NJC

PAPER

Check for updates

Cite this: New J. Chem., 2019, 43, 1478

Received 2nd November 2018, Accepted 6th December 2018

DOI: 10.1039/c8nj05573d

rsc.li/njc

Introduction

 $Ru_3(CO)_{12}$ as a potent catalyst precursor attracted great interest of researchers in inorganic, organic and catalytic chemistry due to its high reactivity and unique catalytic activity.¹ $Ru_3(CO)_{12}$ has been widely used in the activation of chemical bonds² and in the construction of catalytic reactions.³ Besides, reactions of transition metal clusters containing functionalized alkynes also attracted a lot of attention within the inorganic and organometallic fields because of their potential applications in catalysis and as candidates in microelectronics and nanolithography.⁴ In recent years, carbonyl ruthenium clusters formed *via* the reaction of $Ru_3(CO)_{12}$ and alkyne derivatives were extensively investigated, and some of them have been used in catalytic systems.⁵

Unexpected formation and conversion: role of substituents of 1,3-ynones in the reactivity and product distribution during their reactions with $Ru_3(CO)_{12}$ [†]

Lei Xu, Liping Jiang, Shasha Li, Guofang Zhang, Keiqiang Zhang and Ziwei Gao

The reactions of Ru₃(CO)₁₂ with alkynyl ketones $R_1C \equiv CC(O)R_2$ ($R_1 = Et$, $R_2 = Me$ (**1**); $R_1 = Ph$, $R_2 = Me$ (**2**); $R_1 = n$ -hexyl, $R_2 = Ph$ (**3**); $R_1 = H$, $R_2 = CH_3$ (**4**); and $R_1 = C(O)OCH_3$, $R_2 = OCH_3$ (**5**)) proceeds in toluene with the formation of three ruthenoles (**1a–3a**), four CO-inserted binuclear clusters (**1b–2b**, **1c** and **3c**), a tetranuclear cluster **4a**, a binuclear cluster **5a** and a cyclotrimerization product **5b**. Clusters **1a–3a**, **1b**, **2b**, **1c** and **3c** were isolated from the reactions of $Ru_3(CO)_{12}$ with two equivalents of the corresponding ketones **1–3**; **4a** and **5a** were collected by adding **4** and **5** to $Ru_3(CO)_{12}$ in molar ratios of 1:1 and 1:3, respectively; **5b** was obtained by adding **5** to **5a** in a molar ratio of 2:1. All compounds were characterized by NMR, FT-IR, and MS-ESI, and most of them were structurally verified by single crystal X-ray diffraction. Although the reaction products of **1–3** and $Ru_3(CO)_{12}$ exhibit similar cluster frameworks of usual ruthenoles and CO-inserted binuclear clusters, the isolation of the clusters **1b–2b**, **1c** and **3c** reveals their strong dependence on both electronic and steric effects of the substituents of the 1,3-ynones **1–3**. In addition, detailed investigations suggested that the high reactivity of the terminal hydrogen atom and electron-withdrawing property of the carbonyl group in **4** play a key role in the formation of **4a**, and that the structurally unusual **5a** is an intermediate in the formation of **5b**.

To understand the mechanisms of their reactions, the reactions of Ru₃(CO)₁₂ with NHCs, arenes, alkenes and alkynes were extensively investigated.6 It was found that coordination atoms usually play a very important role in the activation of neighboring chemical bonds and construction of compound skeletons.7 Meanwhile, it is well known that triruthenium clusters, ruthenoles, CO-inserted diruthenium clusters and tetrahedral tetraruthenium clusters are the most common ruthenium cluster skeletons produced during the reactions of alkynes with Ru₃(CO)₁₂:⁸ for example, P. J. Low and co-workers synthesized the tetrahedral tetraruthenium cluster $Ru_4(CO)_{12}(\mu_4-\eta^1:\eta^2:\eta^2:\eta^2-Me_3SiC \equiv$ $CC_2C \equiv CSiMe_3$) and ruthenole $Ru_2(CO)_6 \{\mu - \eta^2 - \eta^4 - C(C \equiv CSiMe_3) =$ $C(C \equiv CSiMe_3)C(C \equiv CSiMe_3) = C(C \equiv CSiMe_3)$ by the reaction of Ru₃(CO)₁₂ with 1,6-bis(trimethylsilyl)hexa-1,3,5-triyne;⁹ P. Mathur and co-workers isolated a triruthenium cluster [Ru₃(CO)₁₀- $\{\mu_3$ -FcC₂C \equiv CFc $\}$, a ruthenole $[Ru_2(CO)_6 \{C_4Fc_2(C \equiv CFc)_2\}_2]$, COinserted diruthenium clusters $[Ru_2(CO)_6]\mu-\eta^1:\eta^2:\eta^2-FcC \equiv$ CCC(Fc)-C(O)-C(Fc)CC = CFc}]] and $[Ru_2(CO)_6[\mu-\eta^1:\eta^1:\eta^2:\eta^2 FcC \equiv CCC(Fc)-C(O)-C(-C \equiv CFc)C(Fc)]$ through the reaction of $FcC \equiv CC \equiv CFc$ (Fc = ferrocenyl) with $Ru_3(CO)_{12}$.¹⁰ In addition, T. Takahashi and co-workers reported that an electron-withdrawing group activates an alkyne and that an electron-donating group deactivates an alkyne.¹¹ In our recent studies, we have found that

CHEMISTRY

View Article Online

Key Laboratory of Applied Surface and Colloid Chemistry, MOE/School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, China. E-mail: gfzhang@snnu.edu.cn

[†] Electronic supplementary information (ESI) available. Crystal structures of **1c** and **2a**, CIF, checkcif, ¹H NMR spectra, ¹³C{¹H} NMR spectra, FT-IR spectra and other electronic format. CCDC 1865423 (**1a**), 1865427 (**1c**), 1865428 (**2a**), 1865429 (**2b**), 1865430 (**3c**), 1865433 (**4a**), 1865431 (**5a**) and 1865432 (**5b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c8nj05573d

Paper

trirutheniums and ruthenoles are important intermediates in the reactions of 1,3-ynones with Ru₃(CO)₁₂.¹² We have also found that electronic and steric effects of substituents in 1,3-ynones play very important roles in the formation and conversion of ruthenoles: (1) an electron-withdrawing group is beneficial to the formation and conversion of ruthenoles; (2) an electron-donating group favors the formation of ruthenoles, but disfavors the conversion of ruthenoles: and (3) a substituent with large steric hindrance prefers only the formation of tail-to-tail coupling ruthenoles.¹² Although reactions of Ru₃(CO)₁₂ and different alkyne derivatives have been well explored, the studies usually focus on the reactions of Ru₃(CO)₁₂ and alkynes with aromatic substituents.⁸⁻¹² Herein, we choose 1,3-ynones containing alkyl groups or an acetyl group to study the influence of the substituents on the product distribution and their molecular structures during reactions of the 1,3-vnones with $Ru_3(CO)_{12}$.

In this paper, we examined in detail the reaction process of $\operatorname{Ru}_3(\operatorname{CO})_{12}$ with 1,3-ynones $\operatorname{R}^1 \subset = \operatorname{CC}(\operatorname{O})\operatorname{R}^2(\operatorname{R}^1 = \operatorname{Et}, \operatorname{R}^2 = \operatorname{Me}(1);$ $\operatorname{R}^1 = \operatorname{Ph}, \operatorname{R}^2 = \operatorname{Me}(2); \operatorname{R}^1 = n$ -hexyl, $\operatorname{R}^2 = \operatorname{Ph}(3); \operatorname{R}^1 = \operatorname{H}, \operatorname{R}^2 = \operatorname{CH}_3(4);$ and $\operatorname{R}^1 = \operatorname{C}(\operatorname{O})\operatorname{OCH}_3$, $\operatorname{R}^2 = \operatorname{OCH}_3(5)$). The couplings and coordination of the 1,3-ynones with $\operatorname{Ru}_3(\operatorname{CO})_{12}$ formed three ruthenoles (1a–3a), four CO-inserted binuclear clusters (1b–2b, 1c and 3c), a tetranuclear cluster 4a, a binuclear cluster intermediate 5a and a cyclotrimerization product 5b. Through a detailed examination of the reaction processes, we found that the product distribution of the CO-inserted diruthenium clusters is dependent strongly on both electronic and steric effects of the substituents of the 1,3-ynones. Additionally, both the terminal hydrogen atom and the carbonyl group in 3-butyn-2-one are very important for the formation of 4a, and 5a, whose structure is not similar to that of the usual triruthenium clusters, was found to be an intermediate in the formation of the cyclotrimerization compound **5b**.

Results and discussion

Syntheses and characterization

The thermal reactions of 1,3-ynones (1-5) with Ru₃(CO)₁₂ were carried out in toluene at 90 °C in a nitrogen atmosphere. The reaction courses were monitored by the TLC technique. After slow cooling, the solvents were removed and the residues were chromatographed on silica gel with dichloromethane as the eluent.Scheme 1 illustrates the product distribution according to the experimental results. The crystal and refinement data for **1a**, **1c**, **2a**, **2b**, **3c**, **4a**, **4b** and **5a** are listed in Table 1.

The reaction of ynones (1-3) with Ru₃(CO)₁₂

1,3-Ynones 1–3 were each stirred in toluene at 90 °C in a nitrogen atmosphere in a molar ratio of 2:1 with $Ru_3(CO)_{12}$ for 1 h to yield three usual $Ru(CO)_3(\eta^4$ -ruthenole) derivatives 1a–3a and two types of CO-inserted binuclear clusters 1b–2b and 1c, 3c. The two expected clusters 2c and 3b were not detected by the TLC, however. The structural characterizations showed that each of the ruthenoles (1a–3a) contains a metallacyclopentadienyl framework, similar in structure to the ruthenoles we reported previously,¹² in which two 1,3-ynone molecules are coupled by the C \equiv C units in the head-to-tail mode. Accordingly, we choose 1a (Fig. 1) from 1a–3a as an example to describe the molecular structures of these clusters. The molecular structure of



Scheme 1 The product distribution of the reaction between $Ru_3(CO)_{12}$ and ynones (1–5). $R^1 = Et$, $R^2 = Me$ (1); $R^1 = Ph$, $R^2 = Me$ (2); and $R^1 = n$ -hexyl, $R^2 = Ph$ (3).

