Journal of Organometallic Chemistry, 445 (1993) 211–217

JOM 23145

Cluster chemistry

LXXXVI *. Metallation of pyridine in reactions with an Ru_5 cluster. X-Ray structures of $Ru_4\{\mu_4\text{-}C_2H(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}NC_5H_4)(CO)_{10} \cdot CH_2Cl_2$ and $Ru_6(\mu_6\text{-}C_2H)(\mu_3\text{-}NC_5H_4)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{12} \cdot 1.25CHCl_3$

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(Received July 29, 1992)

Abstract

Reaction of the open Ru_5 cluster $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (1) with pyridine yields $Ru_4\{\mu_4\text{-}C_2H(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}NC_5H_4)(CO)_{10}$ (3) and $Ru_6(\mu_6\text{-}C_2H)(\mu_3\text{-}NC_5H_4)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{12}$ (4). The metal core of 4 has an unusual structure, being a *nido* pentagonal pyramid, although a better representation is based on a metallated pseudo-octahedral C_2Ru_4 skeleton. Complex 3 contains a vinylidene $[C{=}CH(PPh_2)]$, whereas 4 contains the first example of a μ_6-alkynyl ligand (C_2H), formed by a P–C bond cleavage in the C_2PPh_2 ligand in 1. Both clusters contain a 2-metallated pyridine ligand, with the displaced H atom adding to the C_2PPh_2 group. The X-ray crystal structures of 3 and 4 were determined. Crystals of 3 were monoclinic, space group $P2_1/c$, $a = 14.148(4)$, $b = 16.491(11)$, $c = 21.026(12)$ Å, $\beta = 115.22(3)°$; $V = 4438$ Å^3, $Z = 4$; 6802 observed data ($I \geq 3\sigma(I)$) were refined to $R = 0.033$ ($R_w = 0.041$). Crystals of 4 were monoclinic, space group $C2/c$, $a = 34.139(9)$, $b = 14.689(4)$, $c = 22.006(7)$ Å, $\beta = 96.08(2)°$; $V = 10973$ Å^3, $Z = 8$; 6127 observed data were refined to $R = 0.043$ ($R_w = 0.044$).

1. Introduction

We have been interested in the synthesis of cluster complexes containing the C_2 ligand, starting from the open Ru_5 cluster $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (1; Scheme 1); reactions with CO [2] and Me_2S_2 [3] have given such species. More recently, we communicated an account of a third complex, $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{11}(py)_2$ (2), obtained from the reaction between 1 and pyridine [4]. From this reaction, we have also isolated two other complexes, the yellow tetranuclear derivative $Ru_4\{\mu_4\text{-}C_2H(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}NC_5H_4)(CO)_{10}$ (3) and the black hexanuclear cluster $Ru_6(\mu_6\text{-}C_2H)(\mu_3\text{-}NC_5H_4)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{12}$ (4), both of which have been fully characterized by X-ray crystallographic studies and are described below.

2. Results

The reaction between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (1) and pyridine was carried out in benzene at 90°C for 4 h. Preparative thin-layer chromatography was used to separate three major products, which were identified as $Ru_4\{\mu_4\text{-}C_2H(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}NC_5H_4)(CO)_{10}$ (3), $Ru_6(\mu_6\text{-}C_2H)(\mu_3\text{-}NC_5H_4)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{12}$ (4) and $Ru_5(\mu_5\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{11}(py)_2$ (2) by single-crystal X-ray studies.

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* For Part LXXXV, see ref. 1.

