FISEVIER



Journal of the Indian Chemical Society

journal homepage: www.editorialmanager.com/JINCS/default.aspx

Triruthenium clusters containing mono and bidentate phosphines: Synthesis, structure, thermal reactivity and fluxional behavior



Partha S. Roy, Md. Abdullah A. Mamun, Roknuzzaman, Shishir Ghosh **, Shariff E. Kabir

Department of Chemistry, Jahangirnagar University, Savar, Dhaka 1342, Bangladesh

A R T I C L E I N F O <i>Keywords:</i> Ruthenium Carbonyl 1,2-bis(diphenylphosphino)ethane tri(2-thienyl)phosphine tri(2-furyl)phosphine Fluxional behavior X-ray structures	A B S T R A C T		
	The syntheses, structures and thermal reactions of $[Ru_3(CO)_9{P(C_4H_3E)_3}(\mu-dppe)]$ (2, $E = S$; 3, $E = O$; dppe = 1,2-bis(diphenylphosphino)ethane) are described. These triphosphine-substituted clusters can be easily obtained in high yield from the Me ₃ NO initiated room temperature reaction between $[Ru_3(CO)_{10}(\mu-dppe)]$ (1) and $P(C_4H_3E)_3$. Both clusters have been structurally characterized which reveals that the functionalized phosphine $P(C_4H_3E)_3$ is coordinated to the remote ruthenium atom using the phosphorus atom, while the NMR spectroscopic data indicate that both clusters are fluxional in solution mainly due to the ring-flipping process involving the dppe ligand which has been probed by VT NMR spectroscopy. Thermolysis of 2 at 66 °C affords 1 <i>via</i> $P(C_4H_3S)_3$ dissociation, whilst that of 3 under similar experimental conditions also furnishes the diruthenium σ,π -furyl complex $[Ru_2(CO)_6(\mu,\eta^2-C_4H_3O)_{\{\mu-P(C_4H_3O)_2\}}$ (4) in addition to 1.		

1. Introduction

The chemistry of functionalized phosphines such as tri(2-thienyl) phosphine and tri(2-furyl)phosphine (Chart 1) is a subject of continuing interest due to their importance in transition metal catalysis [1–3], since catalysts employing these ligands are often more active than traditional triphenylphosphine based catalysts [1,2]. In addition, the chemistry of phosphine ligands containing pyrrolyl and thienyl substituents has been widely studied because of their respective importance in the hydrodenitrogenation [4] and hydrodesulfurization [5] processes, and some recent developments reveal the intriguing reactivity patterns of these phosphines towards metal carbonyl clusters [6].

In this context, we have been studying the coordination chemistry of tri(2-theinyl)phosphine and tri(2-furyl)phosphine over the years [7–13] which reveals that these phosphines are not only potential alternatives to triphenylphosphine in a range of stoichiometric and catalytic transformations [1,2], but may also function as a source of novel alkynyl derivatives based on thiophyne (C₄H₂S) and furyne (C₄H₂O) platforms, which are generated as a result of both carbon-phosphorus and carbon-hydrogen bond activation [7,8]. For example, the triruthenium bis(diphenylphosphino)methane (dppm) complexes [Ru₃(CO)₉{P(-C₄H₃E)₃}(μ -dppm)] convert cleanly to give the thiophyne and furyne clusters [HRu₃(CO)₇(μ ₃-C₄H₂E){ μ -P(C₄H₃E)₂}(μ -dppm)] in good yield

upon mild heating (Scheme 1) [7], thus allowing their chemistry to be explored. In contrast, the triruthenium complexes $[Ru_3(CO)_9{P(-C_4H_3E)_3}(\mu-dppf)]$, that contain a more flexible 1,1'-bis(diphenylphosphino)ferrocene (dppf) instead of relatively rigid dppm, do not undergo any discernible change upon mild heating. However, the dppf complexes slowly undergo thermal rearrangement only at 80 °C to afford the cyclometalated clusters $[HRu_3(CO)_7{\mu_3-(EH_2C_4)P(C_4H_3E)_2}(\mu-dppf)]$ (Scheme 1) [9]. These observations clearly indicate that the thermal rearrangement of this type of triphosphine-substituted clusters, $[Ru_3(CO)_9{P(-C_4H_3E)_3}(\mu-diphosphine)]$, is influenced by the flexibility of the diphosphine backbone. In order to further explore this area, we have now synthesized the triruthenium 1,2-bis(diphenylphosphino)ethane (dppe) complexes $[Ru_3(CO)_9{P(C_4H_3E)_3}(\mu-dppe)]$ (2, E = S; 3, E = O) and investigated their thermal reactions the details of which are described in this paper.

