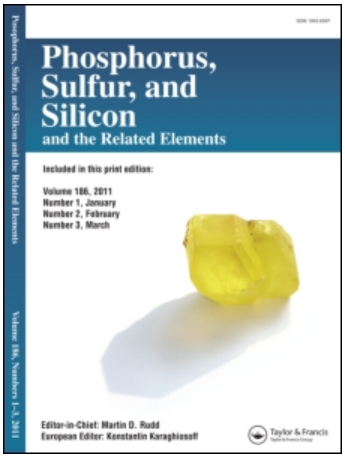

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REACTIONS OF 1,2,3-TRIPHENYL-1,2,3-TRIPHOSPHAINDAN WITH TRIRUTHENIUM CLUSTER

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*Reactions of 1,2,3-triphenyl-1,2,3-triphosphaindan (**I**), $C_6H_4(PPh)_3$, with $[Ru_3(CO)_{12}]$ under various conditions result in the rupture of the P_3C_2-ring framework in the ligand and the cleavage of the M—M bonds in the parent cluster, leading to the formation of a series of phosphido bridged and phosphinidene capped trinuclear or polyhedral ruthenium clusters: a tetra-nuclear butterfly-like cluster $[Ru_4(CO)_{10}(\mu_3\text{-}PPh)]$ **1**, a tri-nuclear bent-chain skeleton cluster $[Ru_3(CO)_9\{\mu_3\text{-}\eta^3\text{-}PPhC_6H_4(PPh)_2\}]$ **2**, and a nonplanar six-atom-raft rhombic geometry cluster $[Ru_6(CO)_{12}(\mu_3\text{-}PPh)(\mu_4\text{-}PPh)_2(\mu_3\text{-}\eta^2\text{-}C_6H_4)]$ **3**. All compounds have been fully characterized by spectroscopic methods, while the molecular structures of the new compounds **2** and **3** are established by X-ray crystallographic techniques.*

Keywords: Cluster; phosphorus; ruthenium; triphosphaindan

INTRODUCTION

The reactions of homocyclic phosphines $(PR)_n$ (R = Ph,[1a–c] Et,[1c–e] CF_3,[1f] or Bu^t;[2] n = 4 or 5) with Group VIIIA metals (Fe, Ru, Os) carbonyl clusters have been extensively studied; however, less attention has been paid to the heterocyclic polyphosphines. For the investigated ligand 1,2,3-triphenyl-1,2,3-triphosphaindan (**I**), its reactions with Fe_2, Fe_3, and Os_3 carbonyl cluster have been reported by King[3–4] and our group,[5] respectively, to give a series of metal cluster derivatives with coordination of ligand (**I**) either intact or with the cleavage of one or two endocyclic phosphorus-phosphorus bonds, but without the observation of breakage of endocyclic P—C bonds. This paper reports an

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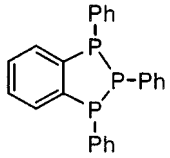
in-depth investigation of the reactions of (**I**) with triruthenium carbonyl clusters.



(**I**)

RESULTS AND DISCUSSION

The reaction of (**I**) with a two-fold molar amount of $[Ru_3(CO)_{12}]$ in toluene at 110°C for 2 h gives rise to a tetra-nuclear butterfly cluster $[Ru_4(CO)_{10}(\mu_3\text{-PPh})]$ **1**, and a tri-nuclear bent-chain cluster $[Ru_3(CO)_9\{\mu_3\text{-}\eta^3\text{-}PPhC_6H_4(PPh)_2\}]$ **2** in moderate yields (15% and 8%, respectively) after TLC separation using CH_2Cl_2-hexane (1/4) as eluent. When the reaction temperature is raised to 150°C, a nonplanar six-atom-raft rhombic geometry cluster $[Ru_6(CO)_{12}(\mu_3\text{-PPh})\ (\mu_4\text{-PPh})_2\ (\mu_3\text{-}\eta^2\text{-}C_6H_4)]$ **3** is afforded in 7% yield. When an equimolar amount of (**I**) reacts with $[Ru_3(CO)_{12}]$ at 100°C, only cluster **2** is isolated and characterized. Cluster **1** has been earlier reported to be the product from the pyrolysis of $[Ru_3(CO)_9(\mu\text{-}PPh_2)(\mu\text{-}H)_2]$.[5]

The spectroscopic data of all the clusters obtained are given in Table I. The carbonyl stretching vibrations fall in the region between 2150 and 1900 cm^{-1}, indicating that all carbonyl groups are terminal. The ^1H NMR spectra only show the resonance signals for the phenyl protons.

TABLE I Spectroscopic Data for Clusters **1** to **3**

Cluster	IR, ν(CO)[a]/cm^{-1}	^1H NMR[b]	$^{31}P\{^1H\}$ NMR[b]
1	2097w, 2061vs,	6.5–7.8	88.7 (s)
	2050m, 2042w, 2010w	(m, Ph)	
2	2069s, 2046vs,	6.6–8.2	112.5 (d, 272.0, P^1/P^2)
	2015s, 2006s,	(m, Ph)	27.6 (dd, 272.0, 20.4, P^1/P^2)
	1985w, 1975w		9.2 (d, 20.4, P^3)
3	2080w, 2061s,	6.8–8.2	87.2 (d, P^2 and P^3)
	2038s, 2027s, 2002w	(m, Ph)	−51.2 (t, 272.0, 20.4, P^1)

[a] In CH_2Cl_2.
[b] In $CDCl_3$ with $SiMe_4$ for ^1H and 85% H_3PO_4 for ^{31}P as reference.