0022-328X/93/$6.00

2.1. Molecular structure of $Ru_4\{\mu_4\text{-}C_2H(PPh_2)\}(\mu\text{-}PPh_2)(\mu\text{-}NC_5H_4)(CO)_{10}$ (3)

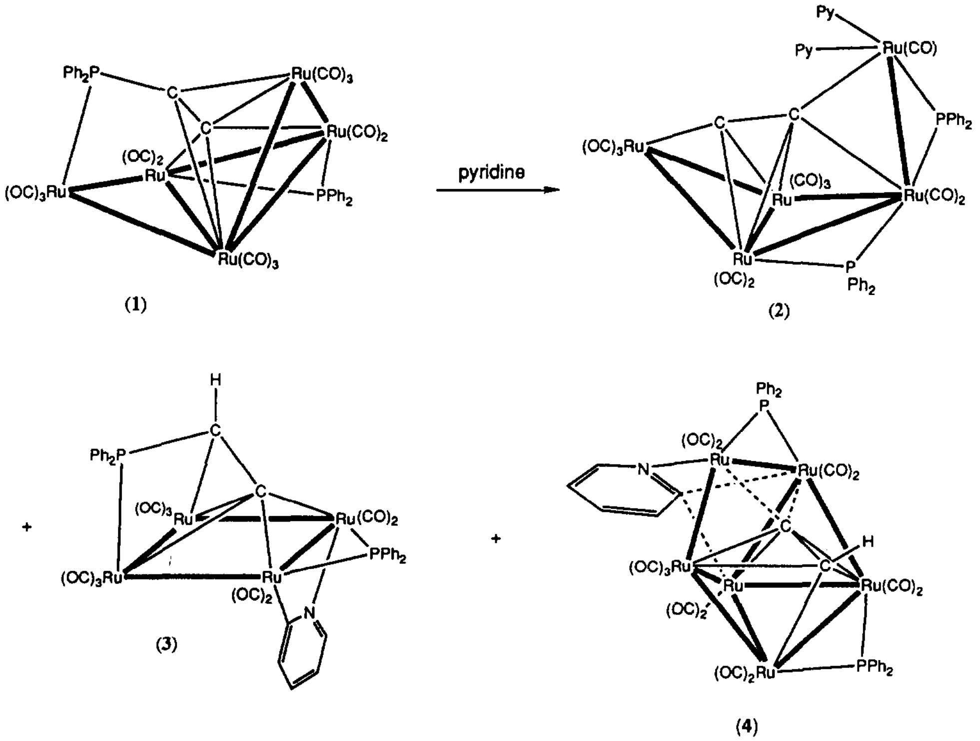
A molecule of **3** is depicted in Fig. 1 and selected bond parameters are given in Table 1. The molecule consists of an Ru_4 rhombus with edges between 2.783(1) and 3.018(1) Å; the Ru_4 core is bent about the Ru(2) ··· Ru(4) axis with a dihedral angle of 161.93(5)°. The C_2P unit is attached to all four Ru atoms via Ru–C σ bonds to C(2) [Ru–C(2) 2.129–2.217(4) Å], by an η^2 interaction between C(1)–C(2) and Ru(4) [Ru(4)–C(1) 2.204(4), Ru(4)–C(2) 2.064(4) Å] and by P(1) to Ru(1) [Ru(1)–P(1) 2.373(2) Å]. The Ru(2)–Ru(3) edge (the shortest) is also symmetrically bridged by the PPh_2 group [Ru(2)–P(2) 2.309(2), Ru(3)–P(2) 2.317(2) Å] and by a 2-metallated pyridine ligand [Ru(2)–C(102) 2.085(4), Ru(3)–N(101) 2.119(4) Å]. The latter distances are similar to those found in the two isomers of $Ru_5C(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_{14}$ [Ru–C 2.080(5), 2.131(15); Ru–N 2.169(4), 2.134(12) Å, for isomers **a**, **b**, respectively] [5].

Location and refinement of a difference map residue near C(1) suggests that a hydrogen atom is attached to this atom, probably originating from the pyridine molecule. The C(1)–C(2) separation is long at 1.459(7) Å and angle P(1)–C(1)–C(2) is 102.5(3)°, both more consistent with a coordinated C=C double bond than with the C≡C triple bond originally present in the C_2PPh_2 ligand in **1**. The ligand is thus best viewed as a μ_4-vinylidene, C=CH(PPh_2), of which C(2) is strongly bonded to Ru(2) and Ru(3) and less so to Ru(1); the C(1)–Ru(4) bond is similar to that found in $Ru_5(\mu_5\text{-}C_2H)(\mu\text{-}SPh)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{11}$ (**5**) [6].

The ^1H and ^{13}C NMR spectra are also consistent with the formulation as a metallated vinylidene. The ^1H NMR spectrum contains a resonance at δ 4.67 (d, J(HP) = 5.1 Hz) which is assigned to the CCH(PPh_2) proton. The ^{13}C NMR spectrum contains resonances at δ 89.79 and δ 231.22 (d, J(CP) = 10.6 Hz) which are

TABLE 1. Selected bond lengths (Å) and angles (°) for $Ru_4(\mu_4\text{-}C_2H(PPh_2))(\mu\text{-}PPh_2)(\mu\text{-}NC_5H_4)(CO)_{10}$ (3)

Ru(1)–Ru(2)	3.018(1)	Ru(3)–N(101)	2.119(4)
Ru(1)–Ru(4)	2.857(1)	Ru(1)–C(2)	2.217(4)
Ru(2)–Ru(3)	2.783(1)	Ru(2)–C(2)	2.129(5)
Ru(3)–Ru(4)	2.898(1)	Ru(3)–C(2)	2.164(4)
Ru(1)–P(1)	2.373(2)	Ru(4)–C(2)	2.064(4)
Ru(2)–P(2)	2.309(2)	Ru(4)–C(1)	2.204(4)
Ru(3)–P(2)	2.317(2)	C(1)–C(2)	1.459(7)
Ru(2)–C(102)	2.085(4)	C(1)–P(1)	1.769(4)
Ru–CO	Range 1.885–1.940(5), av. 1.912 Å		
C–O	Range 1.126–1.146(6), av. 1.136 Å		
P–C(Ph)	Range 1.819–1.832(6), av. 1.824 Å		
Ru(1)–Ru(2)–Ru(3)	88.58(4)	Ru(2)–Ru(1)–Ru(4)	87.57(5)
Ru(1)–Ru(4)–Ru(3)	89.57(4)	Ru(2)–Ru(3)–Ru(4)	91.41(4)



Scheme 1.

assigned to C(1) and C(2), respectively. The NMR spectra contain other signals in the aromatic regions, as expected from the other groups present; resonances at δ 121.5 (C(105)), 152.7 (C(106)) and 180.9 (C(102)) ppm could be assigned to three of the pyridine carbons as indicated. The resonances of the CO groups are found between δ 188–206 ppm. No Ru–H resonance was detected in the ^1H NMR spectrum.

The cluster is electron-precise at 64e; each Ru atom has an 18e configuration if C(2) is considered to be σ bonding to Ru(2) and Ru(3) and the C=C group is π-bonded to Ru(4). Although Ru(4) is within bonding distance of C(2), no formal electron donation is required from this carbon. The CRu_4 moiety is a common feature of complexes derived from **1** and it is likely that detailed calculations of its electronic structure would reveal a stable electronic configuration for this unit.