Table 1 Crystal and refinement data for 1a, 1c, 2a, 2b, 3c, 4a, 4b and 5a

Compounds	1a	1c	2a	2b
Formula	$C_{18}H_{16}O_8Ru_2$	$C_{19}H_{16}O_9Ru_2$	$C_{26}H_{16}O_8Ru_2$	C27H16O9Ru2
$F_{\rm w} ({\rm g \ mol^{-1}})$	562.45	590.46	658.53	686.54
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
<i>T</i> (K)	293(2)	153(2)	153(2)	153(2)
Crystal system	Triclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$Pna2_1$	$P\bar{1}$	$P2_1/c$
a(A)	9.536(3)	14.632(5)	7.9800(14)	9.4633(13)
b (Å)	9.886(3)	15.540(4)	8.6097(16)	11.7500(15)
$c(\dot{A})$	10.826(3)	9.194(3)	18.970(3)	23.323(3)
α	91.241(10)	90.00	86.303(5)	90.00
β()	94.723(10)	90.00	88.063(6)	99.820(5)
v (°)	95.765(10)	90.00	74.729(5)	90.00
$V(A^3)$	1011.6(5)	2090.6(11)	1254.5(4)	2555.4(6)
Z	2	4	2	4
$D_{\rm c}$ (Mg m ⁻³)	1.847	1.876	1.743	1.784
Absorption coefficient (mm^{-1})	1.534	1.493	1.251	1.235
F(000)	552	1160	648	1352
Crystal sizes (mm)	$0.18 \times 0.15 \times 0.12$	$0.16 \times 0.13 \times 0.12$	$0.14 \times 0.13 \times 0.12$	$0.17 \times 0.14 \times 0.12$
Collected/unique	22 225/3916	22 236/4072	45 958/4922	27 930/5015
<i>P</i> .	0.0348	0.0348	0.0383	0.0519
Data/restraints/parameters	3916/0/254	4072/1/272	4922/0/328	5015/1/3/3
$GOE \text{ on } F^2$	1 1 95	1 120	1 050	1 067
$P = WP \left[I > 2\sigma(I) \right]$	0.0205 0.0507	0.0222 0.0567	0.0160 0.0420	0.0204 0.0601
$R_1, WR_2 [I \ge 20(I)]$ $P_1 WP_2 (all data)$	0.0203, 0.0397	0.0250, 0.0576	0.0170 0.0423	0.0294, 0.0091
Largest diff. peak/hole (e $Å^{-3}$)	0.585, -0.463	1.193, -0.620	0.554, -0.385	1.679, -0.579
Compounds	3c	4a	ba	30
Compounds Formula	3c		Sa C14HcO12R112	50 CacHacOa4
Compounds Formula $E_{\rm cr}$ (σ mol ⁻¹)	3c C ₃₇ H ₃₆ O ₉ Ru ₂ 826.80	4a C ₁₆ H ₃ O ₁₃ Ru ₄ 807.46	5a C ₁₄ H ₆ O ₁₂ Ru ₂ 568.33	C ₃₆ H ₃₆ O ₂₄ 852.65
Compounds Formula F_w (g mol ⁻¹) Wavelength (Å)	3c C ₃₇ H ₃₆ O ₉ Ru ₂ 826.80 0.71073	4a C ₁₆ H ₃ O ₁₃ Ru ₄ 807.46 0.71073	5a C ₁₄ H ₆ O ₁₂ Ru ₂ 568.33 0.71073	C ₃₆ H ₃₆ O ₂₄ 852.65 0.71073
Compounds Formula F_w (g mol ⁻¹) Wavelength (Å) T (K)	3c C ₃₇ H ₃₆ O ₉ Ru ₂ 826.80 0.71073 153(2)	$\begin{array}{c} \textbf{4a} \\ \hline \\ C_{16}H_{3}O_{13}Ru_{4} \\ 807.46 \\ 0.71073 \\ 153(2) \end{array}$	C ₁₄ H ₆ O ₁₂ Ru ₂ 568.33 0.71073 153(2)	C ₃₆ H ₃₆ O ₂₄ 852.65 0.71073 153(2)
Compounds Formula F_w (g mol ⁻¹) Wavelength (Å) T (K) Crystal system	3c C ₃₇ H ₃₆ O ₉ Ru ₂ 826.80 0.71073 153(2) Triclinic	4a C ₁₆ H ₃ O ₁₃ Ru ₄ 807.46 0.71073 153(2) Monoclinic	5a C ₁₄ H ₆ O ₁₂ Ru ₂ 568.33 0.71073 153(2) Monoclinic	SD C ₃₆ H ₃₆ O ₂₄ 852.65 0.71073 153(2) Triclinic
Compounds Formula F_w (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group	3c C ₃₇ H ₃₆ O ₉ Ru ₂ 826.80 0.71073 153(2) Triclinic Pī	4a C ₁₆ H ₃ O ₁₃ Ru ₄ 807.46 0.71073 153(2) Monoclinic <i>P</i> _{2.} /n	5a C ₁₄ H ₆ O ₁₂ Ru ₂ 568.33 0.71073 153(2) Monoclinic C ² /c	$\begin{array}{c} & \\ & C_{36}H_{36}O_{24} \\ & 852.65 \\ & 0.71073 \\ & 153(2) \\ & Triclinic \\ & p_{\bar{1}} \end{array}$
Compounds Formula F_w (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group q (Å)	$\begin{array}{c} 3c \\ C_{37}H_{36}O_{9}Ru_{2} \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \end{array}$	$\begin{array}{c} 4a \\ \hline C_{16}H_{3}O_{13}Ru_{4} \\ 807.46 \\ 0.71073 \\ 153(2) \\ Monoclinic \\ P2_{1}/n \\ 13,736(4) \end{array}$	C ₁₄ H ₆ O ₁₂ Ru ₂ 568.33 0.71073 153(2) Monoclinic C2/c 13 385(5)	C ₃₆ H ₃₆ O ₂₄ 852.65 0.71073 153(2) Triclinic <i>P</i> Ī 10 292(4)
Compounds Formula F_{w} (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å)	$\begin{array}{c} 3c \\ \hline C_{37}H_{36}O_{9}Ru_{2} \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \end{array}$	$\begin{array}{c} 4a\\ \hline C_{16}H_{3}O_{13}Ru_{4}\\ 807.46\\ 0.71073\\ 153(2)\\ Monoclinic\\ P2_{1}/n\\ 13.736(4)\\ 10.403(3)\\ \end{array}$	C ₁₄ H ₆ O ₁₂ Ru ₂ 568.33 0.71073 153(2) Monoclinic C2/c 13.385(5) 11 395(3)	$\begin{array}{c} \text{SD} \\ \hline C_{36}\text{H}_{36}\text{O}_{24} \\ 852.65 \\ 0.71073 \\ 153(2) \\ \text{Triclinic} \\ P\bar{1} \\ 10.292(4) \\ 11.043(4) \end{array}$
Compounds Formula F_{w} (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å)	$\begin{array}{c} 3c \\ \hline C_{37}H_{36}O_{9}Ru_{2} \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \end{array}$	$\begin{array}{r} 4a \\ \hline C_{16}H_{3}O_{13}Ru_{4} \\ 807.46 \\ 0.71073 \\ 153(2) \\ Monoclinic \\ P2_{1}/n \\ 13.736(4) \\ 10.403(3) \\ 15.643(5) \end{array}$	$\begin{array}{c} & \\ & C_{14}H_6O_{12}Ru_2 \\ & 568.33 \\ & 0.71073 \\ & 153(2) \\ & Monoclinic \\ & C2/c \\ & 13.385(5) \\ & 11.395(3) \\ & 11.933(4) \end{array}$	$\begin{array}{c} \text{SD} \\ \hline C_{36}\text{H}_{36}\text{O}_{24} \\ 852.65 \\ 0.71073 \\ 153(2) \\ \text{Triclinic} \\ P\bar{1} \\ 10.292(4) \\ 11.043(4) \\ 18.767(6) \end{array}$
Compounds Formula F_{w} (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) c (Å)	$\begin{array}{c} 3c \\ \hline C_{37}H_{36}O_{9}Ru_{2} \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\overline{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \end{array}$	$\begin{array}{c} 4a\\ \hline \\ C_{16}H_3O_{13}Ru_4\\ 807.46\\ 0.71073\\ 153(2)\\ Monoclinic\\ P2_1/n\\ 13.736(4)\\ 10.403(3)\\ 15.643(5)\\ 90.00\\ \end{array}$	$\begin{array}{c} \text{Sa} \\ \hline \\ C_{14}H_6O_{12}Ru_2 \\ 568.33 \\ 0.71073 \\ 153(2) \\ \text{Monoclinic} \\ C2/c \\ 13.385(5) \\ 11.395(3) \\ 11.933(4) \\ 90.00 \\ \end{array}$	$\begin{array}{c} \text{SD} \\ \hline \\ \text{C}_{36}\text{H}_{36}\text{O}_{24} \\ \text{852.65} \\ 0.71073 \\ 153(2) \\ \text{Triclinic} \\ P\bar{1} \\ 10.292(4) \\ 11.043(4) \\ 18.767(6) \\ 76 244(12) \end{array}$
Compounds Formula F_{w} (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) a (°) β (°)	$\begin{array}{c} 3c \\ \hline \\ C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ \end{array}$	$\begin{array}{c} 4a \\ \hline \\ C_{16}H_3O_{13}Ru_4 \\ 807.46 \\ 0.71073 \\ 153(2) \\ Monoclinic \\ P2_1/n \\ 13.736(4) \\ 10.403(3) \\ 15.643(5) \\ 90.00 \\ 91.786(9) \end{array}$	$\begin{array}{c} \text{Sa} \\ \hline \\ C_{14}H_6O_{12}Ru_2 \\ 568.33 \\ 0.71073 \\ 153(2) \\ \text{Monoclinic} \\ C2/c \\ 13.385(5) \\ 11.395(3) \\ 11.933(4) \\ 90.00 \\ 100.958(13) \end{array}$	$\begin{array}{c} \text{SD} \\ \hline \\ \text{C}_{36}\text{H}_{36}\text{O}_{24} \\ \text{852.65} \\ 0.71073 \\ 153(2) \\ \text{Triclinic} \\ P\overline{1} \\ 10.292(4) \\ 11.043(4) \\ 18.767(6) \\ 76.244(12) \\ \text{87} 402(12) \\ \end{array}$
Compounds Formula F_w (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) a (°) β (°) α (°)	$\begin{array}{c} 3c \\ \hline \\ C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\overline{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.952(8) \\ \end{array}$	$\begin{array}{c} 4a \\ \hline \\ C_{16}H_3O_{13}Ru_4 \\ 807.46 \\ 0.71073 \\ 153(2) \\ Monoclinic \\ P2_1/n \\ 13.736(4) \\ 10.403(3) \\ 15.643(5) \\ 90.00 \\ 91.786(9) \\ 90.00 \\ \end{array}$	$\begin{array}{c} \text{Sa} \\ \hline C_{14}H_6O_{12}\text{Ru}_2 \\ 568.33 \\ 0.71073 \\ 153(2) \\ \text{Monoclinic} \\ C2/c \\ 13.385(5) \\ 11.395(3) \\ 11.933(4) \\ 90.00 \\ 100.958(13) \\ 90.00 \\ 00 \\ 00 \\ \end{array}$	$\begin{array}{c} \text{SD} \\ \hline \text{C}_{36}\text{H}_{36}\text{O}_{24} \\ \text{852.65} \\ 0.71073 \\ 153(2) \\ \text{Triclinic} \\ P\overline{1} \\ 10.292(4) \\ 11.043(4) \\ 18.767(6) \\ 76.244(12) \\ 87.402(12) \\ 74.255(12) \\ \end{array}$
