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Coupling of two alkynes with a carbon and an oxygen atom on an Ru_3 cluster *

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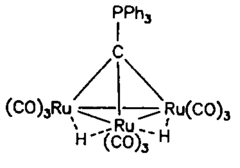
Abstract

The phosphonio alkylidyne bridged cluster $H_2Ru_3(CO)_9(\mu_3\text{-}C \cdot PPh_3)$ (1) reacts with hexyne-3 under increasingly forcing conditions to form successively the products $HRu_3(CO)_8(\mu_3\text{-}C \cdot PPh_3)(\mu\text{-}EtC=CHEt)$ (2), $Ru_3(CO)_7(\mu_3\text{-}C \cdot PPh_3)(\mu\text{-}EtC=CHEt)_2$ (3), and $Ru_3(CO)_8(PPh_3)(\mu_3\text{-}C_5Et_3Ac)$ (4). The constitution of 4 has been elucidated by a crystal structure determination. It contains an open $Ru_3(CO)_8(PPh_3)$ triangle held together by a (1-rutheno, 2,3,4,-triethyl, 5-acetyl) cyclopentadienyl ligand. The formation of this ligand appears to involve the combination of two hexyne-3 molecules with a CCO unit. Of the latter, one C and one O atom are incorporated into the metallocyclopentadienyl ligand while one C atom is expelled as CH_4.

1. Introduction

The motivation for the investigation of organic reactions in the ligand sphere of clusters rests heavily on the cluster-surface analogy [1] which states that stoichiometric cluster reactions may act as models of catalytic reactions on metal surfaces. Our interest in this field [2] has been centred mainly on trinuclear clusters containing isolelectronic E_2R_2 ligands ($E_2 = C_2$, CN, N_2) in the $\mu_3\text{-}\eta^2$ bonding mode [3]. Like others [4–6], we have observed that alkynes are good reagents for inducing interconversions of such substrates attached to several metal atoms [7–9].

We recently found a new substrate for cluster-centred interconversions in the form of the phosphonioalkylidyne ligand in the ruthenium cluster 1 [10]. We showed [11] that the reactivity of 1 towards alkynes corresponds essentially to that of the analogous μ_3-alkylidyne bridged clusters $H_2Ru_3(CO)_9(\mu_3\text{–}CR)$ [12] and $H_2Os_3(CO)_9(\mu_3\text{–}CR)$ [13] which undergo insertion of the RC≡CR unit into the M–H or M–(μ_3–C) bonds. Thus with hexyne-3, Ru–H insertion produced the μ-vinyl bridged cluster 2. We have now observed that 2 is only the starting point of a reaction sequence leading to the incorporation of two alkyne units and their combination with the alkylidyne carbon atom and a CO molecule to form a new organic molecule acting as a $\mu_3\text{-}\eta^7$ ligand.



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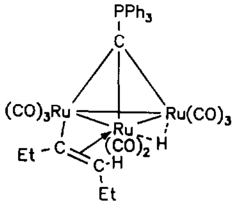

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2. Reactions and product identification

During the previously described synthesis of 2 from 1 and hexyne-3 in boiling cyclohexane for short periods [11], a mass spectrometric investigation of the raw product revealed a minor by-product 3 with a mass of about 940. It has now been shown that extending the reaction time to several hours increases the amount of this by-product which, however, is difficult to separate from 2. Use of the higher-boiling solvent toluene allowed the reaction (which was monitored by IR spectroscopy) to be taken to complete disappearance of 2 and gave the new compound 3 as the main product. At the same time, a further new product 4 was observed,

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* Dedicated to Professor Gian Paolo Chiusoli in recognition of his important contributions to organometallic chemistry.

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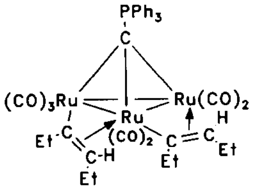
TABLE 1. IR (CH_2Cl_2, cm^{-1}) and ^1H-NMR (CD_2Cl_2, ppm, Hz, int. TMS) data of **3** and **4**