2.2. *Molecular structure of* $Ru_6(\mu_6\text{-}C_2H)(\mu_3\text{-}NC_5H_4)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{12}$ *(4)*

A molecule of **4** is depicted in Fig. 2 and selected bond parameters are given in Table 2. The metal core is best considered as based on a C_2Ru_4 octahedron. Of this, Ru(3) and Ru(5) are the wing-tip atoms and Ru(4) and Ru(6) are the hinge atoms of the Ru_4 butterfly. The Ru(4)–Ru(5) edge is bridged by Ru(1); this part of the cluster resembles the Ru_5 cluster present in **1**. The wing-tip atoms of this "swallow" cluster, Ru(1) and Ru(3), are bridged by Ru(2). The Ru–Ru separations fall into the range 2.719–2.977(1) Å (av. 2.839 Å) with the Ru(3)–Ru(6) separation the shortest and the Ru(1)–Ru(5) vector the longest.

The C_2H ligand interacts with the four Ru atoms of the C_2Ru_4 octahedron in the usual fashion, similar to that found in $Ru_4(\mu_4\text{-}C_2Ph_2)(CO)_{12}$ [7]. Atom C(1) also bridges the Ru(1)–Ru(2) vector [Ru(1)–C(1) 2.143(8), Ru(2)–C(1) 2.274(8) Å]; the C(1)–C(2) separation [1.40(1) Å] is shorter than the corresponding bond in **3**. Consequently, this is the first example of a μ_6-acetylide ligand. It is formed via C–P bond cleavage in the C_2PPh_2 group in **1** along with concomitant addition of an H atom, presumably that from the pyridine ligand. The ^1H and ^{13}C NMR spectra of **4** were consistent with the solid-state structure. In particular, a resonance at δ 6.14 in the ^1H NMR spectrum was assigned to the alkyne proton attached to C(2), which was not refined in the X-ray determination. A standard 2D COSY spectrum showed this peak was not a phenyl or pyridyl proton due to its lack of

TABLE 2. Selected bond lengths (Å) and angles (°) for $Ru_6(\mu_6\text{-}C_2H)(\mu_3\text{-}NC_5H_4)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{12}$ (**4**)

Ru(1)–Ru(2)	2.798(1)	Ru(4)–C(102)	2.340(8)
Ru(1)–Ru(4)	2.835(1)	Ru(2)–N(101)	2.124(6)
Ru(1)–Ru(5)	2.977(1)	Ru(1)–C(1)	2.143(8)
Ru(2)–Ru(3)	2.825(1)	Ru(2)–C(1)	2.274(8)
Ru(3)–Ru(4)	2.880(1)	Ru(3)–C(1)	2.148(9)
Ru(3)–Ru(6)	2.719(1)	Ru(4)–C(1)	2.178(8)
Ru(4)–Ru(5)	2.774(1)	Ru(5)–C(1)	2.455(9)
Ru(4)–Ru(6)	2.877(1)	Ru(3)–C(2)	2.244(8)
Ru(5)–Ru(6)	2.869(1)	Ru(5)–C(2)	2.307(9)
Ru(1)–P(2)	2.317(2)	Ru(6)–C(2)	2.217(8)
Ru(2)–P(2)	2.316(2)	C(1)–C(2)	1.40(1)
Ru(5)–P(1)	2.254(3)	Ru(3)–C(32)	1.959(9)
Ru(6)–P(1)	2.289(3)	Ru(6)–C(32)	2.45(9)
Ru(1)–C(102)	2.129(8)		
Ru–CO	Range 1.83(1)–1.928(8), av. 1.886 Å		
C–O	Range 1.11–1.17(1), av. 1.14 Å		
P–C(Ph)	Range 1.806–1.842(9), av. 1.829 Å.		
Ru(2)–Ru(1)–Ru(5)	106.39(3)	Ru(3)–Ru(4)–Ru(6)	56.36(3)
Ru(1)–Ru(2)–Ru(3)	93.56(3)	Ru(5)–Ru(4)–Ru(6)	60.99(3)
Ru(2)–Ru(3)–Ru(6)	126.47(4)	Ru(2)–Ru(1)–Ru(4)	83.43(3)
Ru(1)–Ru(5)–Ru(6)	108.92(4)	Ru(2)–Ru(3)–Ru(4)	82.14(3)
Ru(3)–Ru(6)–Ru(5)	93.74(4)	Ru(1)–C(102)–Ru(4)	78.6(3)
Ru(1)–Ru(4)–Ru(3)	91.61(3)	Ru(3)–C(32)–O(32)	158.1(9)
Ru(1)–Ru(4)–Ru(5)	64.12(3)		
Dihedrals:	Ru(1)–Ru(4)–Ru(5)/Ru(4)–Ru(5)–Ru(6) 40.37(4)° Ru(3)–Ru(4)–Ru(6)/Ru(4)–Ru(5)–Ru(6) 64.87(4)° Ru(1)–Ru(3)–Ru(5)–Ru(6)/Ru(1)–Ru(2)–Ru(3)– Ru(4) 42.79(3)°		

coupling to any other resonances. No resonances were observed in the metal hydride region. The ^{13}C spectrum contained resonances at δ 89.77 and 319.29 assigned to C(2) and C(1), respectively; three of the five pyridine carbons were found at δ 121.4, 152.7 and 180.7 ppm.

