Indian Journal of Chemistry
Vol. 60A, February 2021, pp. 177-184

Revisiting the reactivity of $Ru_3(CO)_{12}$ with PhC≡CPh (diphenylacetylene)-new findings of a thermic effect towards higher nuclearity

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Received 20 October 2020; revised and accepted 02 December 2020

In this paper, we report tri- and tetranuclear ruthenium carbonyl compounds containing PhC≡CPh ligand showing μ_3-η^2, μ_3-η^4, μ_4-η^2 coordination modes. A one-pot reaction between $[Ru_3(CO)_{12}]$ and PhC≡CPh in THF (tetrahydrofuran) at 66 °C has given the new trinuclear compound $[Ru_3(CO)_6(\mu\text{-}CO)_2(\mu_3\text{-}\eta^4\text{-}C_4Ph_4)]$ (**2**) in 30% yield together with the previously reported $[Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)_2]$ (**1**) in 25% yield. Compound **1** converts to **2** under refluxing condition in THF. A similar reaction involving $[Ru_3(CO)_{12}]$ with PhC≡CPh in refluxing benzene (80 °C) afforded previously reported *closo*-tetraruthenium compounds $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)]$ (**3**) and $[Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)_2]$ (**4**) in 25 and 16% yields, respectively, along with **2** in 20% yield. Compounds **1**, **2** and **4** have been characterized by single-crystal X-ray diffraction analysis in addition to IR and ^{1}H NMR spectroscopic methods.

Keywords: Ruthenium clusters, Carbonyls, Diphenylacetylene, Coordination mode, X-ray structures

The chemistry of alkynes coordinated to trimetallic clusters of ruthenium and osmium has been extensively studied due to the unusual transformations which these molecules undergo when they are attached to the cluster core.[1–27] The coordination mode of an alkyne to metal clusters has been shown to depend both on the identity of the metal and the types of substituents present on the alkyne.[2] For instance, the reactions of terminal alkynes, HC≡CR, with trimetallic clusters $[Os_3(CO)_{10}(NCMe)_2]$ give the triply bridging alkyne compounds $[Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-alkyne})]$, which often lead to hydrogen transfer to the metal, affording $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-alkyne})(\mu\text{-}H)]$. The unsaturation resulting from the loss of CO is compensated by oxidative addition with C−H bond cleavage.[21] In contrast, with substituted alkynes of RC≡CR type, either a perpendicular μ_3-$\eta^2(\perp)$ mode or, more commonly, a parallel μ_3-$\eta^2(\|)$ mode of coordination is observed.[2] The perpendicular co-ordination mode of alkyne is found in $[Fe_3(CO)_9(PhC_2Ph)]$,[8] $[Fe_2Ru(CO)_9(RC_2R)]$[9] (R = Et or Ph) and $[Os_3(CO)_9(PhC_2Ph]$[28] while the parallel co-ordination mode is observed in $[M_3(CO)_{10}(RC_2R)]$[10–15] (R = Me, Et, Ph, CO_2H or CO_2Me) and $[M_3(CO)_9(C_8H_8)(\mu\text{-}H)_2]$[16] (M = Ru or Os) and several other heterometallic alkyne compounds[17] (Fig. 1). It thus appears that the perpendicular co-ordination mode is observed in 46-electron unsaturated clusters, and is stabilized by back donation from the metal atoms to alkyne.[29–31] Furthermore, when the back-donation ability is decreased, the alkyne adopts a parallel co-ordination mode and a 48-electron cluster results. Thus, the compound $[Fe_3(CO)_9\{\mu_3\text{-}\eta^2(\perp)\text{-}RC_2R\}]$ (R = Et or Ph) is stable whereas the decreased back donatibility of ruthenium or osmium compared to iron leads to the formation of $[M_3(CO)_{10}\{\mu_3\text{-}\eta^2(\|)\text{-}RC_2R\}]$ (M = Ru or Os). However, the electrochemical addition of two electrons to the 46-electron triiron cluster causes the co-ordination mode of the alkyne to change from perpendicular to parallel in a chemically reversible manner.[32]

A number of other groups have investigated reactions of $[M_3(CO)_{12}]$ [M = Os, Ru] and their phosphine derivatives with alkynes (e.g., acetylene, ethylene, and their derivatives) and have shown to produce a variety of different complexes containing either the cluster-bound alkyne or fortuitous ligands formed by coupling of two or more alkyne molecules. Several crystal structures of the compounds of the type $[M_3(CO)_{10}(\text{alkyne})]$ (M = Ru or Os) and their tertiary phosphine substituted derivatives[33–39] have been reported along with the related ligand dynamics.[40] There are a number of reports on the reactivity of PhC≡CPh with polynuclear transition metal carbonyl complexes. For example, the reaction of $[Ru_3(CO)_{12}]$ with PhC≡CPh was first investigated by Ceteni *et al.*[41] in 1969 and obtained nine compounds but none was structurally characterized. Later they described the crystal structure of