2. Experimental

2.1. Methods and materials

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques unless otherwise noted. Reagent grade solvents were dried using appropriate drying agents and distilled prior to

https://doi.org/10.1016/j.jics.2021.100023

Received 28 November 2020; Received in revised form 7 January 2021; Accepted 5 March 2021 0019-4522/© 2021 Indian Chemical Society. Published by Elsevier B.V. All rights reserved.

^{*} Corresponding author.

^{**} Corresponding author.

E-mail addresses: sghosh_006@yahoo.com (S. Ghosh), skabir_ju@yahoo.com (S.E. Kabir).



Scheme 1. Thermal reactions of $[Ru_3(CO)_9{P(C_4H_3E)_3}(\mu-diphosphine)]$ (E = S, O; diphosphine = dppm, dppf) [7,9].

use by standard methods. Infrared spectra were recorded on a Shimadzu FTIR Prestige 21 spectrophotometer, and the NMR spectra were recorded 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 NMR solvent (¹H) or external 85% H₃PO₄ (³¹P), as appropriate. Elemental analyses were performed by the Microanalytical Laboratory of Wazed Miah Science Research Center at Jahangirnagar University. [Ru₃(CO)₁₂] was purchased from Strem Chemical Inc. and used without further purification. Tri(2-thienyl)phosphine [P(C₄H₃S)₃], tri(2-furyl)phosphine [P(C₄H₃O)₃] and bis(diphenylphosphino)ethane (dppe) were purchased from Acros Organics and used as received. The starting cluster [Ru₃(CO)₁₀(µ-dppe)] (1) was prepared according to a published procedure [14]. All products reported herein were separated in the air by TLC plates coated with 0.25 mm of silica gel (HF₂₅₄-type 60, E. Merck, Germany).

2.2. Reaction of $[Ru_3(CO)_{10}(\mu-dppe)]$ (1) with $P(C_4H_3S)_3$

 $[Ru_3(CO)_{10}(\mu-dppe)]$ (1) (100 mg, 0.102 mmol) and P(C₄H₃S)₃ (36 mg, 0.128 mmol) was dissolved in 20 mL CH₂Cl₂ in a three-neck round-bottom flask with the aid of a magnetic stirrer. A freshly prepared CH₂Cl₂ solution (15 mL) of Me₃NO (8 mg, 0.107 mmol) was added dropwise to this solution. After the addition of Me₃NO was completed, the reaction mixture was further stirred at room temperature for 1 h. The solvent was then removed under reduced pressure and the residue was recrystallised from *n*-hexane/CH₂Cl₂ at 4 °C which afforded [Ru₃(CO)₉{P(C₄H₃S)₃}(μ -dppe)] (2) (113 mg, 90%) as red crystals.

Data for **2**: Anal. Calcd. for $C_{47}H_{33}O_9P_3Ru_3S_3$: C, 45.74; H, 2.70. Found: C, 45.98; H, 2.81%. IR (ν_{CO} , CH₂Cl₂): 2051 m, 1995 vs, 1974 vs, 1937 sh, 1922 sh cm⁻¹. ¹H NMR (CDCl₃): δ 7.64 (m, 3H), 7.52 (m, 8H), 7.42 (m, 12H), 6.70 (m, 3H), 6.44 (m, 3H), 2.20 (m, 4H). ³¹P{¹H} NMR (CDCl₃): δ 38.7 (d, J 22 Hz, 1P), 37.7 (s, 1P), -15.1 (d, J 22 Hz, 1P).