Phosphido groups symmetrically bridge the Ru(1)–Ru(2) [Ru(1)–P(2) 2.317(2), Ru(2)–P(2) 2.316(2) Å] and Ru(5)–Ru(6) vectors [Ru(5)–P(1) 2.254(2), Ru(6)–P(1) 2.289(3) Å]. The 2-metallated pyridine group is attached to Ru(2) by N(101) [Ru(2)–N(101) 2.124(6) Å] while C(102) asymmetrically bridges Ru(1) and Ru(4) [Ru(1)–C(102) 2.129, Ru(4)–C(102) 2.340(8) Å]. The Ru(3)–Ru(6) vector is semi-bridged by a CO group [Ru(3)–C(32) 1.959(9), Ru(6)–C(32) 2.45(1) Å; Ru(3)–C(32)–O(32) 158.1(9)°].

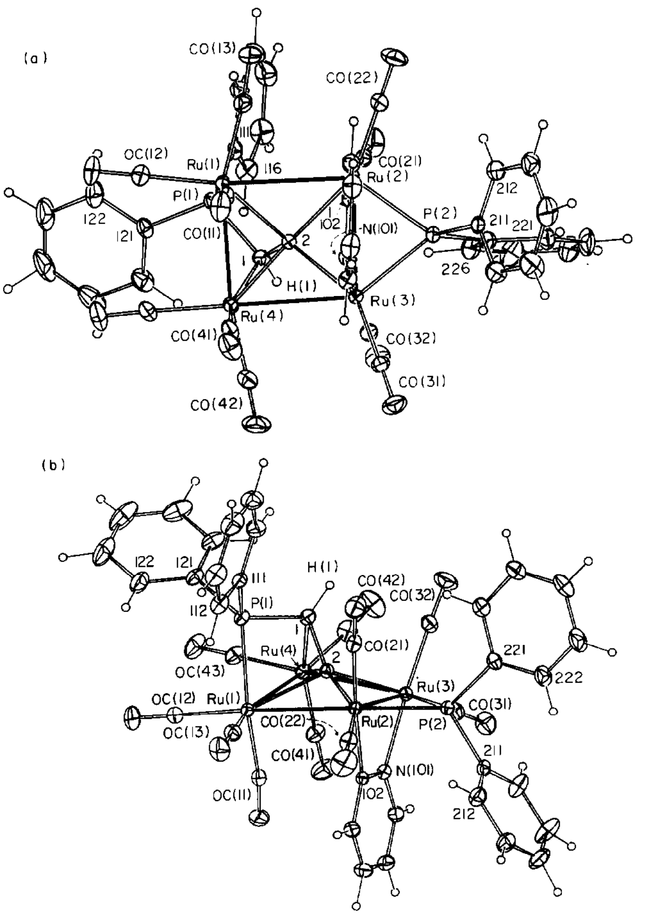


Fig. 1. Plot of molecule of $Ru_4(\mu_4\text{-}C_2H(PPh_2))(\mu\text{-}PPh_2)(\mu\text{-}NC_5H_4)(CO)_{10}$ (3) (a) normal and (b) oblique to the Ru_4 "plane" ($\chi^2 = 4.6\times10^5$; deviations of Ru(1-4) 0.1701, −0.1467, 0.1547, −0.1749(5) Å) showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

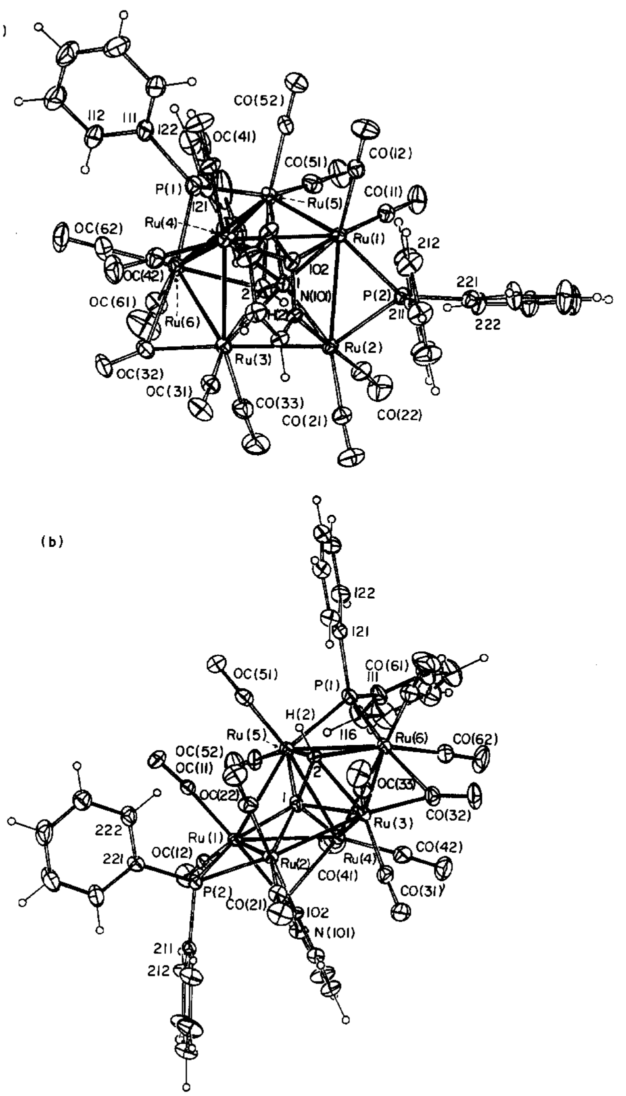


Fig. 2. Plot of a molecule of $Ru_6(\mu_6\text{-}C_2H)(\mu_3\text{-}NC_5H_4)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{12}$ (4) (a) normal and (b) oblique to the Ru_4 "plane" ($\chi^2 = 2.2\times10^5$; deviations of Ru(1-4) ± 0.28 Å), showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

The electron count based on a $[C_2Ru_4 + Ru_2]$ polyhedron is 88e as required, there being nine Ru–Ru bonds; the structure contains a novel core geometry for an Ru_6 cluster.