Compounds Formula $F_w (g \text{ mol}^{-1})$ Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) a (°) β (°) γ (°) $V(A^3)$	$\begin{array}{c} 3\mathbf{c} \\ \\ C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\overline{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.953(8) \\ 1785.9(7) \end{array}$	$\begin{array}{c} 4a\\ \hline \\ C_{16}H_3O_{13}Ru_4\\ 807.46\\ 0.71073\\ 153(2)\\ Monoclinic\\ P2_1/n\\ 13.736(4)\\ 10.403(3)\\ 15.643(5)\\ 90.00\\ 91.786(9)\\ 90.00\\ 2324_3(11)\\ \end{array}$	$\begin{array}{c} \text{Sa} \\ \hline C_{14}\text{H}_6\text{O}_{12}\text{Ru}_2 \\ 568.33 \\ 0.71073 \\ 153(2) \\ \text{Monoclinic} \\ C2/c \\ 13.385(5) \\ 11.395(3) \\ 11.933(4) \\ 90.00 \\ 100.958(13) \\ 90.00 \\ 1786.9(10) \\ \end{array}$	$\begin{array}{c} \text{SD} \\ \hline C_{36}\text{H}_{36}\text{O}_{24} \\ 852.65 \\ 0.71073 \\ 153(2) \\ \text{Triclinic} \\ P\overline{1} \\ 10.292(4) \\ 11.043(4) \\ 18.767(6) \\ 76.244(12) \\ 87.402(12) \\ 74.255(12) \\ 1993.6(12) \end{array}$
Compounds Formula F_{w} (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) a (°) β (°) γ (°) γ (°) γ (°) γ (°) γ (°)	$\begin{array}{c} 3c \\ \\ C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.953(8) \\ 1785.9(7) \\ 2 \end{array}$	$\begin{array}{c} 4a \\ \\ C_{16}H_3O_{13}Ru_4 \\ 807.46 \\ 0.71073 \\ 153(2) \\ Monoclinic \\ P2_1/n \\ 13.736(4) \\ 10.403(3) \\ 15.643(5) \\ 90.00 \\ 91.786(9) \\ 90.00 \\ 2234.3(11) \\ 4 \end{array}$	Sa C ₁₄ H ₆ O ₁₂ Ru ₂ 568.33 0.71073 153(2) Monoclinic C2/c 13.385(5) 11.395(3) 11.933(4) 90.00 100.958(13) 90.00 1786.9(10) 4	$\begin{array}{c} \text{SU} \\ \hline C_{36}\text{H}_{36}\text{O}_{24} \\ 852.65 \\ 0.71073 \\ 153(2) \\ \text{Triclinic} \\ P\overline{1} \\ 10.292(4) \\ 11.043(4) \\ 18.767(6) \\ 76.244(12) \\ 87.402(12) \\ 74.255(12) \\ 1993.6(12) \\ 2 \end{array}$
Compounds Formula F_{w} (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z D (Mg m ⁻³)	$\begin{array}{c} 3c \\ \hline C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.953(8) \\ 1785.9(7) \\ 2 \\ 1 \\ 537 \\ \end{array}$	$\begin{array}{c} 4a \\ \\ C_{16}H_3O_{13}Ru_4 \\ 807.46 \\ 0.71073 \\ 153(2) \\ Monoclinic \\ P2_1/n \\ 13.736(4) \\ 10.403(3) \\ 15.643(5) \\ 90.00 \\ 91.786(9) \\ 90.00 \\ 2234.3(11) \\ 4 \\ 2.400 \\ \end{array}$	Sa C ₁₄ H ₆ O ₁₂ Ru ₂ 568.33 0.71073 153(2) Monoclinic C2/c 13.385(5) 11.395(3) 11.933(4) 90.00 100.958(13) 90.00 1786.9(10) 4 2 113	$\begin{array}{c} \text{SU}\\ \hline \\ \text{C}_{36}\text{H}_{36}\text{O}_{24}\\ \text{852.65}\\ 0.71073\\ 153(2)\\ \text{Triclinic}\\ P\bar{1}\\ 10.292(4)\\ 11.043(4)\\ 18.767(6)\\ 76.244(12)\\ 87.402(12)\\ 74.255(12)\\ 1993.6(12)\\ 2\\ 1420\end{array}$
Compounds Formula F_{w} (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å ³) Z D_{c} (Mg m ⁻³) Δ broantion coefficient (mm ⁻¹)	$\begin{array}{c} 3c \\ \hline C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.953(8) \\ 1785.9(7) \\ 2 \\ 1.537 \\ 0.898 \end{array}$	$\begin{array}{c} 4a \\ \\ C_{16}H_{3}O_{13}Ru_{4} \\ 807.46 \\ 0.71073 \\ 153(2) \\ Monoclinic \\ P2_{1}/n \\ 13.736(4) \\ 10.403(3) \\ 15.643(5) \\ 90.00 \\ 91.786(9) \\ 90.00 \\ 2234.3(11) \\ 4 \\ 2.400 \\ 2.716 \end{array}$	$\begin{array}{c} \text{Sa} \\ \hline \\ C_{14}\text{H}_6\text{O}_{12}\text{Ru}_2 \\ 568.33 \\ 0.71073 \\ 153(2) \\ \text{Monoclinic} \\ C2/c \\ 13.385(5) \\ 11.395(3) \\ 11.933(4) \\ 90.00 \\ 100.958(13) \\ 90.00 \\ 1786.9(10) \\ 4 \\ 2.113 \\ 1.754 \end{array}$	$\begin{array}{c} \text{SU} \\ \hline C_{36}\text{H}_{36}\text{O}_{24} \\ 852.65 \\ 0.71073 \\ 153(2) \\ \text{Triclinic} \\ P\bar{1} \\ 10.292(4) \\ 11.043(4) \\ 18.767(6) \\ 76.244(12) \\ 87.402(12) \\ 74.255(12) \\ 1993.6(12) \\ 2 \\ 1.420 \\ 0.122 \end{array}$
Compounds Formula F_{w} (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å ³) Z D_{c} (Mg m ⁻³) Absorption coefficient (mm ⁻¹)	$\begin{array}{c} 3\mathbf{c} \\ \hline \\ C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.953(8) \\ 1785.9(7) \\ 2 \\ 1.537 \\ 0.898 \\ 826 \end{array}$	$\begin{array}{c} 4a\\ \\ C_{16}H_{3}O_{13}Ru_{4}\\ 807.46\\ 0.71073\\ 153(2)\\ Monoclinic\\ P2_{1}/n\\ 13.736(4)\\ 10.403(3)\\ 15.643(5)\\ 90.00\\ 91.786(9)\\ 90.00\\ 2234.3(11)\\ 4\\ 2.400\\ 2.716\\ 1516\end{array}$	$\begin{array}{c} \text{Sa} \\ \hline \\ C_{14}H_6O_{12}Ru_2 \\ 568.33 \\ 0.71073 \\ 153(2) \\ \text{Monoclinic} \\ C2/c \\ 13.385(5) \\ 11.395(3) \\ 11.933(4) \\ 90.00 \\ 100.958(13) \\ 90.00 \\ 1786.9(10) \\ 4 \\ 2.113 \\ 1.754 \\ 1006 \end{array}$	$\begin{array}{c} \text{SU} \\ \hline C_{36}\text{H}_{36}\text{O}_{24} \\ 852.65 \\ 0.71073 \\ 153(2) \\ \text{Triclinic} \\ P\bar{1} \\ 10.292(4) \\ 11.043(4) \\ 18.767(6) \\ 76.244(12) \\ 87.402(12) \\ 74.255(12) \\ 1993.6(12) \\ 2 \\ 1.420 \\ 0.122 \\ 989 \end{array}$
Compounds Formula F_{w} (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) γ (°) γ (°) γ (°) γ (°) γ (°) Z D_{c} (Mg m ⁻³) Absorption coefficient (mm ⁻¹) F(000)	$\begin{array}{c} 3c \\ \hline \\ C_{37}H_{36}O_{9}Ru_{2} \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.953(8) \\ 1785.9(7) \\ 2 \\ 1.537 \\ 0.898 \\ 836 \\ 0.16 \times 0.14 \times 0.12 \\ \end{array}$	$\begin{array}{c} 4a\\ \\ C_{16}H_{3}O_{13}Ru_{4}\\ 807.46\\ 0.71073\\ 153(2)\\ Monoclinic\\ P2_{1}/n\\ 13.736(4)\\ 10.403(3)\\ 15.643(5)\\ 90.00\\ 91.786(9)\\ 90.00\\ 2234.3(11)\\ 4\\ 2.400\\ 2.716\\ 1516\\ 0.16\times0.12\times0.11\\ \end{array}$	$\begin{array}{c} \text{Sa} \\ \hline C_{14}H_6O_{12}\text{Ru}_2 \\ 568.33 \\ 0.71073 \\ 153(2) \\ \text{Monoclinic} \\ C2/c \\ 13.385(5) \\ 11.395(3) \\ 11.933(4) \\ 90.00 \\ 100.958(13) \\ 90.00 \\ 100.958(13) \\ 90.00 \\ 1786.9(10) \\ 4 \\ 2.113 \\ 1.754 \\ 1096 \\ 0.14 \times 0.12 \times 0.10 \\ \end{array}$	$\begin{array}{c} & & \\$
Compounds Formula F_w (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å3) Z D_c (Mg m ⁻³) Absorption coefficient (mm ⁻¹) F(000) Crystal sizes (mm) Calleated/unique	$\begin{array}{c} 3\mathbf{c} \\ \hline \\ C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\overline{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.953(8) \\ 1785.9(7) \\ 2 \\ 1.537 \\ 0.898 \\ 836 \\ 0.16 \times 0.14 \times 0.13 \\ (4.544/7020) \end{array}$	$\begin{array}{c} 4a\\ \\ \hline C_{16}H_3O_{13}Ru_4\\ 807.46\\ 0.71073\\ 153(2)\\ \\ Monoclinic\\ P2_1/n\\ 13.736(4)\\ 10.403(3)\\ 15.643(5)\\ 90.00\\ 91.786(9)\\ 90.00\\ 2234.3(11)\\ 4\\ 2.400\\ 2.716\\ 1516\\ 0.16 \times 0.13 \times 0.11\\ \\ 77372(4054) \end{array}$	$\begin{array}{c} \text{Sa} \\ \hline \\ C_{14}H_6O_{12}\text{Ru}_2 \\ 568.33 \\ 0.71073 \\ 153(2) \\ \text{Monoclinic} \\ C2/c \\ 13.385(5) \\ 11.395(3) \\ 11.933(4) \\ 90.00 \\ 100.958(13) \\ 90.00 \\ 1786.9(10) \\ 4 \\ 2.113 \\ 1.754 \\ 1096 \\ 0.14 \times 0.13 \times 0.10 \\ 0224/2750 \\ 0.224$	$\begin{array}{c} & & \\$
Compounds Formula F_{w} (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å ³) Z D_{c} (Mg m ⁻³) Absorption coefficient (mm ⁻¹) F(000) Crystal sizes (mm) Collected/unique P	$\begin{array}{c} 3c \\ \\ C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.953(8) \\ 1785.9(7) \\ 2 \\ 1.537 \\ 0.898 \\ 836 \\ 0.16 \times 0.14 \times 0.13 \\ 64.541/7020 \\ 0.0416 \end{array}$	$\begin{array}{c} 4a\\ \\ \hline \\ C_{16}H_3O_{13}Ru_4\\ 807.46\\ 0.71073\\ 153(2)\\ \\ Monoclinic\\ P2_1/n\\ 13.736(4)\\ 10.403(3)\\ 15.643(5)\\ 90.00\\ 91.786(9)\\ 90.00\\ 2234.3(11)\\ 4\\ 2.400\\ 2.716\\ 1516\\ 0.16\times0.13\times0.11\\ 77373/4354\\ 0.0402\\ \end{array}$	$\begin{array}{c} \text{Sa} \\ \hline \\ C_{14}H_6O_{12}\text{Ru}_2 \\ 568.33 \\ 0.71073 \\ 153(2) \\ \text{Monoclinic} \\ C2/c \\ 13.385(5) \\ 11.395(3) \\ 11.933(4) \\ 90.00 \\ 100.958(13) \\ 90.00 \\ 1786.9(10) \\ 4 \\ 2.113 \\ 1.754 \\ 1096 \\ 0.14 \times 0.13 \times 0.10 \\ 9932/1758 \\ 0.0462 \\ \end{array}$	$\begin{array}{c} & & \\ & & C_{36}H_{36}O_{24} \\ & & 852.65 \\ & 0.71073 \\ & 153(2) \\ & & \\ Triclinic \\ P\bar{1} \\ & 10.292(4) \\ & 11.043(4) \\ & 18.767(6) \\ & 76.244(12) \\ & 87.402(12) \\ & 74.255(12) \\ & 1993.6(12) \\ & 2 \\ & 1.420 \\ & 0.122 \\ & 888 \\ & 0.14 \times 0.12 \times 0.10 \\ & 66.879/7815 \\ & 0.0501 \end{array}$