3	IR	2154w, 2124m, 2068w, 2044s, 2008vs, 1990vs, 1930sh, 1792w
	NMR	7.81–6.84(m, 15H, Ph); 3.17(m, 1H, $C\mathit{H}Et$); 2.90–2.62(m, 4H, $CHC\mathit{H}_2CH_3$); 2.22(m, 1H, $C\mathit{H}Et$); 1.50(t, 3H, $J = 7.5$, CH_3); 1.31(t, 3H, $J = 7.8$, CH_3); 1.09(t, 3H, $J = 7.3$, CH_3); 0.93(t, 3H, $J = 7.4$, CH_3); 0.90–0.78(m, 4H, $CC\mathit{H}_2CH_3$)
4	IR	2082m, 2052m, 2040m, 2002vs, 1970sh, 1924w
	NMR	7.44–7.18(m, 15H, Ph); 2.65–2.25(m, 6H, $3xC\mathit{H}_2CH_3$); 1.78(d, 3H, $J_{PH} = 2.2$, $COCH_3$); 1.31(t, 3H, $J = 7.6$, $CH_2C\mathit{H}_3$); 0.97(t, 3H, $J = 7.5$, $CHC\mathit{H}_3$); 0.89(t, 3H, $J = 8.0$, $CH_2C\mathit{H}_3$)

its amount increasing with time. It proved impossible, however, to make **4** the sole reaction product because **3** and **4** started to decompose at elevated temperatures or upon extended reaction times. The best yield of **3** and **4** was around 10% in each case.



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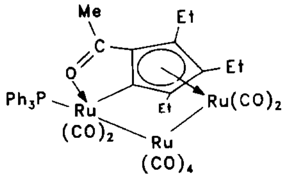

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The identification of **3** rests primarily on the FD mass spectrum, the elemental analyses being unsatisfactory. The formulation of **3** as a bis(vinyl) bridged Ru_3 cluster with an intact μ_3-phosphonio methylidyne unit can be deduced from the ^1H-NMR spectrum (Table 1), which displays the correct intensity ratios for all signals and shows no metal hydride resonance. The chemical shifts for the vinyl CH units and the ethyl CH_2 units are somewhat unusual (see the values for **2** [11]). This must be related to the fact that all four ethyl groups of **3** are in different chemical environments, as can be seen from the four methyl resonances. All the CH and CH_2 signals of **3** show up as multiline multiplets that can be related to the different chemical environments for all H atoms involved. This lack of a clearly unambiguous NMR assignment means that the chemical relationship between **2**, **3** and **4** noted above, is an important feature in the identification of **3**. The IR data for **3** (Table 1) are of no diagnostic value.

The unusual composition and constitution of **4** could only be clarified by an X-ray diffraction study (see below). The ^1H-NMR data (Table 1) are consistent with the structure. All three ethyl groups give rise to separate methyl resonances while their methylene units again give a broad multiplet. The acetyl resonance is clearly separated from the ethyl and phenyl resonances, and the nearness of the PPh_3 ligand results in a small doublet splitting. The IR data for **4** (Table 1) are again of no specific value, but the elemental analyses and the FD mass spectrum showed that the bulk of **4** was identical to the single crystal used for the structure determination.

Details of the structure determination of **4** are given in Section 4. Table 2 lists important bond lengths and angles, and Fig. 1 shows a view of the molecule. The formation of **4** involves a significant molecular reorganization of the structures present in the precursor

TABLE 2. Selected bond distances (pm) and angles (degs.) of **4**

Distances		Angles	
Ru1–Ru2	280.7(1)	Ru1–Ru2–Ru3	80.8(1)
Ru2–Ru3	292.4(1)	C1–C2–C3	108.7(6)
Ru3–P1	236.0(2)	C2–C3–C4	110.1(5)
Ru1–C1	226.5(5)	C3–C4–C5	106.2(7)
Ru1–C2	224.7(6)	C4–C5–C1	109.6(6)
Ru1–C3	224.1(7)	C5–C1–C2	105.4(4)
Ru1–C4	223.1(9)	O1–Ru3–C1	78.4(2)
Ru1–C5	221.5(7)	Ru3–C1–C5	111.3(4)
Ru3–O1	214.2(5)	C1–C5–C6	116.5(5)
Ru3–C1	207.1(4)	C5–C6–C13	126.2(5)
C1–C2	142.2(7)	O1–C6–C13	116.6(5)
C2–C3	144.2(10)	C5–C6–O1	117.2(6)
C3–C4	139.4(12)	C6–O1–Ru3	116.3(4)
C4–C5	144.7(8)		
C5–C1	146.1(9)		
C5–C6	142.5(9)		
C6–C13	149.4(13)		
C6–O1	126.0(7)		