As described earlier [4], **2** was found to be a spiked butterfly holding a C_2 ligand attached to all five metal atoms. Two unmetallated pyridine ligands are attached to the spike Ru atom. Structurally it is related to **4**, but with the C_2 moiety orthogonal to the hinge. In this case, the C_2Ru_4 moiety forms a capped trigonal bipyramid. Alternatively, it can be considered to be an example of a μ_3-$\eta^2(\perp)$-acetylide, the normal substituent of the RC_2 group being replaced by a bridging interaction with the two remaining Ru atoms, as also found in **4**.

The reaction between pyridine and **1** resulted in the formation of at least three complexes. In **2**, addition of pyridine to one Ru atom resulted in cleavage of the P–C(sp) bond of the cluster-bound C_2PPh_2 ligand as well as two Ru–Ru bonds, to give a complex containing the sought-after C_2 ligand. In **3** and **4**, metallation of the pyridine has occurred; in both, migration of the H atom to C_β of the phosphino-acetylide has occurred, probably via the cluster. In **3**, this results in formation of a cluster-bound phosphinovinylidene, whereas in **4**, the P–C(sp) bond cleaves to give the ethynyl ligand. These reactions of the C_2PPh_2 ligand are accompanied by cluster rearrangements and loss (for **3**) or addition (for **4**) of one ruthenium atom. A possible disproportionation of two molecules of a pentanuclear pyridine-containing complex might lead to these complexes, but we have been unable to detect any intermediate of this type.

Several complexes containing the metallated μ-C_5H_4N ligand attached to ruthenium clusters have been described [6], most recently in complexes derived from reactions between $Ru_3(CO)_{12}$ and $Ru(CO)_2(Spy)_2$, which included $Ru_5(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{11}$, containing a pentagonal bipyramidal S_2Ru_5 core [7]. Transfer of hydride to the metal core is usually observed (except in the latter case, where the C_5H_4N ligand is already present in the precursor); as mentioned already, the formation of **3** and **4** requires this hydrogen to migrate further onto the organic ligands.

3. Conclusions

When the open μ_5-C_2PPh_2-containing cluster **1** reacts with pyridine complexes **2** [4], **3** and **4** are obtained. Complex **3** contains a μ_4-metallated vinylidene ligand and **4** containes a μ_6-alkynyl group. In the case of **4**, the μ_6-C_2H was produced from a C–P bond cleavage of the C_2PPh_2 ligand in **1**. Both **3** and **4** contain 2-metallated pyridine ligands, the latter exhibiting a μ_3 bonding mode via carbon bridging an Ru–Ru bond.

4. Experimental details

General experimental conditions were similar to those described earlier [8]. Complex **1** was prepared by the published method [9]. Pyridine (BDH) was used as received.

4.1. Reaction of 1 with pyridine

A solution of complex **1** (300 mg, 0.237 mmol) in benzene (10 cm^3) and pyridine (1 cm^3) was heated in a Carius tube at 90°C for 4 h. The solvent was removed and the residue purified by preparative TLC (petroleum ether/acetone 4:1). A yellow band (R_f 0.6) was recrystallized (CH_2Cl_2/MeOH) to give **3** (92 mg, 33%), m.p. 224–226°C (dec.). Anal. Found: C, 40.92; H, 2.28; N, 1.16; M^+, 1159 (mass spectrometry). $C_{41}H_{25}NO_{10}P_2Ru_4 \cdot CH_2Cl_2$ calc.: C, 40.59; H, 2.19; N, 1.13%; M, 1159. IR (cyclohexane): ν(CO) 2063m, 2037 sh, 2030vs, 2008m, 2000m, 1999sh, 1982m, 1971m, 1958m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.67 (1H, d, J(HP) = 5.1 Hz, $CH(PPh_2)$); 5.98 (2H, t, J(HH) = 5.9 Hz, py + Ph); 6.32 (2H td, J(HH) = 7.6, 1.6 Hz, py + Ph); 6.86 (2H, d, J(HP) = 7.7 Hz, py + Ph); 7.04–7.66 (18H, m, py + Ph). ^{13}C NMR ($CDCl_3$): δ 89.79 (s, C(1)); 121.45 (s, C(105)); 125.95–133.41 (m, Ph); 136.50 (d, J(CP) = 42.3 Hz, *ipso* C (PPh)); 137.56 (d, J(CP) = 11.3 Hz, *ipso* C(PPh)); 139.84 (d, J(CP) = 26.4 Hz, *ipso* C (PPh)); 142.51 (d, J(CP) = 37.0 Hz, *ipso* C (PPh)); 152.74 (s, C(106)); 180.87 (s, C(102)); 188.73 (s, CO); 194.23 (d, J(CP) = 12.8 Hz, CO); 194.69 (s, CO); 196.76 (s, CO); 199.23 (d, J(CP) = 9.1 Hz, CO); 201.13 (d, J(CP) = 9.8 Hz, CO); 201.48 (s, CO); 202.34 (s, CO); 205.63 (s, CO); 231.22 (d, J(CP) = 10.6 Hz, C(2)). FAB MS: m/z 1159, M^+; 1131–879, $[M - nCO]^+$ (n = 1–10). A black band (R_f 0.5) was recrystallized (CH_2Cl_2/MeOH) to give **4** (73 mg, 22%), m.p. 267–271°C (dec.). Anal. Found: C, 36.50; H, 1.82; N, 1.00; M^+, 1445 (mass spectrometry). $C_{44}H_{25}NO_{13}P_2Ru_6$ calc.: C, 36.60; H, 1.74; N, 0.97%; M, 1445. IR (cyclohexane): ν(CO) 2054w, 2026vs, 2004w, 1990s, 1981m, 1965w, 1933w cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.14 (1H, s, C_2H); 6.32 (1H, t, J(HH) = 6.2 Hz, py); 6.67–7.57 (23H, m, Ph and Py). ^{13}C NMR ($CDCl_3$): δ 89.77 (s, C_2H); 121.44 (s, C(105)); 125.95–133.36 (m, Ph); 136.17–137.50 (m, *ipso* C (PPh); 139.83 (d J(CP) = 24.9 Hz, *ipso* C (PPh)); 142.47 (d J(CP) = 38.5 Hz, *ipso* C(PPh)); 152.70 (s, C(106)); 180.67 (s, C(102)); 186.76 (s, CO); 194.3 (s, CO); 194.70 (s, CO); 196.76 (s, CO); 199.21 (s, CO); 201.12 (d, J(CP) = 13.6 Hz, CO); 201.46 (s, CO); 202.32 (d, J(CP) = 9.8 Hz, CO); 205.64 (s, CO); 319.29 (d, J(CP) = 11.3 Hz, C_α). FAB MS: m/z 1445, M^+; 1417–1081 $[M - nCO]^+$ (n = 1–13). A brown band (R_f 0.25) was recrystallized (CH_2Cl_2/MeOH) to yield black crystals of **2** (32 mg, 10%) [4].