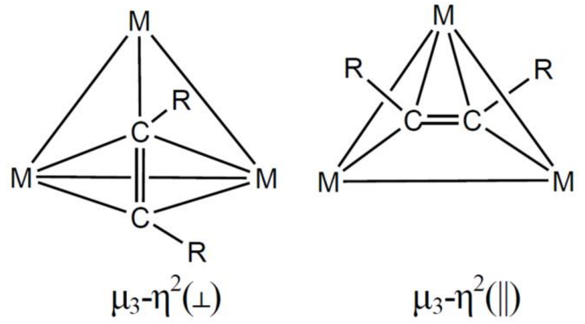


Fig. 1 — Bonding modes of alkynes in trimetallic clusters

$[Ru_3(CO)_9(\mu\text{-}CO)(C_2Ph_2)(\mu\text{-}H)_2]$ being synthesized from reaction of $[Ru_3(CO)_{12}]$ with PhC≡CPh in aqueous methanolic alkali.[42] In 1975, Lewis and Johnson reported the isolation of the tetraruthenium cluster *closo*-$[Ru_4(CO)_{12}(C_2Ph_2)]$ formed upon the reaction of $[Ru_3(CO)_{12}]$ with PhC≡CPh in refluxing hexane,[43] the structure of which was later confirmed by a solid-state structure determination and found to contain a *closo*-Ru_4C_2 unit with the alkyne capping a butterfly arrangement of four ruthenium atoms.[44] A few years later, the tetraruthenium cluster $[Ru_4(CO)_{11}(\mu_4\text{-}C_2Ph_2)_2]$ possessing a *closo*-Ru_4C_4 dodecahedral skeleton as confirmed by X-ray diffraction study, was reported from the Me_3NO initiated reaction between $[Ru_3(CO)_{12}]$ with PhC≡CPh.[45]

These intermittent results intrigued us to revisit the reactions of $[Ru_3(CO)_{12}]$ with diphenylacetylene in different solvent systems at different temperatures in the hope of learning more about the structure and the nuclearity of the products formed. Herein we describe our studies which focused on the characterization of the compounds in our new findings by single-Crystal X-ray diffraction and spectroscopic methods.

Materials and Methods

All reactions were performed under nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Reagent grade solvents were freshly distilled using appropriate drying agents prior to use. Infrared spectra were recorded on a Shimadzu IR Prestige-21 spectrophotometer while NMR spectra were recorded on a on a Bruker Avance III HD (400 MHz) instrument. All chemical shifts are reported in δ units and are referenced to the residual protons of the deuterated solvent. Elemental analyses were performed by Microanalytical Laboratories of Wazed Miah Science Research Centre at Jahangirnagar University. $[Ru_3(CO)_{12}]$ was purchased from Strem Chemicals Inc. and used without further purification. Diphenylacetylene (C_2Ph_2) was purchased from Acros Organics and used as received. Products were separated in air by preparative TLC plates coated with 0.25 mm of silica gel (HF_{254}-type 60, E. Merck, Germany) glass plates.

Reaction of $[Ru_3(CO)_{12}]$ with PhC≡CPh in THF at 66 °C

PhC≡CPh (55 mg, 0.313 mmol) was added to a THF solution (15 mL) of $[Ru_3(CO)_{12}]$ (50 mg, 0.078 mmol) and the solution was heated to reflux (66 °C) for 8 h. The solvent was removed under vacuum and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH_2Cl_2 (8:2, v/v) developed three bands. The first band was unreacted $[Ru_3(CO)_{12}]$ (trace), the second band afforded $[Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)_2]$ (**1**), (17 mg, 25%) as red-violet crystals and the third band gave $[Ru_3(CO)_6(\mu\text{-}CO)_2(\mu_3\text{-}\eta^4\text{-}C_4Ph_4)]$ (**2**) (20 mg, 30%) as yellow crystals after re−Crystallization from hexane/CH_2Cl_2 at −4 °C. Analytical and spectroscopic data for **1**: Anal.(%) Calcd. for $C_{36}H_{20}O_8Ru_3$: C, 48.93; H, 2.28. Found: C, 49.10; H, 2.44. IR (cm^{-1}) (ν(CO), CH_2Cl_2): 2081 m, 2048 vs, 2025 vs,1990 w, 1961 w. ^1H NMR ($CDCl_3$): δ 7.29 (m, 6H), 7.26 (m, 10H), 7.20 (m, 4H). Analytical and spectroscopic data for **2**: Anal. (%) Calcd. for $C_{114}H_{74}O_{24}Ru_9$: C, 50.02; H, 2.72. Found: C, 49.14; H, 2.37. IR (cm^{-1}) (ν(CO), CH_2Cl_2): 2069 s, 2025 s, 1975 s, 1872 m, 1847 m. ^1H NMR ($CDCl_3$): δ 7.39 (m, 4H), 7.18 (m, 2H), 7.12 (m, 4H), 6.87 (m, 6H), 6.24 (m, 4H).