2.3. Reaction of $[Ru_3(CO)_{10}(\mu-dppe)]$ (1) with $P(C_4H_3O)_3$

A CH₂Cl₂ solution (15 mL) of Me₃NO (8 mg, 0.107 mmol) was added dropwise to a CH₂Cl₂ solution (20 mL) of $[Ru_3(CO)_{10}(\mu$ -dppe)] (1) (100 mg, 0.102 mmol) and P(C₄H₃O)₃ (30 mg, 0.129 mmol) and the reaction mixture was stirred at room temperature for 1 h. The solvent was then removed under vacuum and the residue recrystallised from *n*-hexane/CH₂Cl₂ at 4 °C which gave $[Ru_3(CO)_9{P(C_4H_3O)_3}(\mu$ -dppe)] (3) (103 mg, 85%) as red crystals.

Data for **3**: Anal. Calcd. for $C_{47}H_{33}O_{12}P_3Ru_3$: C, 47.60; H, 2.81. Found: C, 47.93; H, 2.90%. IR (ν_{CO} , CH₂Cl₂): 2051 m, 1994 vs, 1973 vs, 1939 sh, 1921 m cm⁻¹. ¹H NMR (CDCl₃, 298K): δ 7.65 (m, 3H), 7.53 (br, s, 8H), 7.43 (br, s, 12H), 6.71 (m, 3H), 6.45 (m, 3H), 2.19 (m, 4H). ³¹P{¹H} NMR (CDCl₃, 298 K): δ 39.1 (s, 1P), 38.1 (s, 1P), 14.6 (s, 1P). ¹H NMR (CDCl₃, 213 K): δ 7.77 (m, 4H), 7.66 (m, 3H), 7.55 (m, 6H), 7.36 (m, 6H), 7.25 (m, 4H), 6.75 (m, 3H), 6.47 (m, 3H), 2.58 (m, 2H) 2.74 (m, 2H). ³¹P{¹H} NMR (CDCl₃, 213 K): δ 40.2 (s, 1P), 39.3 (s, 1P), 15.9 (s, 1P).

2.4. Thermolysis of $[Ru_3(CO)_9{P(C_4H_3S)_3}(\mu-dppe)]$ (2)

A thf solution (20 mL) of 2 (50 mg, 0.041 mmol) was heated to reflux

Table 1

Compound	2	3
CCDC	2045763	2044529
Empirical formula	$C_{47}H_{33}O_9P_3Ru_3S_3\cdot C_6H_{14}$	4C47H33O12P3Ru3
Formula weight	1320.20	4743.41
Temperature (K)	150(1)	220(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	Pbca
Unit cell dimensions:		
a (Å)	18.9980(3)	14.670(3)
b (Å)	13.04878(16)	19.504(4)
c (Å)	23.9536(4)	38.050(8)
α (°)	90	90
β(°)	112.498(2)	90
γ (°)	90	90
Volume (Å ³)	5486.21(17)	10887(4)
Z	4	2
Density (calculated) (Mg/ m ³)	1.598	1.447
Absorption coefficient (mm ⁻¹)	1.070	0.963
F(000)	2648	4704
Crystal size (mm ³)	$0.18 \times 0.18 \times 0.15$	$0.18 \times 0.09 \times 0.06$
2θ Range for data	5.304 to 58.97	5.104 to 54.454
Reflections collected	93626	360459
Independent reflections	$14104 [R_{\odot} = 0.0311]$	$12118 [R_{\odot} - 0.0883]$
[R _{int}]	110 ([A]nt = 0.0011]	12110 [Rint - 0.0000]
Data/restraints/ parameters	14104/0/642	12118/0/586
Goodness-of-fit on F [2]	1.079	1.061
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0249,$	$R_1 = 0.0351,$
	$wR_2 = 0.0514$	$wR_2 = 0.0910$
R indices (all data)	$R_1 = 0.0305,$	$R_1 = 0.0550,$
	$wR_2 = 0.0538$	$wR_2 = 0.0996$
Largest diff. peak and hole (e. $Å^{-3}$)	0.63 and -0.64	0.57 and -0.56

at 66 °C for 3 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with cyclohexane/ CH₂Cl₂ (4:1, v/v) developed three bands. The first and second bands afforded $P(C_4H_3S)_3$ (trace) and $[Ru_3(CO)_{10}(\mu$ -dppe)] (1) (14 mg, 35%), whilst the third was unconsumed **2** (6 mg).