5. Crystallography

Unique diffractometer data sets were measured at *ca.* 295 K within the limit $2\theta_{max} = 50°$ (2θ–θ scan mode; monochromatic Mo Kα radiation, λ 0.7107$_3$ Å); N independent reflections were obtained, N_o with

TABLE 3. Non-hydrogen positional and isotropic displacement parameters (**3**)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.18782(3)	0.38871(2)	0.10547(2)	0.0315(1)
Ru(2)	0.25917(3)	0.29898(2)	0.00859(2)	0.0288(1)
Ru(3)	0.38985(3)	0.20647(2)	0.12305(2)	0.0292(1)
Ru(4)	0.28677(3)	0.26488(2)	0.20735(2)	0.0333(1)
C(11)	0.3171(4)	0.4488(3)	0.1509(3)	0.048(2)
O(11)	0.3871(3)	0.4889(2)	0.1829(2)	0.071(2)
C(12)	0.1342(4)	0.4564(3)	0.1563(3)	0.050(2)
O(12)	0.1024(3)	0.4962(3)	0.1863(2)	0.082(2)
C(13)	0.1360(4)	0.4491(3)	0.0196(3)	0.048(2)
O(13)	0.1055(3)	0.4918(2)	−0.0272(2)	0.072(2)
C(21)	0.1378(3)	0.2361(3)	−0.0511(2)	0.042(2)
O(21)	0.0698(3)	0.2017(3)	−0.0914(2)	0.073(2)
C(22)	0.2353(4)	0.3632(3)	−0.0710(2)	0.049(2)
O(22)	0.2216(3)	0.4037(3)	−0.1183(2)	0.091(2)
C(31)	0.5209(4)	0.1648(3)	0.1852(2)	0.045(2)
O(31)	0.6019(3)	0.1421(2)	0.2236(2)	0.071(2)
C(32)	0.3338(4)	0.1016(3)	0.1176(2)	0.045(2)
O(32)	0.3065(3)	0.0366(2)	0.1177(2)	0.076(2)
C(41)	0.4185(4)	0.3155(3)	0.2641(2)	0.049(2)
O(41)	0.4973(3)	0.3430(3)	0.2990(2)	0.075(2)
C(42)	0.3295(4)	0.1633(3)	0.2540(2)	0.056(2)
O(42)	0.3516(4)	0.1022(2)	0.2816(2)	0.090(2)
C(43)	0.2168(4)	0.3024(3)	0.2633(2)	0.049(2)
O(43)	0.1784(3)	0.3241(3)	0.2975(2)	0.080(2)
C(1)	0.1602(3)	0.2179(3)	0.1103(2)	0.036(2)
C(2)	0.2411(3)	0.2635(2)	0.1001(2)	0.030(2)
P(1)	0.05741(9)	0.28920(7)	0.08655(6)	0.0346(4)
C(111)	−0.0486(3)	0.2677(3)	0.0001(2)	0.038(2)
C(112)	−0.0849(4)	0.3256(3)	−0.0530(2)	0.050(2)
C(113)	−0.1681(4)	0.3088(4)	−0.1160(3)	0.062(2)
C(114)	−0.2155(4)	0.2346(4)	−0.1275(3)	0.072(3)
C(115)	−0.1814(4)	0.1762(4)	−0.0762(3)	0.068(3)
C(116)	−0.0978(4)	0.1920(3)	−0.0122(3)	0.057(2)
C(121)	−0.0119(3)	0.2778(3)	0.1417(2)	0.043(2)
C(122)	−0.0777(4)	0.3396(4)	0.1437(3)	0.069(3)
C(123)	−0.1323(5)	0.3295(5)	0.1839(4)	0.104(4)
C(124)	−0.1234(5)	0.2610(6)	0.2204(4)	0.111(4)
C(125)	−0.0590(5)	0.2004(5)	0.2192(3)	0.094(4)
C(126)	−0.0036(4)	0.2090(4)	0.1797(3)	0.066(3)
P(2)	0.38238(9)	0.20583(7)	0.01082(6)	0.0323(4)
C(211)	0.4947(3)	0.2449(3)	−0.0007(2)	0.036(2)
C(212)	0.4821(4)	0.2964(3)	−0.0555(3)	0.052(2)
C(213)	0.5681(4)	0.3240(4)	−0.0644(3)	0.067(3)
C(214)	0.6650(4)	0.2998(4)	−0.0186(4)	0.080(3)
C(215)	0.6788(4)	0.2469(5)	0.0341(3)	0.088(3)
C(216)	0.5938(4)	0.2205(4)	0.0445(3)	0.067(3)
C(221)	0.3495(4)	0.1149(3)	−0.0434(2)	0.041(2)
C(222)	0.4068(4)	0.0906(3)	−0.0796(3)	0.059(3)
C(223)	0.3805(5)	0.0222(4)	−0.1211(3)	0.077(3)
C(224)	0.2952(5)	−0.0244(3)	−0.1268(3)	0.075(3)
C(225)	0.2400(5)	−0.0025(3)	−0.0901(3)	0.073(3)
C(226)	0.2651(4)	0.0667(3)	−0.0492(3)	0.054(2)
N(101)	0.4574(3)	0.3217(2)	0.1254(2)	0.036(1)
C(102)	0.3952(3)	0.3636(2)	0.0676(2)	0.030(2)
C(103)	0.4328(4)	0.4370(3)	0.0541(3)	0.045(2)
C(104)	0.5285(4)	0.4656(3)	0.0971(3)	0.054(2)
C(105)	0.5919(4)	0.4213(3)	0.1568(3)	0.054(2)
C(106)	0.5539(3)	0.3500(3)	0.1693(2)	0.043(2)
Cl(1)	−0.0142(2)	0.0066(1)	−0.0820(1)	0.136(2)
Cl(2)	−0.1211(3)	−0.0110(2)	−0.2302(2)	0.257(2)
C(0)	−0.0470(7)	0.0483(6)	−0.1651(4)	0.143(5)