Reaction of $[Ru_3(CO)_{12}]$ with PhC≡CPh in benzene at 80 °C

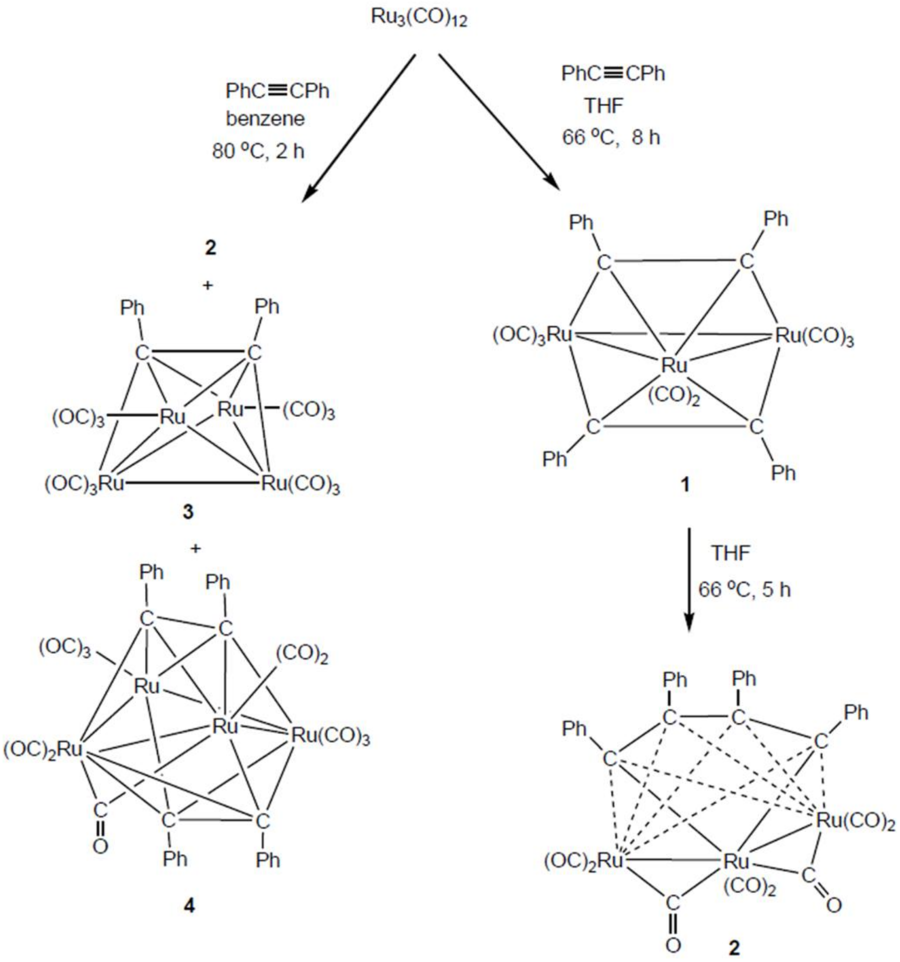
A benzene solution (20 mL) of $[Ru_3(CO)_{12}]$ (50 mg, 0.078 mmol) and diphenylacetylene (55 mg, 0.313 mmol) was heated to reflux for 2 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/CH_2Cl_2 (9:1, v/v) developed three bands which yielded the following compounds in order of elution: **2** (14 mg, 20%), $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)]$ (**3**) (17 mg, 25%), and $[Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)_2]$ (**4**) (13 mg, 16%) as red crystals after recrystallization from hexane/CH_2Cl_2 at −4 °C and an unidentified product (2 mg). Analytical and spectroscopic data for **3**: Anal. (%) Calcd. for $C_{26}H_{10}O_{12}Ru_4$: C, 33.99; H, 1.10. Found: C, 33.89; H, 1.07. IR (cm^{-1}) (ν(CO), CH_2Cl_2): 2092 w, 2067 vs, 2036 vs, 1967 w. ^1H NMR ($CDCl_3$): δ 7.21 (m, 4H), 7.11 (m, 6H). Analytical and spectroscopic data for **4**: Anal. (%) Calcd. for $C_{39}H_{20}O_{11}Ru_4$: C, 43.83; H, 1.89. Found: C, 43.98; H, 1.95. IR (cm^{-1}) (ν(CO), CH_2Cl_2): 2088 m, 2059 s, 2038 vs, 2021 vs, 1975 s, 1818 br. ^1H NMR ($CDCl_3$): δ 6.98 (m, 12H), 6.75 (m, 8H).