2.5. Thermolysis of $[Ru_3(CO)_9{P(C_4H_3O)_3}(\mu-dppe)]$ (3)

A thf solution (20 mL) of **3** (50 mg, 0.042 mmol) was heated to reflux at 66 °C for 3 h. The solvent was removed under vacuum and the residue separated by TLC on silica gel. Elution with cyclohexane/CH₂Cl₂ (4:1, v/ v) developed three bands. The first band afforded the previously reported diruthenium compound [Ru₂(CO)₆(μ , η^2 -C₄H₃O){ μ -P(C₄H₃O)₂] (4) [15] (10 mg, 39%), while the second band yielded [Ru₃(CO)₁₀(μ -dppe)] (1) (17 mg, 41%). The third band was unconsumed **3** (4 mg).

2.6. Crystal structure determination

Suitable single crystals of 2 and 3 were mounted on an Agilent Super



Scheme 2. Reactions of $[Ru_3(CO)_{10}(\mu\text{-dppe})]$ (1) with $P(C_4H_3S)_3$ and $P(C_4H_3O)_3$.



Fig. 1. Molecular structures of $[Ru_3(CO)_9{P(C_4H_3S)_3}(\mu-dppe)]$ (2) (left) and $[Ru_3(CO)_9{P(C_4H_3O)_3}(\mu-dppe)]$ (3) (right) showing 50% probability atomic displacement ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2

Selected structural parameters for $[Ru_3(CO)_9{P(C_4H_3S)_3}(\mu-dppe)]$ (2) and $[Ru_3(CO)_9{P(C_4H_3O)_3}(\mu-dppe)]$ (3) (bond lengths in [Å] and bond angles in [°]).

Compound	2	3
Ru(1)–Ru(2)	2.8307(2)	2.8754(7)
Ru(1)–Ru(3)	2.8667(2)	2.8315(6)
Ru(2)–Ru(3)	2.8468(2)	2.8789(6)
Ru(1)–P(1)	2.3316(5)	2.3061(10)
Ru(2)–P(2)	2.3230(5)	2.3451(10)
Ru(3)–P(3)	2.3231(5)	2.3167(9)
Ru(2)-Ru(1)-Ru(3)	59.953(5)	60.586(10)
Ru(1)-Ru(2)-Ru(3)	60.650(5)	58.953(13)
Ru(2)-Ru(3)-Ru(1)	59.397(5)	60.461(17)
P(1)-Ru(1)-Ru(2)	166.306(13)	106.90(2)
P(1)-Ru(1)-Ru(3)	116.986(13)	166.79(3)
P(2)-Ru(2)-Ru(1)	157.354(13)	158.85(2)
P(2)-Ru(2)-Ru(3)	100.144(12)	101.05(3)
P(3)-Ru(3)-Ru(1)	150.556(13)	162.43(2)
P(3)-Ru(3)-Ru(2)	98.496(13)	103.75(3)

Nova dual diffractometer (Agilent Technologies Inc., Santa Clara, CA) or on a Bruker D8 Venture diffractometer using a Nylon loop and Paratone oil, and the diffraction data were collected at 150(1) K (for **2**) or 220(1) K (for **3**) using Mo-K α radiation ($\lambda = 0.71073$). Unit cell determination, data reduction, and absorption corrections for **2** were carried out using CrysAlisPro [16]. Data reduction and integration for **3** were carried out with SAINT+ [17] and absorption corrections were applied using the program SADABS [18]. The structures were solved with the ShelXS [19] structure solution program by direct methods and refined by full-matrix least-squares on the basis of F^2 using ShelXL [20] or XL [19] within the OLEX2 [21] graphical user interface. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included using a riding model. The asymmetric unit of **2** also contains a disordered *n*-hexane molecule, but we were able to refine it anisotropically and hydrogen atoms were also included in it using a riding model. "Compound **2** shows a 'Level B checkCIF alert' mainly due to omission of a large number of low-order reflections from the (final) least-squares refinement." Additional crystallographic data are given in Table 1.