TABLE 4. Non-hydrogen positional and isotropic displacement parameters (**4**)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.60024(2)	0.53121(5)	0.60969(3)	0.0325(4)
Ru(2)	0.67921(2)	0.51699(5)	0.58740(3)	0.0360(4)
Ru(3)	0.68553(2)	0.70389(5)	0.55985(3)	0.0387(4)
Ru(4)	0.60132(2)	0.68752(5)	0.53432(3)	0.0354(4)
Ru(5)	0.58965(2)	0.71949(5)	0.65533(3)	0.0397(4)
Ru(6)	0.63978(2)	0.84056(5)	0.59662(4)	0.0436(4)
C(11)	0.5973(3)	0.5231(6)	0.6965(4)	0.044(5)
O(11)	0.5941(2)	0.5101(5)	0.7466(3)	0.076(5)
C(12)	0.5472(3)	0.4906(6)	0.5967(4)	0.051(6)
O(12)	0.5156(2)	0.4671(6)	0.5878(3)	0.089(6)
C(21)	0.7228(3)	0.4583(6)	0.5574(4)	0.053(6)
O(21)	0.7496(2)	0.4230(5)	0.5433(3)	0.086(5)
C(22)	0.7100(3)	0.5264(6)	0.6636(4)	0.056(6)
O(22)	0.7297(2)	0.5300(5)	0.7077(3)	0.088(5)
C(31)	0.7003(3)	0.6563(7)	0.4873(4)	0.056(6)
O(31)	0.7102(2)	0.6302(5)	0.4415(3)	0.077(5)
C(32)	0.6898(3)	0.8258(6)	0.5251(4)	0.058(6)
O(32)	0.7010(2)	0.8816(5)	0.4964(4)	0.091(6)
C(33)	0.7383(3)	0.6989(7)	0.6001(4)	0.063(7)
O(33)	0.7681(2)	0.6937(6)	0.6252(3)	0.101(6)
C(41)	0.5465(3)	0.7100(6)	0.5212(4)	0.059(6)
O(41)	0.5139(2)	0.7245(5)	0.5104(4)	0.092(6)
C(42)	0.6090(3)	0.7602(7)	0.4686(4)	0.059(6)
O(42)	0.6130(2)	0.8025(5)	0.4250(3)	0.093(6)
C(51)	0.5934(3)	0.7143(6)	0.7390(4)	0.058(6)
O(51)	0.5939(2)	0.7108(5)	0.7921(3)	0.084(5)
C(52)	0.5362(3)	0.6921(6)	0.6549(4)	0.056(6)
O(52)	0.5039(2)	0.6748(5)	0.6557(4)	0.089(6)
C(61)	0.6780(3)	0.9172(7)	0.6381(5)	0.070(7)
O(61)	0.7011(3)	0.9637(6)	0.6620(4)	0.132(8)
C(62)	0.6230(3)	0.9332(7)	0.5383(4)	0.067(7)
O(62)	0.6122(3)	0.9864(5)	0.5028(3)	0.107(6)
C(1)	0.6425(2)	0.6392(5)	0.6098(4)	0.040(5)
C(2)	0.6563(2)	0.7126(5)	0.6464(3)	0.039(5)
P(1)	0.59168(8)	0.8728(2)	0.6584(1)	0.052(2)
C(111)	0.5503(3)	0.9444(6)	0.6263(5)	0.061(6)
C(112)	0.5579(3)	1.0350(7)	0.6127(5)	0.077(8)
C(113)	0.5288(4)	1.0904(8)	0.5859(6)	0.10(1)
C(114)	0.4923(4)	1.0575(8)	0.5728(6)	0.10(1)
C(115)	0.4835(3)	0.9690(8)	0.5842(7)	0.11(1)
C(116)	0.5136(3)	0.9115(7)	0.6108(6)	0.081(8)
C(121)	0.6061(3)	0.9250(6)	0.7335(4)	0.061(7)
C(122)	0.5820(4)	0.9825(7)	0.7614(5)	0.079(8)
C(123)	0.5948(4)	1.0181(7)	0.8192(5)	0.097(9)
C(124)	0.6308(5)	0.9960(8)	0.8469(5)	0.11(1)
C(125)	0.6545(4)	0.9399(7)	0.8202(5)	0.085(8)
C(126)	0.6429(3)	0.9034(7)	0.7636(5)	0.076(8)
P(2)	0.63753(7)	0.3995(2)	0.6087(1)	0.039(1)
C(211)	0.6271(3)	0.3191(5)	0.5457(4)	0.041(5)
C(212)	0.5896(3)	0.3071(6)	0.5168(4)	0.059(6)
C(213)	0.5832(3)	0.2498(7)	0.4667(5)	0.071(7)
C(214)	0.6139(3)	0.2044(7)	0.4454(5)	0.074(7)
C(215)	0.6506(3)	0.2141(7)	0.4743(5)	0.083(8)
C(216)	0.6575(3)	0.2715(7)	0.5252(5)	0.065(7)
C(221)	0.6457(3)	0.3265(6)	0.6749(4)	0.048(6)
C(222)	0.6602(3)	0.3628(6)	0.7311(4)	0.061(7)
C(223)	0.6651(3)	0.3094(7)	0.7832(5)	0.077(8)
C(224)	0.6563(4)	0.2195(8)	0.7781(5)	0.099(9)
C(225)	0.6435(4)	0.1819(8)	0.7234(5)	0.11(1)
C(226)	0.6374(3)	0.2344(7)	0.6716(5)	0.081(8)
N(101)	0.6426(2)	0.5110(4)	0.5032(3)	0.033(4)
C(102)	0.6049(2)	0.5316(5)	0.5140(4)	0.038(5)