X-ray crystallography

Single crystals of **1**, **2** and **4** suitable for X-ray diffraction analysis were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the compounds at –4 °C. Suitable crystals were mounted on a Bruker APEX3 diffractometer using a Nylon loop (MiTeGen, Dual-Thickness) with an inert oil and the diffraction data were collected at different temperatures for different compounds using Mo–Kα radiation (λ = 0.71073 Å). Unit cell determination, data reduction and absorption corrections were carried out using Apex3 v2016.1-0. The structures were solved by direct methods and refined by full-matrix least-squares on the basis of F^2 using SHELXL[46] within the OLEX2[47] graphical user interface. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included using a riding model. Pertinent crystallographic parameters are given in Table 1.

Table 1 — Crystallographic data and structure refinement for **1**, **2** and **4**

Compound	**1**	**2**	**4**
Identification code	CCDC 2034102	CCDC 2034100	CCDC 2034101
Empirical formula	$C_{36}H_{20}O_8Ru_3$	$C_{114}H_{74}O_{24}Ru_9$	$C_{39}H_{20}O_{11}Ru_4$
Formula weight	883.73	2737.36	1068.83
Temperature/K	193.0	193.0	213.0
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	*C2/c*	*C2/c*	*Pbca*
a/Å	38.118(17)	14.680(7)	9.107(9)
b/Å	8.449(4)	11.938(6)	17.688(17)
c/Å	21.810(10)	59.02(3)	45.15(5)
α/°	90	90	90
β/°	114.69(2)	95.747(18)	90
γ/°	90	90	90
Volume/Å^3	6382(5)	10292(8)	7274(13)
Z	8	4	8
ρ_{calc}g/cm^3	1.839	1.767	1.952
μ/mm^{-1}	1.455	1.356	1.691
F(000)	3456.0	5384.0	4144.0
Crystal size/mm^3	0.211 x 0.105 x 0.081	0. 0.211 x 0.118 x 0.071	0.224 x 0.166 x 0.044
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ range for data collection/°	4.782 to 56.79	4.406 to 54.464	4.694 to 54.292
Index ranges	$-50 \le h \ge 50$, $-11 \le k \ge 11$, $-29 \le l \ge 28$	$-18 \le h \ge 18$, $-15 \le k \ge 15$, $-75 \le l \ge 75$	$-11 \le h \ge 11$, $-22 \le k \ge 22$, $-57 \le l \ge 57$
Reflections collected	55471	62406	165160
Independent reflections	7983 (R_{int} = 0.0398, R_{sigma} = 0.0301)	11466 (R_{int} = 0.0598, R_{sigma} = 0.0540)	8062 (R_{int} = 0.1565, R_{sigma} = 0.0599)
Data/restraints/parameters	9342 / 0 / 672	11466 / 0 / 653	8062 / 0 / 488
Goodness-of-fit on F^2	1.018	1.152	1.127
Final R indexes [I>=2σ (I)]	R_1 = 0.0247, wR_2 = 0.0442	R_1 = 0.0445, wR_2 = 0.0761	R_1 = 0.0530, wR_2 = 0.0795
Final R indexes [all data]	R_1 = 0.0414, wR_2 = 0.0488	R_1 = 0.0708, wR_2 = 0.0817	R_1 = 0.01119, wR_2 = 0.0931
Largest diff. peak/hole e.Å^{-3}	0.53 and –0.43	0.69 and –1.00	1.20 and –1.43



Scheme 1 — Schematic representation for the reaction of [$Ru_3(CO)_{12}$] with PhC≡CPh

Results and Discussion

Reaction of [$Ru_3(CO)_{12}$] with PhC≡CPh (diphenylacetylene) at 66 °C

The reaction of [$Ru_3(CO)_{12}$] with PhC≡CPh in refluxing tetrahydrofuran afforded [$Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)_2$] (**1**) (Scheme 1) in 25% yield, after purification by TLC. Continued reflux in tetrahydrofuran for further 5 h resulted the new compound [$Ru_3(CO)_6(\mu\text{-}CO)_2(\mu_3\text{-}\eta^4\text{-}C_4Ph_4)$] (**2**) in 30% yield. Furthermore, the reaction of [$Ru_3(CO)_{12}$] with PhC≡CPh in benzene at 66 °C gave **1** as the sole product. Thus it appears that the product formation depends on temperature and not on solvents. Compound **1** (Scheme 1) was first reported by Cetini *et al*.[41] and was only characterized spectroscopically. We were successful in growing X-ray quality crystals of **1** and unambiguously characterized by a solid-state structure determination. The molecular structure of **1** is depicted in Fig. 2, crystallographic data are given in Table 1 and selected bond distances and bond angles are listed in Table 2.