Compounds Formula F_{w} (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z D_{c} (Mg m ⁻³) Absorption coefficient (mm ⁻¹) F(000) Crystal sizes (mm) Collected/unique R_{int} Data /rectraints/parameters	$\begin{array}{c} 3c \\ \\ C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.953(8) \\ 1785.9(7) \\ 2 \\ 1.537 \\ 0.898 \\ 836 \\ 0.16 \times 0.14 \times 0.13 \\ 64 541/7020 \\ 0.0416 \\ 7000/0/425 \end{array}$	$\begin{array}{c} 4a\\ \\ \hline C_{16}H_3O_{13}Ru_4\\ 807.46\\ 0.71073\\ 153(2)\\ \\ Monoclinic\\ P2_1/n\\ 13.736(4)\\ 10.403(3)\\ 15.643(5)\\ 90.00\\ 91.786(9)\\ 90.00\\ 2234.3(11)\\ 4\\ 2.400\\ 2.716\\ 1516\\ 0.16\times0.13\times0.11\\ 77.373/4354\\ 0.0408\\ 4254/0/202\\ \end{array}$	$\begin{array}{c} \text{Sa} \\ \hline \\ C_{14}\text{H}_6\text{O}_{12}\text{Ru}_2 \\ 568.33 \\ 0.71073 \\ 153(2) \\ \text{Monoclinic} \\ C2/c \\ 13.385(5) \\ 11.395(3) \\ 11.933(4) \\ 90.00 \\ 100.958(13) \\ 90.00 \\ 100.958(13) \\ 90.00 \\ 1786.9(10) \\ 4 \\ 2.113 \\ 1.754 \\ 1096 \\ 0.14 \times 0.13 \times 0.10 \\ 9932/1758 \\ 0.0463 \\ 1758/0(127) \\ \end{array}$	$\begin{array}{c} & & \\ & & C_{36}H_{36}O_{24} \\ & & 852.65 \\ & & 0.71073 \\ & & 153(2) \\ & & \text{Triclinic} \\ & & P\overline{1} \\ & & 10.292(4) \\ & & 11.043(4) \\ & & 18.767(6) \\ & & 76.244(12) \\ & & 87.402(12) \\ & & 74.255(12) \\ & & 1993.6(12) \\ & & 2 \\ & & 1.420 \\ & & 0.122 \\ & & 888 \\ & & 0.14 \times 0.12 \times 0.10 \\ & & 66.879/7815 \\ & & 0.0691 \\ & & 7815/0/522 \end{array}$
Compounds Formula F_{w} (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z D_{c} (Mg m ⁻³) Absorption coefficient (mm ⁻¹) F(000) Crystal sizes (mm) Collected/unique R_{int} Data/restraints/parameters COE on P^{2}	$\begin{array}{c} 3c \\ \hline \\ C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.953(8) \\ 1785.9(7) \\ 2 \\ 1.537 \\ 0.898 \\ 836 \\ 0.16 \times 0.14 \times 0.13 \\ 64.541/7020 \\ 0.0416 \\ 7020/0/435 \\ 1.197 \end{array}$	$\begin{array}{c} 4a\\ \hline \\ C_{16}H_3O_{13}Ru_4\\ 807.46\\ 0.71073\\ 153(2)\\ Monoclinic\\ P2_1/n\\ 13.736(4)\\ 10.403(3)\\ 15.643(5)\\ 90.00\\ 91.786(9)\\ 90.00\\ 2234.3(11)\\ 4\\ 2.400\\ 2.716\\ 1516\\ 0.16\times 0.13\times 0.11\\ 77373/4354\\ 0.0408\\ 4354/0/298\\ 4.147\\ \end{array}$	Sa $C_{14}H_6O_{12}Ru_2$ 568.33 0.71073 153(2) Monoclinic C2/c 13.385(5) 11.395(3) 11.933(4) 90.00 100.958(13) 90.00 1786.9(10) 4 2.113 1.754 1096 0.14 × 0.13 × 0.10 9932/1758 0.0463 1758/0/127 1.092	$\begin{array}{c} & & & \\ & & C_{36}H_{36}O_{24} \\ & & 852.65 \\ & & 0.71073 \\ & & 153(2) \\ & & \\ Triclinic \\ & & P\bar{1} \\ & & 10.292(4) \\ & & 11.043(4) \\ & & 18.767(6) \\ & & 76.244(12) \\ & & 87.402(12) \\ & & 74.255(12) \\ & & 1993.6(12) \\ & & 2 \\ & & 1.420 \\ & & 0.122 \\ & & 888 \\ & & 0.14 \times 0.12 \times 0.10 \\ & & 66879/7815 \\ & & 0.0691 \\ & & 7815/0/553 \\ & & 1.997 \end{array}$
Compounds Formula $F_{w}(g \text{ mol}^{-1})$ Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) a (Å) a (Å) a (Å) a (Å) f (°) f	$\begin{array}{c} 3c \\ \hline \\ C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.953(8) \\ 1785.9(7) \\ 2 \\ 1.537 \\ 0.898 \\ 836 \\ 0.16 \times 0.14 \times 0.13 \\ 64.541/7020 \\ 0.0416 \\ 7020/0/435 \\ 1.197 \\ 0.2000 0.0504 \\ \end{array}$	$\begin{array}{c} 4a\\ \\ C_{16}H_3O_{13}Ru_4\\ 807.46\\ 0.71073\\ 153(2)\\ Monoclinic\\ P2_1/n\\ 13.736(4)\\ 10.403(3)\\ 15.643(5)\\ 90.00\\ 91.786(9)\\ 90.00\\ 2234.3(11)\\ 4\\ 2.400\\ 2.716\\ 1516\\ 0.16\times 0.13\times 0.11\\ 77373/4354\\ 0.0408\\ 4354/0/298\\ 1.147\\ 0.0411\\ \end{array}$	Sa $C_{14}H_6O_{12}Ru_2$ 568.33 0.71073 153(2) Monoclinic C2/c 13.385(5) 11.395(3) 11.933(4) 90.00 100.958(13) 90.00 1786.9(10) 4 2.113 1.754 1096 0.14 × 0.13 × 0.10 9932/1758 0.0463 1758/0/127 1.083 0.0457 0.0457 0.0457	$\begin{array}{c} & & \\ & C_{36}H_{36}O_{24} \\ & 852.65 \\ & 0.71073 \\ & 153(2) \\ & Triclinic \\ & P\bar{1} \\ & 10.292(4) \\ & 11.043(4) \\ & 18.767(6) \\ & 76.244(12) \\ & 87.402(12) \\ & 74.255(12) \\ & 1993.6(12) \\ & 2 \\ & 1.420 \\ & 0.122 \\ & 888 \\ & 0.14 \times 0.12 \times 0.10 \\ & 66879/7815 \\ & 0.0691 \\ & 7815/0/553 \\ & 1.097 \\ & 2.0462 \\ & 0.1021 \end{array}$
Compounds Formula F_{w} (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z D_{c} (Mg m ⁻³) Absorption coefficient (mm ⁻¹) F(000) Crystal sizes (mm) Collected/unique R_{int} Data/restraints/parameters GOF on F^{2} R_{1} , w R_{2} [$I \ge 2\sigma(I)$]	$\begin{array}{c} 3c \\ \hline \\ C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.953(8) \\ 1785.9(7) \\ 2 \\ 1.537 \\ 0.898 \\ 836 \\ 0.16 \times 0.14 \times 0.13 \\ 64.541/7020 \\ 0.0416 \\ 7020/0/435 \\ 1.197 \\ 0.0208, 0.0594 \\ 0.0690 \\ \end{array}$	$\begin{array}{c} 4a\\ \\ C_{16}H_{3}O_{13}Ru_{4}\\ 807.46\\ 0.71073\\ 153(2)\\ Monoclinic\\ P2_{1}/n\\ 13.736(4)\\ 10.403(3)\\ 15.643(5)\\ 90.00\\ 90.00\\ 91.786(9)\\ 90.00\\ 2234.3(11)\\ 4\\ 2.400\\ 2.716\\ 1516\\ 0.16 \times 0.13 \times 0.11\\ 77373/4354\\ 0.0408\\ 4354/0/298\\ 1.147\\ 0.0168, 0.0411\\ 0.0168, 0.0411\\ 0.0168, 0.0411\\ \end{array}$	$\begin{array}{c} \text{Sa}\\ \hline \\ C_{14}\text{H}_6\text{O}_{12}\text{Ru}_2\\ 568.33\\ 0.71073\\ 153(2)\\ \text{Monoclinic}\\ C2/c\\ 13.385(5)\\ 11.395(3)\\ 11.395(3)\\ 11.933(4)\\ 90.00\\ 100.958(13)\\ 90.00\\ 100.958(13)\\ 90.00\\ 1786.9(10)\\ 4\\ 2.113\\ 1.754\\ 1096\\ 0.14 \times 0.13 \times 0.10\\ 9932/1758\\ 0.0463\\ 1758/0/127\\ 1.083\\ 0.0235, 0.0476\\ 0.0476\\ 0.0235, 0.0476\\ 0.0700\\ \end{array}$	$\begin{array}{c} & \mathbf{SU} \\ & \mathbf{C}_{36}\mathbf{H}_{36}\mathbf{O}_{24} \\ & 852.65 \\ & 0.71073 \\ & 153(2) \\ & \text{Triclinic} \\ & P\bar{1} \\ & 10.292(4) \\ & 11.043(4) \\ & 18.767(6) \\ & 76.244(12) \\ & 87.402(12) \\ & 74.255(12) \\ & 1993.6(12) \\ & 2 \\ & 1.420 \\ & 0.122 \\ & 888 \\ & 0.14 \times 0.12 \times 0.10 \\ & 66879/7815 \\ & 0.0691 \\ & 7815/0/553 \\ & 1.097 \\ & 0.0462, 0.1024 \\ & 0.4401 \end{array}$
Compounds Formula Fow (g mol ⁻¹) Wavelength (Å) T (K) Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å ³) Z D_c (Mg m ⁻³) Absorption coefficient (mm ⁻¹) F(000) Crystal sizes (mm) Collected/unique R_{int} Data/restraints/parameters GOF on F^2 R_1 , w R_2 [$I \ge 2\sigma(I)$] R_1 , w R_2 (all data)	$\begin{array}{c} 3c \\ \hline \\ C_{37}H_{36}O_9Ru_2 \\ 826.80 \\ 0.71073 \\ 153(2) \\ Triclinic \\ P\bar{1} \\ 8.457(2) \\ 10.898(2) \\ 19.590(5) \\ 88.140(8) \\ 83.336(8) \\ 84.953(8) \\ 1785.9(7) \\ 2 \\ 1.537 \\ 0.898 \\ 836 \\ 0.16 \times 0.14 \times 0.13 \\ 64 541/7020 \\ 0.0416 \\ 7020/0/435 \\ 1.197 \\ 0.0208, 0.0594 \\ 0.0231, 0.0608 \\ 0.500 \\ \end{array}$	$\begin{array}{c} 4a\\ \\ \hline \\ C_{16}H_3O_{13}Ru_4\\ 807.46\\ 0.71073\\ 153(2)\\ \\ Monoclinic\\ P2_1/n\\ 13.736(4)\\ 10.403(3)\\ 15.643(5)\\ 90.00\\ 91.786(9)\\ 90.00\\ 2234.3(11)\\ 4\\ 2.400\\ 2.716\\ 1516\\ 0.16\times0.13\times0.11\\ 77373/4354\\ 0.0408\\ 4354/0/298\\ 1.147\\ 0.0168, 0.0411\\ 0.0176, 0.0416\\ 0.0176, 0.0416\\ \end{array}$	$\begin{array}{c} 5a\\ \hline \\ C_{14}H_6O_{12}Ru_2\\ 568.33\\ 0.71073\\ 153(2)\\ Monoclinic\\ C2/c\\ 13.385(5)\\ 11.395(3)\\ 11.933(4)\\ 90.00\\ 100.958(13)\\ 90.00\\ 100.958(13)\\ 90.00\\ 1786.9(10)\\ 4\\ 2.113\\ 1.754\\ 1096\\ 0.14\times0.13\times0.10\\ 9932/1758\\ 0.0463\\ 1758/0/127\\ 1.083\\ 0.0235, 0.0476\\ 0.0303, 0.0500\\ \end{array}$	$\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & &$