TABLE 4 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(103)	0.5752(3)	0.5336(6)	0.4649(4)	0.049(6)
C(104)	0.5841(3)	0.5132(7)	0.4068(4)	0.068(7)
C(105)	0.6221(3)	0.4866(7)	0.3972(4)	0.059(6)
C(106)	0.6500(2)	0.4857(6)	0.4483(4)	0.043(5)
C(01)	0.7370(4)	0.665(1)	0.8319(6)	0.12(1)
Cl(11)	0.6876(1)	0.6498(4)	0.8187(2)	0.184(5)
Cl(12)	0.7523(1)	0.6535(4)	0.9064(2)	0.186(5)
Cl(13)	0.7488(2)	0.7668(4)	0.8016(3)	0.220(6)
C(02) [a]	0.4982(–)	0.3103(–)	0.7352(–)	0.17(3)
Cl(21) [a]	0.4687(–)	0.2832(–)	0.6769(–)	0.25(1)
Cl(22) [a]	0.4716(–)	0.3257(–)	0.7905(–)	0.44(3)
Cl(23) [a]	0.5243(–)	0.2281(–)	0.7548(–)	0.35(2)

[a] Population parameter = 0.25, isotropic refinement.

$I > 3\sigma(I)$ being considered "observed" and used in the full matrix least squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R′ on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 2.6 program system [10] implemented by Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the figures and tables.

TABLE 5. Crystal data and refinement details for **3** and **4**

Compound	**3**	**4**
Formula	$C_{41}H_{25}NO_{10}P_2Ru_4 \cdot CH_2Cl_2$	$C_{44}H_{24}NO_{13}P_2Ru_6 \cdot 1.25CHCl_3$
MW	1251.7	1592.3
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a (Å)	14.148(4)	34.139(9)
b (Å)	16.491(11)	14.689(4)
c (Å)	21.026(12)	22.006(7)
β (°)	115.22(3)	96.08(2)
U (Å^3)	4438.0	10973
Z	4	8
D_c (g cm^{-3})	1.87	1.93
$F(000)$	2424	6126
Crystal size (mm)	0.40×0.31×0.50	0.15×0.40×0.48
A^* (min, max)	1.43, 1.50	1.43, 1.79
μ (cm^{-1})	14.1	17.3
N	7802	9509
N_0	6802	6127
R	0.033	0.043
R_w	0.041	0.044

5.1. Abnormal features / variations in procedure

The core hydride of **3** was located as a difference map residue and refined in (x, y, z, U_{iso}); that of **4** was observed in a final difference map. Assignment of core-bonded pyridine C,N atoms in both structures was made on the basis of refinement behaviour and associated geometries **4** decomposed by ~ 10% during data collection and data were scaled accordingly.

Acknowledgements

We thank the Australian Research Council for financial support and Johnson Matthey Technology Centre for a generous loan of $RuCl_3 \cdot nH_2O$.

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