The structure consists of an approximate isosceles triangle of ruthenium atoms with two significantly shortened and approximately equal metal−metal bonds [Ru(1)-Ru(2) 2.6460(9), Ru(1)-Ru(3) 2.6553 (11) Å] and one relatively long metal−metal bond [Ru(2)-Ru(3) 2.7192(13) Å] with eight terminal carbonyl ligands. Two carbonyls are bonded to Ru(1) and three to each of Ru(2) and Ru(3). The average Ru−Ru distance of 2.667 Å is considerably shorter than the average Ru−Ru separation of 2.854 Å in [$Ru_3(CO)_{12}$].[48] The structure confirms usual μ_3-η^1:η^1:η^2 coordination mode of the two C_2Ph_2 ligands, with C(9)−C(10) and C(11)−C(12), bonds to the Ru_3 cluster. Each of the ligands is attached by two σ bonds to Ru(2) and Ru(3) atoms and the Ru−C σ bond distances associated with the Ru_2C_2 core range from 2.155(2) to 2.188(2) Å and these distances show an asymmetric pattern. The π-type interactions of the

Table 2 — Selected bond distances (Å) and angles (^{o}) for compounds **1**, **2** and **4**

Compound	Bond distances (Å)	Bond angles (^{o})	Symmetry code
1	Ru(1)–Ru(2) 2.6460(9)	Ru(1)–Ru(2)–Ru(3) 59.31(3)	
	Ru(2)–Ru(3) 2.7192(13)	Ru(1)–Ru(3)–Ru(2) 58.972(9)	
	Ru(1)–Ru(3) 2.6553(11)	Ru(2)–Ru(1)–Ru(3) 61.72(3)	
	Ru(1)–C(1) 1.882(3)	C(9)–Ru(1)–Ru(2) 53.01(6)	
	Ru(2)–C(3) 1.935(3)	C(9)–Ru(1)–Ru(3) 73.58(6)	
	Ru(3)–C(6) 1.936(3)	C(10)–Ru(1)–Ru(2) 75.20(6)	
	Ru(1)–C(9) 2.132(2)	C(10)–Ru(1)–Ru(3) 52.35(6)	
	Ru(1)–C(10) 2.126(2)	C(10)–Ru(1)–C(9) 38.38(8)	
	Ru(1)–C(11) 2.120(2)	C(9)–Ru(2)–Ru(3) 71.53(6)	
	Ru(1)–C(12) 2.133(2)	C(10)–Ru(3)–Ru(2) 73.08(6)	
	Ru(2)–C(11) 2.188(2)	C(11)–Ru(2)–Ru(3) 71.59(6)	
	Ru(3)–C(12) 2.155(2)	C(12)–Ru(3)–Ru(2) 73.05(6)	
	Ru(2)–C(9) 2.181(2)	C(9)–Ru(2)–Ru(1) 51.33(6)	
	Ru(3)–C(10) 2.162(2)	C(10)–Ru(3)–Ru(1) 51.12(6)	
	C(11)–C(12) 1.400(3)	C(11)–Ru(2)–Ru(1) 50.94(6)	
	C(9)–C(10) 1.400(3)	C(12)–Ru(3)–Ru(1) 51.36(6)	
2	Ru(1)–Ru(2) 2.6712(10)	Ru(3)–Ru(2)–Ru(1) 88.90(4)	-X,+Y,3/2-Z; -X,1-Y,1-Z
	Ru(2)–Ru(3) 2.6601(10)	Ru(1)−C(3)−Ru(2) 78.87(16)	
	Ru(1)−C(3) 2.018(5)	Ru(1)−C(12)−Ru(2) 73.31(13)	
	Ru(2)−C(3) 2.182(4)	Ru(2)−C(12)−Ru(3) 72.20(12)	
	Ru(2)−C(6) 2.152(5)	Ru(1)−C(12)−Ru(3) 111.44(17)	
	Ru(3)−C(6) 2.014(5)	C(12)–Ru(1)–Ru(2) 53.27(10)	
	Ru(2)−C(9) 2.176(4)	C(12)–Ru(2)–Ru(3) 54.66(10)	
	Ru(1)−C(9) 2.339(4)	C(11)–Ru(1)–Ru(2) 78.96(10)	
	Ru(1)−C(10) 2.328(4)	C(11)–Ru(3)–Ru(2) 79.59(10)	
	Ru(3)−C(10) 2.354(4)	C(10)–Ru(1)–Ru(2) 77.75(11)	
	Ru(3)−C(9) 2.306(4)	C(10)–Ru(3)–Ru(2) 77.54(10)	
	Ru(1)−C(12) 2.239(4)	C(9)–Ru(3)–Ru(2) 51,36(10)	
	Ru(2)−C(12) 2.235(4)	C(9)–Ru(1)–Ru(2) 50.95(10)	
	Ru(3)−C(12) 2.279(4)	C(9)–Ru(2)–Ru(3) 56.60(11)	
	Ru(1)−C(11) 2.329(4)	C(12)–Ru(2)–Ru(1) 53.41(10)	
	Ru(3)−C(11) 2.306(4)	C(12)–Ru(3)–Ru(2) 53.13(10)	
	C(9)−C(10) 1.436(5)		
	C(10)−C(11) 1.470(6)		
	C(11)−C(12) 1.447(6)		
4	Ru(1)−Ru(2) 2.884(3)	Ru(3)–Ru(1)–Ru(2) 86.87(2)	
	Ru(1)−Ru(3) 2.762(3)	Ru(4)–Ru(2)–Ru(1) 86.86(2)	
	Ru(2)−Ru(4) 2.763(3)	Ru(1)–Ru(3)–Ru(4) 87.15(2)	
	Ru(3)−Ru(4) 2.831(3)	Ru(2)–Ru(4)–Ru(3) 87.09(2)	
	Ru(1)−C(26) 2.196(7)	C(12)–Ru(1)–Ru(2) 48.78(17)	
	Ru(4)−C(27) 2.171(7)	C(13)–Ru(4)–Ru(3) 49.62(17)	
	Ru(1)−C(12) 2.283(7)	C(27)–Ru(4)–Ru(2) 58.43(18)	
	Ru(2)−C(12) 2.178(7)	C(26)–Ru(2)–Ru(1) 49.09(17)	
	Ru(4)−C(12) 2.494(7)	C(12)–Ru(1)–Ru(2) 48.78(17)	
	Ru(1)−C(13) 2.362(7)	Ru(1)–C(26)–Ru(2) 78.2(2)	
	Ru(3)−C(13) 2.208(7)	Ru(4)–C(27)–Ru(2) 72.9(2)	
	Ru(3)−C(11) 2.055(7)		
	Ru(1)−C(11) 2.026(7)		
	Ru(2)−C(27) 2.463(7)		
	Ru(3)−C(27) 2.299(7)		
	Ru(1)−C(26) 2.196(7)		
	C(12)−C(13) 1.409(9)		
	C(26)−C(27) 1.406(9)		