1a contains a metallacyclopentadienyl moiety, which is similar in structure to the carbonyl complexes $[M(CO)(\eta^4\text{-metallole})](M = Fe, Ru, Os)$ formed by a combination of alkynes with group 8 metals.^{12,13} The FT-IR absorption bands in the range of 2014–2088 cm⁻¹ were assigned to the terminal CO groups of 1a. The ¹³C chemical shifts of the carbon atoms of the C \equiv C bond in 1a, located at 96.5 and 92.4 ppm in 1, moved downwards to 127.86 and 122.90 ppm, respectively, confirming a strong interaction between the C \equiv C bonds and the three Ru atoms. The distance of the Ru–Ru bond is 2.7163(7) Å. The lengths of the C–C bonds (1.4010(3)–1.4668(3) Å) in the metallacyclopentadiene (Ru₂C₃C₄C₉C₁₀) reflect the interactions between

the Ru1 atom and the alkyne molecule, and most of the Ru–C bond lengths in the metallacyclopentadiene fall into two distinct ranges, 2.2140(5)–2.3034(5) Å and 2.0655(4)–2.0843(5) Å. In addition, the structure of **1a** shows an eclipsed conformation of the carbonyls on the two ruthenium centers, with the dihedral angle of Ru1–Ru2–C15_{plane} and Ru1–Ru2–C17_{plane} being 3.612(6)°. The special arrangement geometrically prevents an apical carbonyl from being close enough to the ring metal Ru1 for a CO bridging conformation. Hence, all carbonyls are terminal with almost parallel Ru–C–O angles.

The crystal structures of the ruthenium carbonyl clusters **1b–2b**, **1c** and **3c** exhibit a similar binuclear ruthenium



Fig. 1 ORTEP view of cluster **1a** showing 50% ellipsoids. Selected bond lengths (Å) and bond angles (°): Ru1–Ru2 = 2.7163(7); Ru1–C3 = 2.2532(5); Ru1–C4 = 2.2503(4); Ru1–C9 = 2.2140(5); Ru1–C10 = 2.3034(5); Ru2–C3 = 2.0843(4); Ru2–C10 = 2.0655(5); C3–C4 = 1.4010(3); C4–C9 = 1.4668(3); C9–C10 = 1.4192(3); C2–C3 = 1.4923(3); C8–C9 = 1.5165(3); C2–O1 = 1.2066(3); C8–O2 = 1.1987(3); and C3–Ru2–C10 = 77.566(9).

framework to that reported by A. J. Blake and co-workers in the reaction of Ru₃(CO)₉(μ_3 - η^2 : η^2 : η^2 -C₁₆H₁₆) and 1,2-diphenylethyne earlier.¹⁴ The molecular structure of **2b**, as an example, is depicted in Fig. 2. The crystal structure of **2b** exhibits a routine staggered conformation of carbonyls, two C \equiv C units being linked through an inserted carbonyl group in the tail-to-tail coupling mode (**1b–2b**). The distance of the Ru–Ru bond is 2.7383(3) Å, and the dihedral angles between C7–C27–C17_{plane} and C7–Ru1–C18_{plane}, C8–Ru2–C17_{plane} are 22.227° and 39.054°, respectively. Two phenylacetylene units are connected through a carbonyl group; the FT-IR spectrum can demonstrate this point by a band



Fig. 2 ORTEP view of cluster **2b** showing 50% ellipsoids. Selected bond lengths (Å) and bond angles (°): Ru1–Ru2 = 2.7383(3); Ru1–C7 = 2.2713(2); Ru1–C8 = 2.1759(3); Ru1–C18 = 2.0583(3); Ru2–C8 = 2.0896(2); Ru2–C17 = 2.3084(2); Ru2–C18 = 2.1948(2); C7–C8 = 1.4166(1); C17–C18 = 1.4206(1); C7–C27 = 1.5188(2); C17–C27 = 1.5031(1); C27–O9 = 1.2063(1); C18–C19 = 1.4980(1); C19–O1 = 1.2140(2); C8–C9 = 1.4991(2); C9–O1= 1.2166(1); and C7–C27–C17 = 114.762(8).



Fig. 3 ORTEP view of cluster **3c** showing 50% ellipsoids. Selected bond lengths (Å) and bond angles (°): Ru1–Ru2 = 2.7471(6); Ru1–C8 = 2.2104(4); Ru1–C9 = 2.2836(4); Ru1–C24 = 2.0933(4); Ru2–C8 = 2.0715(4); Ru2–C23 = 2.2942(5); Ru2–C24 = 2.2546(4); C8–C9 = 1.4124(3); C23–C24 = 1.4054(3); C23–C31 = 1.5027(3); C9–C31 = 1.4978(3); C22–C23 = 1.5217(3); C7–C8 = 1.5008(3); C22–O2 = 1.2129(3); C7–O1 = 1.2175(2); C31–O3 = 1.2097(3); and C9–C31–C23 = 114.594(18).

displaying at 1681 cm⁻¹. Each of the 1,3-ynone molecules bonds to the ruthenium dimer *via* one π and one σ interactions, therefore providing each metal atom three electrons. Apart from this, each metal also has three terminal carbonyl groups, and the effective atomic number rule is obeyed for the Ru–Ru bond.

On comparison of the structures of **1c** and **3c** with **1b–2b**, the crystal structures of **1c** and **3c** (taking **3c** shown in Fig. 3 as an example) each also show the usual staggered conformation of the carbonyls, but two $C \equiv C$ units are joined through an inserted carbonyl group in the head-to-tail coupling mode. The structure of **3c** consists of six terminal and one bridging carbonyls. The distance of the Ru–Ru bond is 2.7471(6) Å. The dihedral angles between C9–C31–C23_{plane} and C24–Ru1–C9_{plane}, C8–Ru2–C23_{plane} are 27.955(19)° and 34.554(21)°, respectively. The lengths of the Ru–C bonds fall mostly in the range of 2.0715(4)–2.2942(5) Å, and the FT-IR absorption band at 1673 cm⁻¹ confirms the existence of a bridging carbonyl group between C23 and C9 atoms.

The reaction of 3-butyn-2-one (4) with $Ru_3(CO)_{12}$

Treatment of 3-butyn-2-one (4) with Ru₃(CO)₁₂ in a molar ratio of 1:1 in toluene at 90 °C for 1 h in a nitrogen atmosphere yielded a single product [Ru₄(CO)₁₂{ $\mu_4-\eta^1:\eta^2:\eta^1:\eta^2-$ (CH₃C(O))CC}] (4a). In addition, adding one equivalent of Ru₃(CO)₁₂ or 4 in 4a in toluene at 90 °C did not give any new ruthenium clusters after 2 h under stirring. The molecular structure of compound 4a has been established by X-ray crystallography and depicted in Fig. 4. The molecular structure of 4a consists of an octahedral arrangement of four ruthenium atoms and two carbon atoms, with Ru-Ru bond distances being in the range of 2.7235(5)–2.8068(8) Å. In addition, the distance between C3 and C4 is 1.4771(4) Å, which is elongated significantly, falling between the typical C-C single bond and double bond.¹⁵ The alkyne ligand coordinates with Ru1 and Ru4 in a η^1 mode, but with Ru2 and Ru3 in a η^2 mode. The Ru–C bond distances in the octahedron fall in the range of



Fig. 4 ORTEP view of cluster **4a** showing 50% ellipsoids. Selected bond lengths (Å) and bond angles (°): Ru1–Ru2 = 2.7734(5); Ru1–Ru3 = 2.7235(5); Ru1–Ru4 = 2.8068(8); Ru2–Ru4 = 2.7359(5); Ru3–Ru4 = 2.7756(6); Ru1–C3 = 2.1354(5); Ru2–C3 = 2.1752(6); Ru2–C4 = 2.1885(5); Ru3–C3 = 2.1863(5); Ru3–C4 = 2.1792(5); Ru4–C4 = 2.1249(6); C3–C4 = 1.4771(14); C2–C3 = 1.5114(4); C2–O1 = 1.2090(3); Ru3–Ru3–C4 = 39.552(7)°; and Ru1–C39–Ru2 = 89.885(7)°.

2.1752(6)–2.1885(5) Å, reflecting the interactions between the Ru atoms and the alkyne ligands. The dihedral angles between C3–C4–Ru4–Ru1_{plane} and C3–Ru3–C4_{plane}, C3–Ru2–C4_{plane} are 70.880° and 71.117°, respectively. M. I. Bruce and co-workers synthesized the cluster $Ru_4(\mu_4$ -PhC₂CCPh)(CO)₁₂, which is similar in structure to **4a**, by the reaction of more active $Ru_3(CO)_{10}$ (MeCN)₂ and PhC₂C₂Ph.¹⁶ Although the reactivity of $Ru_3(CO)_{12}$ is usually lower than that of $Ru_3(CO)_{10}$ (MeCN)₂, the easy loss of the terminal H atom of the C–C triple bond improves the reactivity of **4**.

The reaction of dimethyl acetylenedicarboxylate (5) with $Ru_3(CO)_{12}$

The reaction of Ru₃(CO)₁₂ with dimethyl acetylenedicarboxylate (5) in a molar ratio of 1:3 in toluene at 90 °C for 30 min in a nitrogen atmosphere afforded [Ru(CO)₄{ μ_2 - η^1 : η^1 -(CH₃OC(O))CC-(C(O)OCH₃)Ru(CO)₄}] (5a) *via* the binding of the C=C bond and the ruthenium dimer. The crystal structure of 5a (Fig. 5) exhibits a binuclear ruthenium skeleton, with each Ru atom binding with four terminal carbonyls and the Ru–Ru bond distance being 2.8850(9) Å. The coordination of the alkynyl ketone (5) with Ru1 and Ru2 is in a η^1 : η^1 mode. The distance of Ru1–C3 is 2.1330(6) Å, and the C3–C3A bond length is 1.3308(4) Å, which is between the typical C–C double bond and triple bond.¹⁵

When the reaction time of the above reaction was prolonged from 0.5 h to 2 h, **5b**, a cyclotrimerization product of **5**, was separated. The structure of **5b** is illustrated in Fig. 6. The isolation of **5b** demonstrated that the reaction of $\text{Ru}_3(\text{CO})_{12}$ and **5** afforded a structurally similar cyclotrimerization compound to those we reported previously.¹²

To clarify the formation process of the products at each step, the reaction of $Ru_3(CO)_{12}$ with dimethyl acetylenedicarboxylate (5) was studied in detail and monitored by the TLC technique. It was observed that **5a** was isolated as the main product when the



Fig. 5 ORTEP view of cluster **5a** showing 50% ellipsoids. Selected bond lengths (Å) and bond angles (°): Ru1–Ru1A = 2.8850(9); Ru1–C3A = 2.1330(6); Ru1–C3 = 2.1330(6); C3–C3A = 1.3308(4); C2A–C3A = 1.4892(3); C2A–O2A = 1.2064(4); C2A–O1A = 1.3481(3); C2–C3 = 1.4892(3); C2–O2 = 1.2064(4); and C2–O1 = 1.3481(3).