3. Results and discussion

3.1. Reaction of $[Ru_3(CO)_{10}(\mu-dppe)]$ (1) with $P(C_4H_3E)_3$ (E = S, O)

Room temperature reaction between $[Ru_3(CO)_{10}(\mu-dppe)]$ (1) and $P(C_4H_3E)_3$ in the presence of Me_3NO led to the formation of $[Ru_3(CO)_9{P(C_4H_3E)_3}(\mu-dppe)]$ (2, E = S; 3, E = O) as red, air-stable crystalline solid in *ca.* 90% yield, after usual chromatographic separation and workup (Scheme 2). Both new clusters have been characterized by elemental and spectroscopic data in addition to single crystal X-ray diffraction analyses.

ORTEP diagrams of the molecular structure of 2 and 3 are depicted in Fig. 1 and selected bond lengths and angles are listed in Table 2. Both molecules contain a triruthenium core ligated by nine carbonyls, a dppe and a P(C₄H₃S)₃ or P(C₄H₃O)₃ ligands. The effect of P(C₄H₃E)₃ substitution on the Ru3-triangle is unremarkable, as the average Ru-Ru distance (2.8481 Å in 2 and 2.8619 Å in 3) being not significantly different from that found for 1 (2.853 Å) [14] or even for [Ru₃(CO)₁₂] (2.851 Å) [22]. The diphosphine (dppe) acts in bridging capacity and the non-planarity of the resulted Ru-P-C-C-P-Ru ring, a feature also observed in the parent cluster 1, is one of the main structural features of 2 and 3. In both clusters, all three phosphorus atoms occupy an equatorial coordination site on each ruthenium atoms, and the average Ru-P bond distance (2.3259 Å in 2 and 2.3226 Å in 3) are very similar to that observed for related clusters such as [Ru₃(CO)₉{P(C₄H₃S)₃}(µ-dppm)] (2.3324 Å) [7] and $[Ru_3(CO)_9{P(C_4H_3O)_3}(\mu-dppf)]$ (2.3375 Å) [9]. The nine carbonyls are equally distributed between the three ruthenium



Fig. 2. Variable-temperature ¹H NMR spectra in the aliphatic region for 3 recorded over the temperature range 213–298 K.



tri(2-thienyl)phosphine $[P(C_4H_3S)_3]$ tri(2-furyl)phosphine [P(C_4H_3O)₃]

Chart 1. Chemical structures of tri(2-thienyl) phosphine and tri(2-furyl) phosphine.

atoms, and are bound to the metal centers in terminal fashion. In both clusters, the axial OC–Ru–CO directions are not perpendicular to the Ru₃

plane but are screwed with respect to each other. This type of distortion is common and also observed in the structure of the parent cluster 1 [14], and even to a small extent in the structures of $[M_3(CO)_{12}]$ (M = Ru, Os) [22,23].

The spectroscopic data indicate that both clusters are fluxional in solution. At room temperature, the ¹H NMR spectra of both clusters show a multiplet in the aliphatic region (δ 2.20 for **2** and δ 2.19 for **3**) for the four methylene protons of the dppe ligand in addition to a series of multiplets in the aromatic region for the phenyl and theinyl or furyl ring protons. The appearance of the four methylene protons resonance as a single multiplet can be attributed to the ring-flipping process involving the dppe ligand as shown in Scheme 3, which was also reported for the dppe-bridged triosmium complex [Os₃(CO)₁₀(μ -dppe)] [24] and its protonated derivative [Os₃(CO)₁₀(μ -H)(μ -dppe)][PF₆] [24]. To confirm this assumption, we have carried out a VT NMR experiment for **3** the results of which is shown in Fig. 2. At 213 K, the methylene protons of the dppe ligand indeed appear as two multiplets at δ 2.58 and 1.73 which



(E = S, O; X = CH₂, Fc')

Scheme 4. Phosphine migration between equatorial positions of the unique ruthenium atom of $[Ru_3(CO)_9{P(C_4H_3E)_3}(\mu-diphosphine)]$ [7,9].



