5); 1.838(4)	1.837(3); 1.839(3)	1.818(4); 1.845(4)	1.833(3); 1.845(3) 1.841(3); 1.845(3)	1.830(5); 1.838(5)	1.835(4); 1.838(4)
P–Ru1–Ru2	171.44(3)	173.893(15)	168.63(3)	167.74(2) 169.60(2)	166.77(3)	169.20(2)
Ru1–Ru2–Ru2′	162.510(18)	171.917(12)	164.538(18)	165.570(12) 162.888(12)	165.10(2)	162.620(16)

[a] Molecule has no crystallographic centre of symmetry; second set of values is for the right half of the molecule.

Separation of the crude product by TLC with DCM as eluent gave a pink solid. Crystals of X-ray diffraction quality were grown by slow evaporation of a diethyl ether solution at 4 °C.

Yield = 21.8 mg (54%).

IR (KBr): ν_{CO} 2038 (vs), 1982 (s), 1927 (m) cm^{-1}. IR (DCM): ν_{CO} 2048 (vs), 1986 (s), 1977 (s), 1917 (w) cm^{-1}. ^{1}H NMR (C_6D_6): δ 3.41 (d, OMe, 18H, J = 11.6 Hz), 1.18 (s, ^{t}Bu, 36H) ppm. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 108.5 ppm. ESI-MS^{+} m/z: 1281.88 M^{+}, 1179.81 $[M-^{t}BuCOO]^{+}$. Elemental Analysis (%) calcd for $C_{34}H_{54}O_{22}P_2Ru_4$: C 31.88, H 4.25; found: C 31.75, H 4.10. UV–vis (300–900 nm, solid, λ_{max}): 548, 324 nm.

4.7. *Synthesis of $[Ru_2(CO)_4(\mu\text{-}OOC^{t}Bu)_2(PPh_3)\{P(OMe)_3\}]$, 7*

Complex **5d** (5.7 mg, 0.00421 mmol) was added into 4 mL of C_6D_6 in an NMR tube. $P(OMe)_3$ (1.04 mg, 0.00841 mmol) was added and the orange-red solution immediately turned yellow. The NMR tube was left to stir for 10 min and analysis showed the formation of **7**. However, **7** was not isolated as it was found to equilibrate in solution with its symmetric homologues $[Ru_2(CO)_4(\mu\text{-}OOC^{t}Bu)_2(PPh_3)_2]$ (**6a**) and $[Ru_2(CO)_4(\mu\text{-}OOC^{t}Bu)_2\{P(OMe)_3\}_2]$ (**6a′**). To determine the equilibrium constant, **6a** (2.9 mg, 0.00274 mmol) and **6a′** (2.1 mg, 0.00274 mmol) were dissolved in C_6D_6 and added into an NMR tube and left to stir at rt in a water bath. The reaction was monitored by NMR spectroscopy. NMR analysis showed that **7** was formed readily upon addition of **6a** and **6a′**.

^{1}H NMR (C_6D_6): δ 1.07 (s, ^{t}Bu, 18H), 3.56 (d, OMe, J = 11.6 Hz), 7.03–7.76 (aromatic) ppm. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 128.3 (d, $P(OMe)_3$, $^{3}J_{p,p}$ = 181 Hz), 14.2 (d, PPh_3, $^{3}J_{p,p}$ = 181 Hz) ppm.

4.8. *X-ray crystallographic studies of 5 and 6*

X-ray data was collected at 103 K on a Bruker Kappa diffractometer equipped with a CCD detector, employing Mo Kα radiation (λ = 0.71073 Å), with the Apex II suite of programs [19]. The data was processed and corrected for Lorentz and polarisation effects with SAINT [20], and for absorption effects with SADABS [21]. Structural solution and refinement were carried out with the SHELXTL suite of programs [22]. There was a disorder of one of the pivalate group for the orthorhombic crystal of **5b′**. This was modelled with two alternative positions, and appropriate distance and thermal parameter restraints were applied. Crystal and refinement data are summarized in Table S2.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.11.005.

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