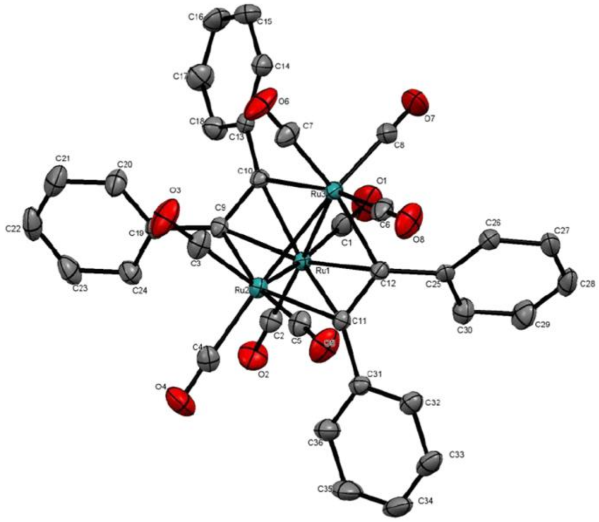


Fig. 2 — Molecular structure of $[Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)_2]$ (**1**) showing 50% probability of thermal ellipsoids. The hydrogen atoms are omitted for clarity

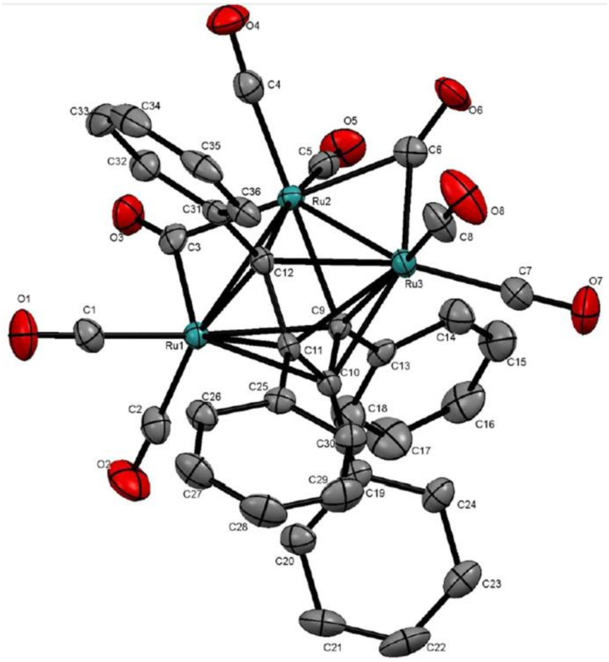


Fig. 3 — Molecular structure of $[Ru_3(CO)_6(\mu\text{-}CO)_2(\mu_3\text{-}\eta^4\text{-}C_4Ph_4)]$ (**2**) showing 50% probability of thermal ellipsoids. The hydrogen atoms are omitted for clarity