Scheme 5. Thermal reactions of $[Ru_3(CO)_9{P(C_4H_3E)_3}(\mu-dppe)]$ (2, E = S; 3, E = O).

coalesce at about 253 K to give a broad singlet (δ 2.19) at 273 K. The ³¹P 1 H} NMR spectrum of **2** displays two doublets at δ 38.7 and -15.1 (*J* 22 Hz) and a sharp singlet at δ 37.7 at room temperature due to the phosphorus atoms of the dppe and P(C₄H₃S)₃ ligands, respectively, indicating that the P(C₄H₃S)₃ ligand does not move between equatorial positions of the unique ruthenium atom which is quite common for [Ru₃(CO)₉(PR₃)(µ-diphosphine)] complexes [7,9,25]. For example, such movement of P(C₄H₃E)₃ ligand has also been reported for $[Ru_3(CO)_9{P(C_4H_3E)_3}(\mu-dppm)]$ (E = S, O) [7] and $[Ru_3(CO)_9{P(C_4H_3E_3$ (µ-dppf)] (E = S, O) [9] (Scheme 4). In contrast, the ³¹P{¹H} NMR spectrum of **3** displays three singlets at δ 39.1, 38.1 and 14.6 at room temperature, and the spectrum does not show any discernible change upon cooling to 213 K. This suggests that a second fluxional process such as movement of the P(C₄H₃O)₃ ligand between equatorial positions of the unique ruthenium atom or a more complex fluxional process is occurring in solution for 3.

3.2. Thermolysis of $[Ru_3(CO)_9{P(C_4H_3E)_3}(\mu-dppe)]$

We next examined the thermal stability of $[Ru_3(CO)_9\{P(C_4H_3E)_3\}(\mu-dppe)]$ (2, E = S; 3, E = O) in order to study the rearrangement of the coordinated $P(C_4H_3E)_3$ ligand. Heating a CH_2Cl_2 solution of 2 at 40 °C in the presence of equimolar amount of Me₃NO only led to unspecific decomposition, but $[Ru_3(CO)_{10}(\mu-dppe)]$ (1) was isolated from the reaction mixture when 2 was heated at 66 °C in the absence of Me₃NO (Scheme 5). This indicates that decomposition of 2 upon heating is triggered by loss of $P(C_4H_3S)_3$ ligand, and the isolation of 1 from this thermal reaction can be attributed to the CO capture by the putative 46-electron cluster $[Ru_3(CO)_9(\mu-dppe)]$ generated *in situ* upon phosphine dissociation.

On the contrary, thermolysis of **3** at 66 °C led to the isolation of the diruthenium σ,π -furyl complex [Ru₂(CO)₆(μ,η^2 -C₄H₃O){ μ -P(C₄H₃O)₂] (**4**) [15] and **1** in 39 and 41% yield (Scheme 5). Complex **4** results *via* C–P bond cleavage of the coordinated P(C₄H₃O)₃ ligand followed by coordination of the dissociated furyl moiety to the diruthenium center in σ,π -alkenyl fashion. The dppe ligand is probably lost as [Ru(CO)₃(κ^2 -dppe)] during the formation of **4** from **3** which we assume undergoes decomposition since we could not isolate it from the reaction mixture. Complex **4** was previously reported and structurally characterized by Wong and coworkers [15], obtained from the direct reaction between [Ru₃(CO)₁2] and P(C₄H₃O)₃ at 66 °C.

4. Conclusions

In summary, we have investigated the reactions of $[Ru_3(CO)_{10}(\mu-dppe)]$ (1) with two functionalized phosphines $P(C_4H_3S)_3$ and $P(C_4H_3O)_3$. Two new triruthenium clusters $[Ru_3(CO)_9\{P(C_4H_3E)_3\}(\mu-dppe)]$ (2, E = S; 3, E = O) have been isolated in high yield from these reactions and the molecular structure of each product established by X-ray crystallography. Thermolysis of 2 at 66 °C leads to the formation of 1 *via* $P(C_4H_3S)_3$ dissociation with subsequent capture of a CO from the reaction mixture. In contrast, the diruthenium σ,π -furyl complex $[Ru_2(CO)_6(\mu,\eta^2-C_4H_3O)_{\{\mu-P(C_4H_3O)_2\}}$ (4) [15] formed by C–P bond