Fig. 6 ORTEP view of cluster **5b** showing 50% ellipsoids. Selected bond lengths (Å) and bond angles (°): C1-C2 = 1.3932(4); C2-C3 = 1.3952(3); C3-C4 = 1.3998(5); C4-C5 = 1.3899(4); C5-C6 = 1.3935(3); C1-C7 = 1.5021(4); C2-C9 = 1.5048(5); C3-C11 = 1.4989(4); C4-C13 = 1.5088(4); C5-C15 = 1.5023(5); C6-C17 = 1.5016(4); C7-O1 = 1.2024(3); C7-O2 = 1.3269(4); C9-O3 = 1.1951(3); C9-O4 = 1.3286(4); C11-O5 = 1.1979(3); C11-O6 = 1.3249(7); C13-O7 = 1.1998(4); C13-O8 = 1.3248(4); C15-O9 = 1.2015(3); C15-O10 = 1.3280(4); C17-O11 = 1.2019(3); and C17-O12 = 1.3232(4).

reaction was performed at 90 °C for 30 min in a nitrogen atmosphere. The mixing of **5a** with $Ru_3(CO)_{12}$ in toluene did not give any new ruthenium clusters, however. By adding two equivalents of **5** in the cluster **5a** in toluene at 90 °C, a cyclotrimerization product **5b** was obtained. The formation of **5b** by the reaction of **5a** with **5** confirmed that **5a** is a key intermediate in the generation of **5b**.

Transformation process from 1,3-ynones to products

The reactions of Ru₃(CO)₁₂ and alkyne derivatives have been well researched,⁸⁻¹² and the electronic and steric effects of the substituents of the alkynes were also investigated in detail by T. Takahashi,¹¹ and the results showed that substituents of the alkynes direct, to some degree, the formation and conversion of the intermediate products. We have also found a similar tendency in the reactions of Ru₃(CO)₁₂ and 1,3-ynones.¹² We previously paid much attention to the reactions of $Ru_3(CO)_{12}$ with 1,3-ynones containing aromatic substituents, which are usually electron withdrawing groups. For gaining insight into the effects of electron donating groups on the product distribution and molecular structures of the isolated clusters during the reactions of 1,3-ynones with $Ru_3(CO)_{12}$, the reactions of Ru₃(CO)₁₂ with 1,3-ynones (1-3) were investigated in detail and their reaction courses were traced by the TLC technique. Experimental results showed that the reaction processes in the formation of 1a-3a were similar to those we reported earlier.12 However, it was found that different substituents in the 1,3-vnones led to divergent product distribution in the reaction processes. For example, the larger steric hindrance of the substituents in 3 results in the formation of 3c as the unique CO-inserted product in the reaction of 3 with $Ru_3(CO)_{12}$. And, according to the explanations of T. Takahashi,¹¹ the larger steric hindrance and the electron-withdrawing property of the phenyl ring in 2 exert 2b as the unique CO-inserted product in the reaction of 2 with $Ru_3(CO)_{12}$.

4a is the unique product in the reaction of 3-butyn-2-one 4 with $Ru_3(CO)_{12}$. However, the reaction of FPC \equiv C–H (FP = (η^5 -C₅H₅)-Fe(CO)₂) and Ru₃(CO)₁₂ afforded a triruthenium cluster Ru₃(CO)₉- $[\mu_3-\eta^1:\eta^2:\eta^2-C\equiv C-FP]$, which is different in structure from 4a.¹⁷ Concerning the structural difference between the two ruthenium clusters whilst both precursors are terminal alkynes, we consider that although the loss of the terminal hydrogen atom improves the reactivity of $C \equiv C$ bonds in both alkynes, the weak influence of the FP group in FPC=C-H induces it to strongly coordinate with a ruthenium atom of $Ru_3(CO)_{12}$ in a η^1 mode, and then its $C \equiv C$ bond interacts further with the other two ruthenium atoms of the $Ru_3(CO)_{12}$ molecule in a η^2 mode to finish the formation of the triruthenium carbonyl cluster. Meanwhile, besides activating the $C \equiv C$ bond of 3-butyn-2-one by its terminal hydrogen atom, the electron-withdrawing property of the carbonyl group of 3-butyn-2-one promotes electron movement towards the carbonyl side of the triple bond. Thus an unstable triruthenium intermediate is probably generated by the coordination of the triple bond with the $Ru_3(CO)_{12}$ molecule, and the C \equiv C bond interacts further with a ruthenium atom of another Ru₃(CO)₁₂ molecule or a $Ru(CO)_5$ molecule produced by the decomposition of $Ru_3(CO)_{12}$,¹⁸ in a η^2 mode to generate the tetranuclear ruthenium carbonyl cluster 4a. Thus, both the high reactivity of the terminal hydrogen atom and the electron-withdrawing property of the carbonyl group in 3-butyn-2-one favor the formation of 4a.

The reaction of $\text{Ru}_3(\text{CO})_{12}$ with acetylenedicarboxylate 5 afforded a binuclear cluster **5a** and a cyclotrimerization product **5b**. **5b** can be detected after adding 5 in the cluster **5a** in toluene at 90 °C. Unlike the structure of the triruthenium clusters we reported previously, 5a is a binuclear ruthenium cluster.¹² We speculate that the electron-withdrawing property of the carbonyl group in 5 makes a great contribution to the formation of 5a and 5b. Because 5 is a symmetric molecule with two electron-withdrawing acetyl groups at the two sides of the $C \equiv C$ bond, they make the electrons shift towards the carbonyl groups from the $C \equiv C$ unit, thus helping coordination of the $C \equiv C$ bond with two ruthenium atoms of the Ru₃(CO)₁₂ molecule in a $\eta^1:\eta^1$ mode, and the $C \equiv C$ bond has therefore no ability to interact with another ruthenium atom of the Ru₃(CO)₁₂ molecule to complete the formation of a triruthenium cluster or to couple with another alkynyl molecule to generate an usual stable ruthenole. In this situation, an unstable metallacyclopentadienyl-containing intermediate might be formed initially, and then the unstable intermediate reacts quickly with another 5 molecule to produce 5b. Therefore, 5a is an intermediate in the formation of 5b.

Experimental

General procedures

All manipulations were carried out using standard Schlenk, and the solvents were purified, dried and distilled in a nitrogen atmosphere prior to use. Preparative TLC was performed on 20×20 cm glass plates coated with silica gel (Merck GF254, 0.5 mm thick). FT-IR spectra were recorded on a Bruker Tensor 27 Fourier-transform spectrometer. ¹H and ¹³C{¹H} MMR spectra were performed on a Bruker Avance 400 MHz spectrometer. ESI-mass spectra were recorded on a Thermo Deca Max (LCMS) mass spectra were recorded in the ESI mode on a Waters UPLC-Q-TOF mass spectrometer. Elemental analyses were performed by using a Vario EL III Elemental Analyzer. The structural measurements of single crystals were carried out with a Bruker SMART APEX-II CCD detector.

Synthesis

1,3-Diphenylprop-2-yn-1-one (1), 1-(2-chloro-phenyl)-3-phenylprop-2yn-1-one (2), 1-(4-nitro-phenyl)-3-phenylprop-2-yn-1-one (3), 1-(2-amino-phenyl)-3-phenylprop-2-yn-1-one (4) and 2-(3-phenylpropioloyl)phenylacetate (5) were used to react with Ru₃(CO)₁₂, respectively. In order to get an optimum reaction condition for the reactions of 1–5 with Ru₃(CO)₁₂, influences of the molar ratio of Ru₃(CO)₁₂ to 1–5 (1:1–1:5), reaction time (20 min–3 h) and reaction temperature (60–110 °C) were investigated. The reaction of 1 with Ru₃(CO)₁₂ was taken as an example. It was found that the optimum molar ratio, reaction temperature and reaction time are 1:2, 90 °C and 1 h, respectively. Their detailed synthetic procedures are described as follows.

3-Hexyn-2-one (1) (0.0577 g, 0.6 mmol) and $Ru_3(CO)_{12}$ (0.1918 g, 0.3 mmol) were added to 15 mL toluene and heated at 90 °C for 1 h, until the reaction solution changed from red to red-brown. The red-brown solution was cooled to room temperature and the unreacted orange-red $Ru_3(CO)_{12}$ was precipitated and recovered (0.0493 g 0.0771 mmol). The residue was chromatographed by a chromatographic column (457 mm

length and 26 mm internal diameter) on silica gel with dichloromethane and petroleum ether, and the main products were eluted in the order of **1a**, **1b** and **1c**, with the eluents being dichloromethane/petroleum ether (v/v) 1:10, 1:4 and 1:3, respectively. And then the products were recrystallized by dichloromethane and hexane. The yields of the products were calculated based on the $Ru_3(CO)_{12}$ added at the beginning of a reaction.

[Ru(CO)₃{ $\mu_4-\eta^{1:}\eta^{2:}\eta^{1:}\eta^{1}$ (MeC(O))CC(Et)C(MeC(O))C(Et)Ru(CO)₃}] (1a). Yield: 21% (0.0354 g, 0.063 mmol). FT-IR (KBr, cm⁻¹): 2976 m, 2937 m, 2879 m, 2088 vs, 2057 vs, 2014 vs, 1675 s. ¹H NMR (400 MHz, CDCl₃) δ 2.40–2.58 (m, 4H, CH₂, CH₃), 2.34–2.17 (m, 6H, CH₃), 1.11–1.20 (m, 6H, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 205.02 (CO), 204.86 (CO), 201.78 (CO), 196.08 (CO), 195.39 (CO), 194.95 (CO), 194.82 (CO), 194.74 (CO), 194.43 (CO), 181.99 (CO), 127.86 (C≡C), 122.90 (C≡C), 36.33 (CH₃), 33.06 (CH₃), 29.34 (CH₂), 23.87 (CH₂), 18.88 (CH₃), 16.30 (CH₃). MS (*m*/*z*, ESI⁺), 565.893 (M⁺), 537.896 (M⁺ – CO), 509.901 (M⁺ – 2CO). Anal. calcd for C₁₈H₁₆O₈Ru₂: 565.894. Anal. found: C, 38.35; H, 3.01. C₁₈H₁₆O₈Ru₂ requires: C, 38.44; H, 2.87. M.p.: 139.3–140.5 °C.

[Ru(CO)₃{ μ_2 -η¹:η²: μ_2 -η²:η¹-(MeC(O))CC(Et)C(O)C(Et)C(MeC-(O))Ru(CO)₃]] (1b). Yield: 21% (0.0378 g, 0.064 mmol). FT-IR (KBr, cm⁻¹): 2970 m, 2933 m, 2877 m, 2852 m, 2096 vs, 2034 vs, 1967 vs, 1774 s, 1674 s. ¹H NMR (400 MHz, CDCl₃) δ 2.02–2.64 (m, 10H, CH₂, CH₃), 1.06–1.26 (m, 6H, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 199.52 (CO), 196.70 (CO), 192.06 (CO), 173.52 (CO), 110.96 (C=C), 106.33 (C=C), 53.43 (CH₃) 31.38 (CH₂), 30.38 (CH₂), 20.35 (CH₂), 17.34 (CH₃), 16.16 (CH₃). MS (*m*/*z*, ESI⁺), 593.885 (M⁺), 537.892 (M⁺ – 2CO). Anal. calcd for C₁₉H₁₆O₉Ru₂: 593.889. Anal. found: C, 38.53; H, 2.80. C₁₉H₁₆O₉Ru₂ requires: C, 38.65; H, 2.73. M.p.: 136.7 °C (dec.).