C_2 units with Ru(1) are [Ru(1)−C(9) 2.132(2), Ru(1)−C(10) 2.126(2) and Ru(1)−C(11) 2.120(2), Ru(1)−C(12) 2.133(2) Å]. The carbon−carbon bond distance of alkynes [C(9)−C(10) = C(11)−C(12)] 1.400(3) Å] is lengthened by coordination to the cluster. Cetini *et al*. isolated two isomers of **1**, the violet isomer and the yellow isomer.[41] The spectroscopic data of **1** in solution are consistent with the solid-state structure and similar to those reported for the violet isomer.[41] Compound **2** has been fully characterized by elemental analysis, spectroscopic data and single crystal X-ray analysis. The molecular structure of **2** is depicted in Fig. 3, crystallographic data and structure refinement parameters are given in Table 1 and selected bond distances and bond angles in Table 2. For symmetry generated atoms, the symmetry codes are provided in Table 2. The structure is based on a Ru_3 unit with two Ru−Ru bonds [Ru(1)−Ru(2) 2.6712(10), Ru(2)−Ru(3) 2.6601(10) Å] which are significantly shorter than the average Ru−Ru separation of 2.854 Å in $[Ru_3(CO)_{12}]$[48] but is comparable to those found in 1. The non-bonding Ru(1)…..Ru(3) distance of 3.733 Å suggests that there is no direct contact between these two ruthenium atoms in the molecule. The molecule also contains six terminal and two bridging carbonyl ligands and a C_4Ph_4 ligand formed by coupling of two C_2Ph_2 molecules on the triruthenium center. There are two terminal CO groups associated with each ruthenium atom to complete the ligand shell of cluster. The Ru(1)−Ru(2) and Ru(2)−Ru(3) edges are asymmetrically bridged by two CO ligands [Ru(1)−C(3) 2.018(5), Ru(2)−C(3) 2.182(4), Ru(2)−C(6) 2.152(5), Ru(3)−C(6) 2.014(5) Å]. The C_4Ph_4 ligand is attached to Ru(2) via two σ bonds [Ru(2)−C(9) 2.176(4) and Ru(2)−C(12) 2.235(4) Å] and to Ru(1) and Ru(3) by an η^4 interaction with the C_4 (diene) system [Ru(1)−C(9) 2.339(4), Ru(1)−C(10) 2.328(4), Ru(1)−C(11) 2.329(4), Ru(1)−C(12) 2.239(4) Å] and [Ru(3)−C(9) 2.306(4), Ru(3)−C(10) 2.354(4), Ru(3)−C(11) 2.306(4), Ru(3)−C(12) 2.279(4) Å]. Thus, the bonding of the C_4Ph_4 ligand to three metal atoms via 2σ and 4π interactions donating a total of ten electrons to the cluster orbitals is remarkable. To our knowledge analogous complexes in which the buta-1,3-dien-1,4-diyl type ligands interact with only two metal centers in $2\eta^1{:}\eta^4$-fashion have been previously reported in $[Ru_3(CO)_6(\mu_3\text{-}CH_2PPh_2(\mu_3\text{-}C_4Ph_4)(\mu\text{-}H)]$[49] and $[Ru_3(CO)_6\{\mu_3\text{-}PPhCH_2PPh(C_6H_4)\}\{\mu\text{-}C_4(CO_2Me)_4\}]$.[50] Considering the C_4Ph_4 ligand as ten-electron donor, compound **2** contains 50 CVE as expected for an electron-precise trinuclear cluster containing two metal−metal bonds instead of three.

The spectroscopic data of **2** in solution are consistent with the solid-state structure. The IR spectrum exhibits three strong CO bands at 2069, 2025 and 1975 cm^{-1} assigned to terminal carbonyls and two medium intensity bands at 1872 and 1847 cm^{-1} indicating the presence of bridging carbonyl groups. The ^1H NMR spectrum shows five well separated multiplets at δ 7.39, 7.18, 7.12, 6.87 and 6.24 in a relative intensity of 4 : 2 : 4 : 6 : 4 for phenyl protons of the C_4Ph_4 ligand. Compound **1** converts to **2** by refluxing in THF at 66 °C. Heating **1** in refluxing THF at 66 °C resulted double decarbonylation and cleavage of a metal−metal edge followed by dimerization of the coordinated diphenylacetylene ligands leading to the formation of compound **2** which is electron-precise and exhibits a 50 electron count, assuming the C_4Ph_4 ligand functions as 10e donor ligand. This is an interesting example of thermic effect in organometallic clusters to rearrange to thermodynamically stable structure at elevated temperature.