cleavage of the coordinated $P(C_4H_3O)_3$ ligand is also isolated in addition to **1** from the thermal reaction of **3** under similar experimental conditions. The thermolytic behavior of **2** and **3** is in sharp contrast with those observed for their dppm and dppf analogues $[Ru_3(CO)_9{P(-C_4H_3E)_3}(\mu-dppm)]$ (E = S, O) [7] and $[Ru_3(CO)_9{P(C_4H_3O)_3}(\mu-dppf)]$ (E = S, O) [9], respectively (Scheme 1). Thus, the present study also underscores the influence of flexibility of the diphosphine backbone on the thermal rearrangement of triphosphine-substituted clusters of the general formula $[Ru_3(CO)_9{P(C_4H_3E)_3}(\mu-diphosphine)]$ (E = S, O).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Financial support from the Ministry of Science and Technology, the Government of the People's Republic of Bangladesh (SG and SEK) is acknowledged. We thank the Wazed Miah Science Research Center, Jahangirnagar University, Bangladesh for providing some technical facilities required for this work. We also thank Prof. Derek A. Tocher for X-ray structure analysis of **2**.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://do i.org/10.1016/j.jics.2021.100023.

References

- (a) Anderson NG, Keay BA. Chem. Rev. 2001;101:997. (b) Sakai M, Hayashi H, Miyaura N. Organometallics 1997;16:4229. (c) Shirakawa E, Yamasaki K, Hiyama T. Synthesis 1998:1544. (d) Trost BM, Rhee YH. J. Am. Chem. Soc. 1999; 121:11680. (e) Anderson JC, Namli H, Roberts CA. Tetrahedron 1997;53:15123.
- [2] (a) Farina V. Pure Appl. Chem. 1996;68:73.(b) Wong W-Y, Ting F-L, Lin Z. Organometallics 2003;22:5100.(c) Santelli-Rouvier C, Coin C, Toupet L, Santelli M. J. Organomet. Chem. 1995;495:91.
- [3] (a) Klement I, Rottländer M, Tucker CE, Majid TN, Knöchel P, Venegas P, Cahiez G. Tetrahedron 1996;52:7201 (b) Herrmann WA, Brossmer S, Öfele K, Beller M, Fischer H. J. Mol. Catal. Chem. 1995;103:133 (c) Farina V, Baker SR, Benigni DA, Sapino C. Tetrahedron Lett. 1988;29:5739.
- [4] (a) Laine RM. Ann. N. Y. Acad. Sci. 1983;415:271 (b) Fish RH. Ann. N. Y. Acad. Sci. 1983;415:292.(c) Eisenstadt A, Giandomenico CM, Frederick MF, Laine RM. Organometallics 1985;4:2033.(d) Chisholm MH. Polyhedron 1997;16:3071.
- [5] Angelici RJ. In: King RB, editor. Encyclopedia of Inorganic Chemistry, vol. 3. New York: Wiley-VCH; 1994. p. 1433.
- [6] (a) Arce AJ, Deeming AJ, Sanctis Y De, Johal SK, Martin CM, Shinhmar M, Speel DM, Vassos A. J. Chem. Soc., Chem. Commun. 1998:233.(b) Bodensieck U, Varenkamp H, Rheinwald G, Stoeckli-Evans H. J. Organomet. Chem. 1995;85: 488.(c) Deeming AJ, Jaysuriya SN, Arce AJ, De Sanctis Y. Organometallics 1996; 15:786.
- [7] Uddin MN, Begum N, Hassan MR, Hogarth G, Kabir SE, Miah MA, Nordlander E, Tocher DA. Dalton Trans. 2008:6219.
- [8] Rahman MA, Begum N, Ghosh S, Hossain MK, Hogarth G, Tocher DA, Nordlander E, Kabir SE. J. Organomet. Chem. 2011;696:607.
- [9] Hossain MK, Rajbangshi S, Rahaman A, Chowdhury MAH, Siddiquee TA, Ghosh S, Richmond MG, Nordlander E, Hogarth G, Kabir SE. J. Organomet. Chem. 2014;760: 231.

P.S. Roy et al.