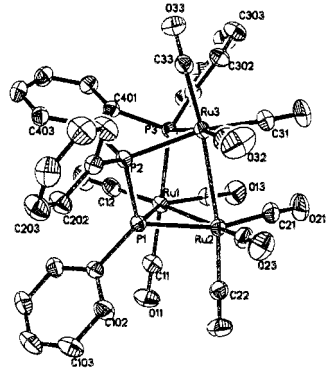


FIGURE 1 Molecular structure of **2** with H-atom omitted. Selected bond distances: Ru(1)-Ru(2) 2.8620(3); Ru(2)-Ru(3) 2.9456(3); Ru(1)...Ru(3) 3.903; Ru(1)-P(1) 2.3467(6); Ru(1)-P(3) 2.4041(6); Ru(2)-P(1) 2.3042(6); Ru(3)-P(2) 2.3552(6); Ru(3)-P(3) 2.3861(6); P(1)-P(2) 2.1806(8).

Molecular Structure of 2

The $^{31}P\{^{1}H\}$ NMR spectrum of **2** exhibits an AMX spin pattern, as indicated in Table I. From the ^{31}P NMR spectrum, we can deduce that the P_3C_2-ring framework of the ligand (**I**) moiety in the cluster has been ruptured with the cleavage of one P—P bond. The elemental analysis results are in accordance with the formula $C_{33}H_{19}O_9P_3Ru_3$: C, 42.28(41.46); H, 2.35 (1.99); P, 9.02(9.74).

The molecular structure of **2** is shown in Figure 1, together with the atomic labeling scheme and the selected bond parameters listed below. Analogous structures containing Fe and Os have been reported before.[3b,4] The skeleton contains a bent-chain arrangement of triruthenium atoms with an angle of 84.450(7)°, which is supported by the ligand **I** fragments with one of the P—P bonds broken. The three Ru atoms and three P atoms define the vertices of a distorted trigonal prism with a nonbonded P—P edge linked to two carbon atoms of the fused phenyl ring.

Molecular Structure of 3

The molecular structure of **3** is illustrated in Figure 2, together with atomic labeling scheme and some selected bond parameters that are listed below. In the structure of **3**, six Ru atoms constitute a nonplanar six-atom-raft rhombic (or two edge-fused butterflies) geometry skeleton, with the two internal triangles approximately coplanar (with dihedral angle of 165.8°) and each of the two external triangles nearly

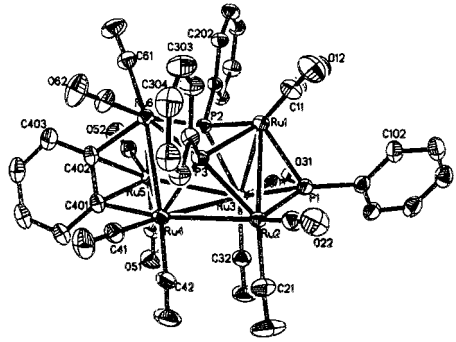


FIGURE 2 Molecular structure of **3** with H-atom omitted. Selected bond distances: Ru(1)-Ru(2) 2.8696(3); Ru(1)-Ru(3) 2.8650(3); Ru(2)-Ru(3) 2.8842(3); Ru(2)-Ru(4) 2.8136(3); Ru(3)-Ru(4) 3.0914(3); Ru(3)-Ru(5) 2.8083(3); Ru(4)-Ru(5) 2.7241(3); Ru(4)-Ru(6) 2.8774(3); Ru(5)-Ru(6) 2.7589(3).

perpendicular to its corresponding internal triangle (with dihedral angles of 78.3 and 79.4°, respectively). The six Ru atoms constitute a boat configuration. The two edge-fused butterfly geometry metal skeleton supports the ligands; a μ_3-PPh, two μ_4-PPh, and a μ_3-η^2-C_6H_4, which are formed by formal cleavage of the two P—P bonds and the two P—C(sp) bonds in the P_3C_2-ring of the ligand (**I**). One of the external triangles (Ru(1)Ru(2)Ru(3)) is capped asymmetrically by the μ_3-phosphinidene P(1) with P(1)-Ru(2) (2.2096(8) Å) a little shorter than the other two P—Ru bonds (average 2.2826(8) Å), while the other one is capped by the μ_3-η^2-benzyne, which derives from the formal cleavage of two P—C(sp) bonds in the fused phenyl ring of the ligand. The two μ_4-phosphinidenes each caps the two wing-tip atoms Ru(1), Ru(6) and an edge of the base of the boat structure comprising the six Ru atoms. The Ru-Ru distances cover a wide range of 2.7241(3)–3.0914(3) Å. The longest bond is the diagonal of the Ru(2)Ru(3)Ru(4)Ru(5) rhomboid. The valence electron count for cluster **3** leads to 88, which is 2 electrons fewer than the EAN rule for the rhombic-raft geometry.

The $^{31}P\{^1H\}$ NMR spectrum exhibits two kinds of resonance signals with an integration intensity ratio of 2:1, which supports the X-ray structure. Elemental analytical results are in accordance with the formula $C_{36}H_{19}O_{12}P_3Ru_6$: C, 32.58(32.17); H, 1.67(1.41); P, 6.12(6.92).

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