[Ru(CO)₃{ μ_2 -η¹:η²: μ_2 -η²:η¹-(MeC(O))CC(Et)C(O)C(MeC(O))-C(Et)Ru(CO)₃}] (1c). Yield: 23% (0.0407 g, 0.069 mmol). FT-IR (KBr, cm⁻¹): 2969 m, 2922 m, 2850 m, 2100 vs, 2073 vs, 2026 vs, 1676 s. ¹H NMR (400 MHz, CDCl₃) δ 2.32-2.59 (m, 10H, CH₂, CH₃), 1.24-1.28 (s, 6H, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 202.80 (CO), 201.93 (CO), 200.12 (CO), 196.62 (CO), 191.93 (CO), 191.77 (CO), 176.49 (CO), 105.42 (C \equiv C), 98.15 (C \equiv C), 43.17 (CH₃), 31.40 (CH₃), 28.24 (CH₂), 25.99 (CH₂), 20.37 (CH₃), 15.20 (CH₃). MS (*m*/*z*, ESI⁺), 593.886 (M⁺). Anal. calcd for C₁₉H₁₆O₉Ru₂: 593.889. Anal. found: C, 38.51; H, 2.83. C₁₉H₁₆O₉Ru₂ requires: C, 38.65; H, 2.73. M.p.: 135.2 °C (dec.).

[Ru(CO)₃{μ₄-η¹:η²:η¹:η¹-(MeC(O))CC(Ph)C(MeC(O))C(Ph)-Ru(CO)₃]] (2a). 4-Phenyl-3-butyn-2-one (2) (0.0865 g, 0.6 mmol) was used instead of 3-hexyn-2-one (1) to react with Ru₃(CO)₁₂ (0.1918 g, 0.3 mmol) and a similar synthetic procedure was used. The isolated unreacted orange-red Ru₃(CO)₁₂ was 0.0578 g (0.0904 mmol) and the main products 2a and 2b were eluted using 1:6 and 1:5 (v/v) dichloromethane/petroleum ether as eluents, respectively. Yield for 2a: 22% (0.0441 g, 0.067 mmol). FT-IR (KBr, cm⁻¹): 2954 m, 2923 s, 2852 m, 2089 vs, 2058 vs, 2026 vs, 1995 vs, 1967 vs, 1708 m, 1676 m. ¹H NMR (400 MHz, CDCl₃) δ 7.18–7.34 (m, 8H, C₆H₅), 6.96 (S, 2H, C₆H₅), 1.91 (S, 3H, CH₃), 1.84 (S, 3H, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 204.23 (CO), 199.47 (CO), 195.39 (CO), 195.10 (CO), 194.19 (CO), 194.12 (CO), 177.81(C≡C), 146.29 (C≡C), 134.93 (Ph), 133.54 (Ph), 130.30 (Ph), 129.02 (Ph), 128.77 (Ph), 128.20 (Ph), 127.76 (Ph), 122.36 (Ph), 31.61 (CH₃), 28.25 (CH₃). MS (m/z, ESI⁺), 661.892 (M⁺). Anal. calcd for C₂₆H₁₆O₈Ru₂: 661.894. Anal. found: C, 47.37; H, 2.56. C₂₆H₁₆O₈Ru₂ requires: C, 47.42; H, 2.45. M.p.: 143.2–144.8 °C.

[Ru(CO)₃{μ₃-η¹:η²:μ₃-η²:η¹-(MeC(O))CC(Ph)C(O)C(Ph)C(MeC(O))-Ru(CO)₃]] (2b). Yield: 29% (0.0597 g, 0.087 mmol). FT-IR (KBr, cm⁻¹): 2921 vs, 2852 s, 2092 s, 2059 vs, 2018 vs, 1681 m. ¹H NMR (400 MHz, CDCl₃) δ 6.89–7.11 (m, 10H, C₆H₅), 1.90–1.96 (d, 6H, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ = 195.03 (CO), 194.23 (CO), 193.76 (CO), 169.14 (C=C), 163.94 (C=C), 131.08 (Ph), 130.02 (Ph), 128.69 (Ph), 128.28 (Ph), 29.33. (CH₃). MS (m/z, ESI⁺), 689.887 (M⁺), 661.892 (M⁺ – CO). Anal. calcd for C₂₇H₁₆O₉Ru₂: 689.889. Anal. found: C, 47.10; H, 2.44. C₂₇H₁₆O₉Ru₂ requires: C, 47.23; H, 2.35. M.p.: 139.5 °C (dec.).

 $[Ru(CO)_{3}{\mu_{4}-\eta^{1}:\eta^{2}:\eta^{1}:\eta^{1}-(PhC(O))CC(n-hexyl)C(PhC(O))C(n-hexyl)C(PhC(O$ hexyl)Ru(CO)₃] (3a). 1-Phenyl-3-hexyl-2-yn-1-one (3) (0.1286 g, 0.6 mmol) was used instead of 3-hexyn-2-one (1) to react with Ru₃(CO)₁₂ (0.1918 g, 0.3 mmol) and a similar synthetic procedure was employed. The isolated unreacted orange-red Ru₃(CO)₁₂ was 0.0592 g (0.0926 mmol) and the main products 3a and 3c were eluted using 1:5 and 1:4 (v/v) dichloromethane/petroleum ether as eluents, respectively. Yield for 3a: 31% (0.0743 g, 0.093 mmol). FT-IR (KBr, cm⁻¹): 3062 w, 2955 vs, 2924 vs, 2854 vs, 2087 s, 2060 vs, 2021 vs, 1981 s, 1671 s. ¹H NMR (400 MHz, CDCl₃) δ 7.31-8.05 (m, 10H, C₆H₅), 2.10-2.56 (m, 4H, CH₂), 1.08-1.26 (m, 16H, CH₂), 0.77–0.87 (m, 6H, CH₃). ${}^{13}C{}^{1}H$ NMR (101 MHz, $CDCl_3$) δ 197.36, 194.69, 194.26 (CO), 171.47 (C \equiv C), 168.00 (C≡C), 134.95 (Ph), 133.96 (Ph), 133.08 (Ph), 132.33 (Ph), 129.96 (Ph), 128.33 (Ph), 123.60 (Ph), 121.81 (Ph), 33.06 (CH₂), 31.95 (CH₂), 31.17 (CH₂), 31.00 (CH₂), 29.72 (CH₂), 29.68 (CH₂), 22.43 (CH₂), 22.25 (CH₂), 13.98 (CH₃), 13.89 (CH₃). MS (m/z, ESI⁺), 802.050 (M⁺). Anal. calcd for C₃₆H₃₆O₈Ru₂: 802.051. Anal. found: C, 53.97; H, 4.62. C₃₆H₃₆O₈Ru₂ requires: C, 54.13; H, 4.54. M.p.: 146.1–147.5 °C.

[Ru(CO)₃{μ₂-η¹:η²:μ₂-η²:η¹-{PhC(O)}CC(*n*-hexyl)C(O)C(PhC(O))C-(*n*-hexyl)Ru(CO)₃}] (3c). Yield: 27% (0.0678 g, 0.082 mmol). FT-IR (KBr, cm⁻¹): 3065 w, 2955 vs, 2927 vs, 2857 vs, 2086 vs, 2054 vs, 2023 vs, 1971 vs, 1673 m, 1649 m. ¹H NMR (400 MHz, CDCl₃) δ 7.45-8.15 (m, 10H, C₆H₅), 2.07-2.52 (m, 4H, CH₂), 1.17-1.50 (m, 16H, CH₂), 0.69-0.76 (m, 6H, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 197.00 (CO), 196.29 (CO), 196.16 (CO), 195.04 (CO), 194.83 (CO), 194.11 (CO), 179.57 (C=C), 169.45 (C=C), 135.15 (Ph), 134.51 (Ph), 133.86 (Ph), 132.95 (Ph), 129.69 (Ph), 128.94 (Ph), 128.36 (Ph), 126.55 (Ph), 34.06 (CH₂), 32.24 (CH₂), 31.02 (CH₂), 30.56 (CH₂), 29.71 (CH₂), 29.23 (CH₃), 13.74 (CH₃). MS (*m*/*z*, ESI⁺), 825.042 (M⁺), 797.051 (M⁺ – CO). Anal. calcd for C₃₇H₃₆O₉Ru₂: 825.046. Anal. found: C, 53.69; H, 2.53. C₃₇H₃₆O₉Ru₂ requires: C, 53.75; H, 4.39. M.p.: 141.5 °C (dec.).

[Ru₄(CO)₁₂{μ₄-η¹:η²:η¹:η²-(CH₃C(O))CC}] (4a). 3-Butyn-2-one (4) (0.0204 g, 0.3 mmol) was used instead of 3-hexyn-2-one (1) to react with Ru₃(CO)₁₂ (0.1918 g, 0.3 mmol) and the synthetic process was similar. The isolated unreacted orange-red Ru₃(CO)₁₂ was 0.0978 g (0.153 mmol) and the main product 4a was eluted using 1:8 (v/v) dichloromethane/petroleum ether as eluent. Yield: 31% (0.0759 g, 0.094 mmol). FT-IR (KBr, cm⁻¹): 3057 w, 2918 m, 2852 w, 2080 vs, 2030 vs, 2003 vs, 1672 w. ¹H NMR (400 MHz, CDCl₃) δ 3.49 (s, 3H, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 196.85 (CO), 190.45 (CO), 50.89 (C=C), 29.69 (C=C), 26.05 (CH₃). MS (*m*/*z*, ESI⁺), 809.579 (M⁺). Anal. calcd for C₁₆H₃O₁₃Ru₄: 809.577. Anal. found: C, 23.67; H, 0.51. C₁₆H₃O₁₃Ru₄ requires: C, 23.80; H, 0.37. M.p.: 157.6 °C (dec.).

 $[Ru(CO)_{4}\{\mu-\eta^{2}-(CH_{3}OC(O))CC(C(O)OCH_{3})Ru(CO)_{4}\}]$ (5a). Dimethyl acetylenedicarboxylate (5) (0.1279 g, 0.9 mmol) was used instead of 3-hexyn-2-one (1) to react with $Ru_3(CO)_{12}$ (0.1918 g, 0.3 mmol) and the synthetic process was similar. The isolated unreacted orange-red $Ru_3(CO)_{12}$ was 0.0846 g (0.1323 mmol) and the main products 5a and 5b were eluted using 1:10 and 1:2 (v/v) dichloromethane/petroleum ether as eluents, respectively. Yield for 5a: 21% (0.0358 g, 0.063 mmol). FT-IR (KBr, cm⁻¹): 3011 w, 2956 w, 2921 w, 2852 w, 2107 s, 2080 vs, 2053 vs, 2005 s, 1732 s, 1697 s. ¹H NMR (400 MHz, CDCl₃) δ 3.86 (s, 3H, CH₃), 3.70 (s, 3H, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 192.51 (CO), 192.34 (CO), 191.74 (CO), 172.47 (CO), 164.35 (CO), 117.50 (C \equiv C), 53.56 (CH₃), 52.58 (CH₃). MS $(m/z, ESI^{+})$, 566.798 (M⁺), 528.797 (M⁺ – CO). Anal. calcd for C14H6O12Ru2: 566.796. Anal. found: C, 29.46; H, 1.15. C14H6O12Ru2 requires: C, 29.59; H, 1.06. M.p.: 137.3 °C (dec.).

Benzene-1,2,3,4,5,6-hexacarboxylic acid hexamethyl ester (5b). Yield: 64% (0.0822 g, 0.193 mmol). FT-IR (KBr, cm⁻¹): 3013 w, 2958 m, 2918 w, 2851 w, 1736 νs. ¹H NMR (400 MHz, CDCl₃) δ 3.88 (s, 18H, CH₃). ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 165.14 (CO), 133.90 (C=C), 53.48 (CH₃). MS (*m*/*z*, ESI⁺), 426.083 (M⁺). Anal. calcd for $C_{18}H_{18}O_{12}$: 426.080. Anal. found: C, 50.63; H, 4.38. $C_{18}H_{18}O_{12}$ requires: C, 50.71; H, 4.26. M.p.: 188.6–190.5 °C.