- [10] (a) Begum N, Rahman MA, Hassan MR, Tocher DA, Nordlander E, Hogarth G, Kabir SE. J. Organomet. Chem. 2008;693:1645.(b) Uddin MN, Mottalib MA, Begum N, Ghosh S, Raha AK, Haworth DT, Lindeman SV, Siddiquee TA, Bennett DW, Hogarth G, Nordlander E, Kabir SE. Organometallics 2009;28: 1514.(c) Ghosh S, Khatun M, Haworth DT, Lindeman SV, Siddiquee TA, Bennett DW, Hogarth G, Nordlander E, Kabir SE. J. Organomet. Chem. 2009;694: 2941.
- [11] (a) Ghosh S, Rana S, Tocher DA, Hogarth G, Nordlander E, Kabir SE. J. Organomet. Chem. 2009;694:3312.(b) Ghosh S, Das AK, Begum N, Haworth DT, Lindeman SV, Gardinier JF, Siddiquee TA, Bennett DW, Nordlander E, Hogarth G, Kabir SE. Inorg. Chim. Acta. 2009;362:5175.(c) Ghosh S, Hogarth G, Tocher DA, Nordlander E, Kabir SE. Inorg. Chim. Acta. 2010;363:1611.(d) Sikder MDH, Ghosh S, Kabir SE, Hogarth G, Tocher DA. Inorg. Chim. Acta. 2011;376:170.
- [12] (a) Hossain MI, Sikder MDH, Ghosh S, Kabir SE, Hogarth G, Salassa L. Organometallics 2012;31:2546.(b) Ghosh S, Hogarth G, Kabir Shariff E, Nordlander E, Salassa L, Tocher DA. J. Organomet. Chem. 2011;696:1982.(c) Karmaker S, Ghosh S, Kabir SE, Haworth DT, Lindeman SV. Inorg. Chim. Acta. 2012;382:199.(d) Rahaman A, Alam FR, Ghosh S, Haukka M, Kabir SE, Nordlander E, Hogarth G. J. Organomet. Chem. 2013;730:123.
- [13] Rahaman A, Alam FR, Ghosh S, Tocher DA, Haukka M, Kabir SE, Nordlander E, Hogarth G. J. Organomet. Chem. 2014;751:326.(b) Raha AK, Uddin MN, Ghosh S,

Miah AR, Richmond MG, Tocher DA, Nordlander E, Hogarth G, Kabir SE. J. Organomet. Chem. 2014;751:399.(c) Uddin MM, Begum N, Ghosh S, Sarker JC, Tocher DA, Hogarth G, Richmond MG, Nordlander E, Kabir SE. J. Organomet. Chem. 2016;812:197.

- [14] Bruce MI, Hambley TW, Nicholson BK, Snow MR. J. Organomet. Chem. 1982;235: 83.
- [15] Wong W-Y, Ting F-L, Lam W-L. J. Chem. Soc. Dalton Trans. 2001:2981.
- [16] CrysAlisPRO, Agilent Technologies UK Ltd, Yarnton, England.
- [17] Bruker. SAINT (8.37A). Madison, Wisconsin, USA: Bruker AXS Inc.; 2015.
- [18] Bruker. SADABS-2014/5. Madison, Wisconsin, USA: Bruker AXS Inc.; 2014.[19] Sheldrick GM. Acta Crystallogr. 2008;A64:112.
- [20] Sheldrick GM. Acta Crystallogr. 2006;A04.11 [20] Sheldrick GM. Acta Crystallogr. 2015;C71:3.
- [21] Dolomanov OV, Bourhis LJ, Gildea RJ, Howard JAK, Puschmann H. J. Appl. Crystallogr. 2009;42:339.
- [22] Churchill MR, Hollander FJ, Hutchinson JP. Inorg. Chem. 1977;16:2655.
- [23] Churchill MR, DeBoer BG. Inorg. Chem. 1977;16:878.
- [24] Deeming AJ, Donovan-Mtunzi S, Hardcastle KI, Kabir SE, Henrick K, Mcpartlin M. J. Chem. Soc., Dalton Trans. 1988;579.
- [25] Torabi AA, Humphreys AS, Koutsantonis GA, Skelton BW, White AH. J. Organomet. Chem. 2002;655:227.