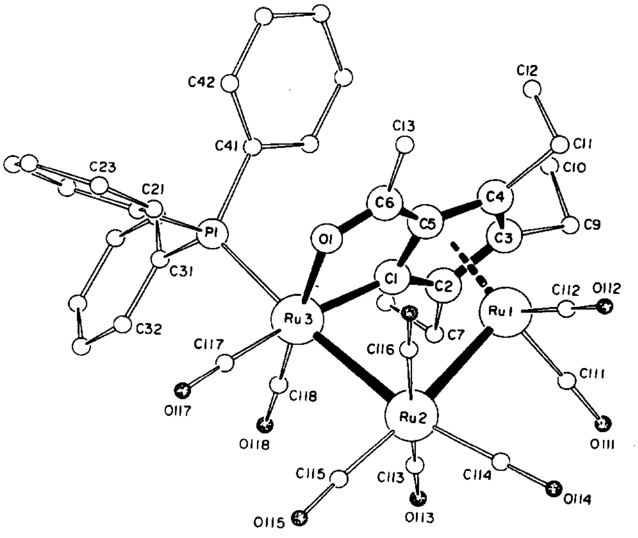

Fig. 1. Molecular structure of **4**.

compounds **1**, **2**, or **3** (see Section 3 below). The constituents of the μ_3-C·PPh$_3$ ligand in these compounds show up as the PPh$_3$ ligand and the C1 atom of the cyclopentadienyl ligand in **4**, which itself arises from C1 and the two incoming hexyne-3 molecules. The Ru$_3$ triangle has been opened by insertion of the 2,3,4-triethyl-5-acetyl-Cp ligand. This ligand acts as a η^5-Cp unit towards Ru1 and forms an oxaruthenol ring with Ru3. Only Ru2 is in a normal metal carbonyl environment, such as in Ru$_3$(CO)$_{12}$.

Although the mode of formation of **4** and its composition are unusual, its molecular details are all normal and can be related to those of well-known compounds. Thus the Ru–Ru distances and the close-to-octahedral ligand environment at Ru2 and Ru3 can be related to those in Ru$_3$(CO)$_{12}$ [14] or Ru$_3$(CO)$_{11}$(PPh$_3$) [15]. The cyclopentadienyl ligand at Ru1 is quite symmetrical (see Ru–C and C–C distances), and comparison can be made with the structures of RuCp$_2$ [16] or [CpRu(CO)$_2$]$_2$ [17], including the piano-stool geometry at Ru1. The acetyl group attached to the Cp ring has normal C–C and C–O bond lengths and angles, and finally the oxaruthenacyclopentadiene ring at Ru3 (Ru3-01-C6-C5-C1) has precedents in our own work [11,18], with a quite similar ring shape and Ru–O and Ru–C distances. Altogether the geometrical situation and bonding pattern in **4** are without strain or unusual electron distributions, thus making it understandable why **4** should be the final product of the observed reaction sequence.

3. Discussion

The reaction sequence leading to **4** is unusual from start to finish. It begins with the two-step oxidative addition of the phosphorus ylide Ph$_3$P=CH$_2$ to Ru$_3$(CO)$_{12}$ to give **1** during which a methylene group is converted into a phosphine-stabilised μ_3-carbide ligand [10]. This carbide unit loses its phosphine "ligand" during the subsequent transformation and is either eliminated as CH$_4$ or ends up as the Ru3-bound C atom of the metallocyclopentadienyl ligand in **4**. The course of this transformation can only partly be defined.

One possible reaction sequence would involve both **2** and **3** as successive intermediates. It could be envisaged that the two vinyl ligands in **3** form a C–C bond being combined to a ruthenacyclopentene (or ruthenacyclopentadiene respectively ruthenol) unit. This metallacycle would then transfer its two Ru–C σ bonds to the μ_3-carbon giving the Ru–C$_5$R$_4$ system and inducing the further interconversions. We do not favour this possibility because it requires the loss or transfer of two hydrogen atoms from the vinyl ligands, and involves an increase in the number of CO ligands from **3** to **4**.