Crystallography

The structural measurements were carried out with a Bruker D8 QUEST with a Photo 100 CMOS detector using a graphite monochromated MoK radiation ($\lambda = 0.71073$). The structure was solved by direct methods (SHELXS-2014/97) and refined by full-matrix least squares against F^2 using SHELXL-2014 and SHELXL-97 software.¹⁹ Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and refined using a riding model.

The single crystals of compounds **1a**, **1c**, **2a**, **2b**, **3c**, **4a**, **5a** and **5b** suitable for single crystal X-ray diffraction were successfully grown from their dichloromethane/hexane solutions after slow evaporation at 0 °C. Relevant crystallographic data are given in Table 1. The crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre: 1865423 (1a), 1865427 (1c), 1865428 (2a), 1865429 (2b), 1865430 (3c), 1865433 (4a), 1865431 (5a) and 1865432 (**5b**).†

Conclusions

We isolated a series of new ruthenium clusters and a cyclotrimerization product by investigating the reactions of five 1,3-ynones with $Ru_3(CO)_{12}$. The activation of the 1,3-ynones and the transformation of the cluster skeletons suggested that the diverse alkyl groups in the 1,3-ynones leads to the difference in their reactivities during their reactions with $Ru_3(CO)_{12}$. More importantly, we revealed that the product distribution of the CO-inserted binuclear ruthenium clusters is dependent strongly on both the electronic and steric effects of the substituents of the acetylenic ketones, and considered that the high reactivity of the terminal H atom and the electronwithdrawing property of the carbonyl group in 3-butyn-2-one are responsible for the formation of 4a. Besides, we found that 5a is an intermediate in the formation of the cyclotrimerization product 5b, implying that cyclotrimerization of a 1,3-ynone undergoes probably a complicated transformation process or one of two transformation processes, in which a triruthenium cluster, a biruthenium cluster and/or a ruthenole are formed as intermediates.

Conflicts of interest

No conflicts of interest to declare.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (21401124, 21171112).

Notes and references

- (a) A. Lennartson, A. Lundin, K. Boerjesson, V. Gray and K. Moth-Poulsen, *Dalton Trans.*, 2016, 45, 8740; (b) F. Xie, M. Zhang, H. Jiang, M. Chen, W. Lv, A. Zheng and X. Jian, *Green Chem.*, 2015, 17, 279; (c) M. Chen, M. Zhang, B. Xiong, Z. Tan, W. Lv and H. Jiang, *Org. Lett.*, 2014, 16, 6028; (d) L. Wang and L. Ackermann, *Chem. Commun.*, 2014, 50, 1083; (e) D. C. Schmitt, J. Lee, A. R. Dechert-Schmitt, E. Yamaguchi and M. J. Krische, *Chem. Commun.*, 2013, 49, 6096; (f) T. C. Johnson, W. G. Totty and M. Wills, *Org. Lett.*, 2012, 14, 5230; (g) J. A. Cabeza, I. del Rio, E. Perez-Carreno and V. Pruneda, *Organometallics*, 2011, 30, 1148.
- 2 (a) J. Liu, C. Kubis, R. Franke, R. Jackstell and M. Beller, ACS Catal., 2016, 6, 907; (b) Z. Fan, J. Ni and A. Zhang, J. Am. Chem. Soc., 2016, 138, 8470; (c) N. Armanino, M. Lafrance and E. M. Carreira, Org. Lett., 2014, 16, 572; (d) Y. Yuki, K. Takahashi, Y. Tanaka and K. Nozaki, J. Am. Chem. Soc., 2013, 135, 17393; (e) S. T. Tan, J. W. Kee and W. Y. Fan, Organometallics, 2011, 30, 4008; (f) X. Guo and C. J. Li, Org. Lett., 2011, 13, 4977.
- 3 (a) W. Li, X. Huang and J. You, Org. Lett., 2016, 18, 666;
 (b) A. Saxena, F. Perez and M. J. Krische, Angew. Chem., Int. Ed., 2016, 55, 1493; (c) A. Saxena, F. Perez and M. J. Krische, J. Am. Chem. Soc., 2015, 137, 5883; (d) W. J. Park, C. H. Lee, D. S. Kim and C. H. Jun, Chem. Commun., 2015, 51, 14667;
 (e) B. Y. Park, T. Luong, H. Sato and M. J. Krische, J. Am. Chem. Soc., 2015, 137, 7652; (f) B. Li, Y. Park and S. Chang, J. Am. Chem. Soc., 2014, 136, 1125; (g) B. Y. Park, T. P. Montgomery,

H. J. Garza and M. J. Krische, *J. Am. Chem. Soc.*, 2013, 135, 16320;
(*h*) L. Wu, I. Fleischer, R. Jackstell and M. Beller, *J. Am. Chem. Soc.*, 2013, 135, 3989;
(*i*) K. Takahashi, M. Yamashita and K. Nozaki, *J. Am. Chem. Soc.*, 2012, 134, 18746;
(*j*) M. Nishiumi, H. Miura, K. Wada, S. Hosokawa and M. Inoue, *Adv. Synth. Catal.*, 2010, 352, 3045.

- 4 (a) A. K. Clarke, J. M. Lynam, R. J. K. Taylor and W. P. Unsworth, ACS Catal., 2018, 8, 6844; (b) A. K. Clarke, M. J. James, P. ÓBrien, R. J. K. Taylor and W. P. Unsworth, Angew. Chem., Int. Ed., 2016, 55, 13798; (c) J. T. R. Liddon, M. J. James, A. K. Clarke, P. ÓBrien, R. J. K. Taylor and W. P. Unsworth, Chem. Eur. J., 2016, 22, 8777; (d) C. S. Yi, S. Y. Yun and I. A. Guzei, J. Am. Chem. Soc., 2005, 127, 5782; (e) C. S. Yi and S. Y. Yun, J. Am. Chem. Soc., 2005, 127, 17000.
- 5 (a) H. Sato, M. Bender, W. J. Chen and M. J. Krische, J. Am. Chem. Soc., 2016, 138, 16244; (b) C. S. Chen, Y. F. Lin and W. Y. Yeh, Chem. – Eur. J., 2014, 20, 936; (c) J. P. Hopewell, J. E. D. Martins, T. C. Johnson, J. Godfrey and M. Wills, Org. Biomol. Chem., 2012, 10, 134; (d) M. Kawatsura, M. Yamamoto, J. Namioka, K. Kajita, T. Hirakawa and T. Itoh, Org. Lett., 2011, 13, 1001; (e) S. V. Osintseva, F. M. Dolgushin, N. A. Shtel'tser, P. V. Petrovskii, A. S. Peregudov, A. Z. Kreindlin and M. Y. Antipin, Organometallics, 2010, 29, 1012.
- 6 (a) C. E. Ellul, J. P. Lowe, M. F. Mahon, P. R. Raithby and M. K. Whittlesey, *Dalton Trans.*, 2018, 47, 4518; (b) J. Yan, Z. Han, D. Zhang and C. Liu, *RSC Adv.*, 2016, 6, 99625; (c) J. A. Cabeza, M. Damonte, P. García-Álvarez, M. G. Hernández-Cruz and A. R. Kennedy, *Organometallics*, 2012, 31, 327; (d) J. A. Cabeza, M. Damonte and E. Pérez-Carreño, *Organometallics*, 2012, 31, 8355; (e) P. Ghosh, P. J. Fagan, W. J. Marshall, E. Hauptman and R. M. Bullock, *Inorg. Chem.*, 2009, 48, 6490; (f) K. Xu, B. Li, S. Xu, H. Song and B. Wang, *Organometallics*, 2009, 28, 4438; (g) S. Ngubane, M. Hakansson, S. Jagner, J. R. Moss and A. Sivaramakrishna, *J. Organomet. Chem.*, 2008, 693, 343; (h) T. Takao, M. Moriya and H. Suzuki, *Organometallics*, 2008, 27, 1044.
- 7 (a) C. S. Chen, Y. F. Lin and W. Y. Yeh, *Chem. Eur. J.*, 2014, 20, 936; (b) S. V. Osintseva, F. M. Dolgushin, N. A. Shtel'tser,

P. V. Petrovskii, A. S. Peregudov, A. Z. Kreindlin and M. Y. Antipin, *Organometallics*, 2010, **29**, 1012.

- 8 (a) P. Mathur, D. K. Rai, R. K. Joshi, B. Jha and S. M. Mobin, Organometallics, 2014, 33, 3857; (b) M. Li, H. Song, S. Xu and B. Wang, Organometallics, 2010, 29, 6092; (c) O. F. Koentjoro, P. J. Low, R. Rousseau, C. Nervi, D. S. Yufit, J. A. K. Howard and K. A. Udachin, Organometallics, 2005, 24, 1284; (d) Y. Yamamoto, Y. Miyabe and K. Itoh, Eur. J. Inorg. Chem., 2004, 3651; (e) P. J. Low, K. A. Udachin, G. D. Enright and A. J. Carty, J. Organomet. Chem., 1999, 578, 103.
- 9 P. J. Low, G. D. Enright and A. J. Carty, J. Organomet. Chem., 1998, 565, 279.
- 10 P. Mathur, A. Das, S. Chatterjee and S. M. Mobin, J. Organomet. Chem., 2008, 693, 1919.
- 11 T. Takahashi, Z. Xi, A. Yamazaki, Y. Liu, K. Nakajima and M. Kotora, *J. Am. Chem. Soc.*, 1998, **120**, 1672.
- 12 (a) L. Xu, S. S. Li, L. P. Jiang, G. F. Zhang, W. Q. Zhang and Z. W. Gao, *RSC Adv.*, 2018, 8, 4354; (b) L. Xu, L. P. Jiang, S. S. Li, G. F. Zhang, W. Q. Zhang and Z. W. Gao, *RSC Adv.*, 2018, 8, 25268; (c) J. D. Yang, W. Q. Zhang, G. F. Zhang and Z. W. Gao, *J. Organomet. Chem.*, 2015, 799, 166; (d) L. Xu, S. S. Li, L. P. Jiang, T. R. Dong, G. F. Zhang, W. Q. Zhang and Z. W. Gao, *Inorg. Chim. Acta*, 2019, 485, 20.
- 13 (a) A. J. Arce, P. Arrojo, A. J. Deeming and Y. De Sanctis, *Dalton Trans.*, 1992, 2423; (b) A. J. Arce, R. Machado, C. Rivas, Y. De Sanctis and A. J. Deeming, *J. Organomet. Chem.*, 1991, **419**, 63.
- 14 A. J. Blake, P. J. Dyson, S. L. Ingham, B. F. G. Johnson and C. M. Martin, *Organometallics*, 1995, 14, 862.
- 15 X. M. Chen and J. W. Cai, *In Single-Crystal Structural Analysis-Principles and Practices*, Science China Press, Beijing, China, 2nd edn, 2004, p. 114.
- 16 M. I. Bruce, N. N. Zaitseva, B. W. Skelton and A. H. White, *Inorg. Chim. Acta*, 1996, **250**, 129.
- 17 M. Akita, S. Sugimoto, H. Hirakawa, S. Kato, M. Terada, M. Tanaka and Y. Morooka, *Organometallics*, 2001, 20, 1555.
- 18 F. Hasanayn, N. H. Nsouli, A. Al-Ayoubi and A. S. Goldman, J. Am. Chem. Soc., 2008, 130, 511.
- 19 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112.