Reaction of $[Ru_3(CO)_{12}]$ with PhC≡CPh at 80 °C

The reaction of $[Ru_3(CO)_{12}]$ with diphenylacetylene in refluxing benzene afforded the triruthenium compound **2** in 20% yield and two tetraruthenium compounds, $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)]$ (**3**) and $[Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)_2]$ (**4**) in 25 and 16% yields, respectively (Scheme 1). Johnson *et al*. reported compound **3** in 1975 from the thermal reaction between $[Ru_3(CO)_{12}]$ and diphenylacetylene[43] and later characterized by a solid-state structure determination.[44] On the other hand, compound **4** was reported to be prepared from Me_3NO initiated reaction of $[Ru_3(CO)_{12}]$ with PhC≡CPh and crystallographically characterized.[45] We have redetermined the structure **4** and found that the molecule had packed in a different unit cell than that reported by Davies *et al*. The molecular structure of **4** is depicted in Fig. 4, crystallographic data are collected in Table 1 and selected bond distances and bond angles are listed in Table 2. The molecule **4** has a crystallographic plane of symmetry consisting of ten terminal and a bridging carbonyl ligand and two diphenylacetylene ligands. The four Ru atoms form a rhombus, bent along the Ru(1)….Ru(4) vector, with two different Ru–Ru distances [Ru(1)−Ru(2) 2.844(3) Å and Ru(1)−Ru(3) 2.762(3)] symmetrically bridged by carbonyl CO(11) [Ru(1)–C(11) 2.026(7), Ru(1)–C(11) 2.005(7) Å]. Angles subtended at one Ru atom by the others are within 86.86(2)-87.15(2)°. The two diphenylacetylene molecules lie on opposite sides of the Ru_4 core, each being bonded by two σ bonds [Ru(1)−C(26) 2.196(7), Ru(4)−C(27) 2.171(7) Å] and one π [Ru−C 2.283–2.362(7) Å] bond. The C(12)−C(13) and C(26)−C(27) separations are 1.409(9) Å, which is lengthened by coordination to the cluster. The structure and the spectroscopic data of **4** in solution are very similar to those reported by Davies and coworkers.

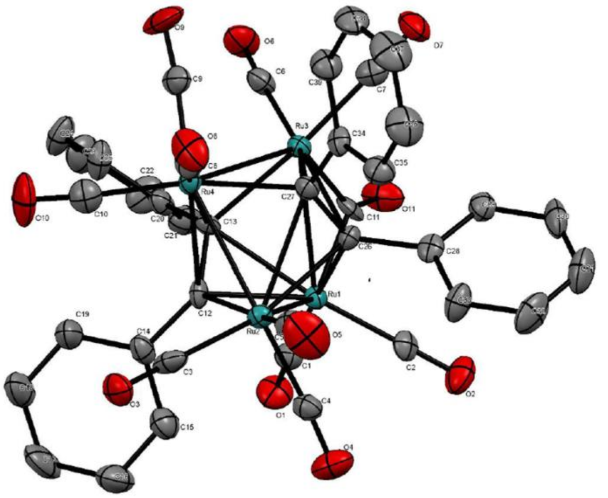


Fig. 4 — Molecular structure of $[Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)_2]$ (**4**) showing 50% probability of thermal ellipsoids. The hydrogen atoms are omitted for clarity

Conclusions

The products obtained from the reaction between $[Ru_3(CO)_{12}]$ and C_2Ph_2 are temperature dependent. The reaction of $[Ru_3(CO)_{12}]$ with C_2Ph_2 in refluxing THF furnished two trinuclear compounds, the new compound $[Ru_3(CO)_6(\mu\text{-}CO)_2(\mu_3\text{-}\eta^4\text{-}C_4Ph_4)]$ (**2**) and the previously reported $[Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)_2]$ (**1**). In contrast, heating $[Ru_3(CO)_{12}]$ with C_2Ph_2 in benzene at 80 °C furnished two tetraruthenium clusters $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)]$ (**3**) and $[Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}\eta^2\text{-}C_2Ph_2)_2]$ (**4**) together with the trinuclear compound **2**. Clusters **1** and **2** have the same molecular formula but different structural motif. They are isomers and we have characterized them structurally. Compound **1** was previously characterized only by spectroscopic methods. Compound **2** provides a unique example of an open triruthenium alkyne cluster in which the C_4Ph_4 ligand is bonded to three metal atoms via two σ and four π interactions supplying a total of ten electrons to the cluster orbitals. This type of bonding for an alkyne in polymetallic compounds is rare, because in transition metal clusters these normally bridge a metal−metal bond as part of a closed triangle interacting with only two metal centers in $2\eta^1{:}\eta^4$-fashion. Heating **1** at 66 °C slowly rearranges to afford **2**, thus implying that **1** is the precursor to **2**.

Supplementary Data

CCDC 2034102, 2034100 and 2034101 contain supplementary crystallographic data for **1**, **2** and **4**, respectively, which may be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif. Supplementary Data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(02)177-184_ SupplData.pdf.

Acknowledgement

This research has been sponsored by the Ministry of Science and Technology, Government of the People's Republic of Bangladesh. We also thank the Wazed Miah Science Research Center, Jahangirnagar University, Bangladesh for providing instrumental facilities required for this work.

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