We assume that a more likely reaction sequence is that which requires reversibility of the formation of **2** and **3** at higher temperatures and which involves a thermal rearrangement of **1** that we have observed before. The key steps in this sequence are (i) the combination of the two alkyne units on the cluster to form a metallole (specifically RuC$_4$Et$_4$) unit, a well-known reaction in cluster–alkyne chemistry [4], which we have found to occur with concomitant opening of the cluster [9], and (ii) exchange of PPh$_3$ and CO at the μ_3-carbon somewhere along the reaction path, as found for the conversion of **1** into H$_2$Ru$_3$(CO)$_8$(PPh$_3$)(μ_3-CCO) [10]. These two steps would produce, in the form of the ketenylidene ligand, the three atomic fragments necessary for the formation of **4**. The first of these fragments, the μ_3-C atom, could be eliminated as CH$_4$, as required by the net reaction **1** + 2 hexyne → **4** + CH$_4$. Although rather unusual in this case, such alkane elimination is a characteristic reaction of Ru$_3$(μ_3-CX) or Os$_3$(μ_3-CX) clusters [19,20]. Next, cleavage of the ketenylidene CO to C and O would have to be invoked; CO cleavage is commonplace in cluster chemistry, and Shriver's cluster-carbide and cluster-ketenylidene work has revealed the formation of both CH$_4$ and H$_2$O from CO ligands on clusters without the use of reducing agents [21]. Thus, both the μ_3-carbon and one CO ligand may be the source of CH$_4$ as well as of the α-C in the Ru–C$_5$ ring. The most difficult step in the reaction sequence is the transfer of the oxygen atom from CO to the methylene carbon of one C-ethyl substituent, turning it into a C-acetyl substituent at the expense of two hydrogen atoms. We could find no precedent for this except for the nucleophilic attack of oxygen-containing substrates on cluster-bound unsaturated ligands [22]. It was therefore tempting to assume that there is, in reality, a CH$_2$ group in place of O1 in **4**, and that H$_2$O is eliminated instead of CH$_4$ [23*]. The main argument against this possibility rests on the absence of ^{1}H-NMR resonances assignable to such a CH$_2$ group, and on the typical chemical shift value of the CH$_3$ resonance for an acetyl group.

Thus, while the suggested mechanistic pathway to **4** involves several hypotheses and uncertainties, the product **4**, as outlined in the discussion of the structure, contains no very unusual structural or bonding features. Combination of alkynes with CO to form organometallic ring systems is commonly observed in cluster chemistry [4,6], and recently combinations of

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* Reference number with asterisk indicates a note in the list of references.

the type alkyne + CH + CO have also been found [11,24]. The formation of **4** involves the combination 2 alkyne + C + O, thereby adding a new variant to the list of stoichiometric models for catalytic reactions.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal coefficients ($pm^2 \times 10^{-1}$) for **4**

Atom	*x*	*y*	*z*	U_{eq}
Ru(1)	2225(1)	8847(1)	1106(1)	58(1)
Ru(2)	3768(1)	6039(1)	1472(1)	56(1)
Ru(3)	4134(1)	7139(1)	2716(1)	37(1)
P(1)	4445(2)	8188(2)	3661(1)	43(1)
C(111)	726(9)	8583(10)	729(4)	88(4)
C(112)	3107(9)	8680(9)	280(4)	81(4)
C(113)	1966(9)	6071(8)	1793(4)	72(4)
C(114)	3383(9)	5724(9)	583(4)	81(4)
C(115)	4901(9)	4186(8)	1805(4)	72(4)
C(116)	5422(8)	6364(7)	1215(3)	65(3)
C(117)	5706(7)	5404(6)	2974(3)	55(2)
C(118)	2837(7)	6579(6)	3104(3)	50(2)
O(111)	−253(8)	8442(9)	525(3)	130(5)
O(112)	3632(8)	8595(8)	−232(3)	123(4)
O(113)	910(7)	6029(7)	1960(3)	100(3)
O(114)	3160(8)	5542(8)	51(3)	117(4)
O(115)	5577(7)	3068(6)	1960(4)	108(3)
O(116)	6409(6)	6518(6)	1032(3)	89(3)
O(117)	6617(6)	4355(5)	3125(3)	90(3)
O(118)	2019(5)	6250(5)	3370(3)	75(3)
C(1)	2623(6)	8902(5)	2212(3)	41(2)
C(2)	1114(6)	9644(6)	2061(3)	52(2)
C(3)	908(7)	10788(7)	1592(4)	70(3)
C(4)	2245(8)	10777(7)	1425(4)	74(3)
C(5)	3329(7)	9615(6)	1810(3)	52(2)
C(6)	4870(7)	9065(6)	1872(3)	53(2)
C(7)	−80(7)	9351(7)	2354(3)	62(2)
C(8)	−594(10)	9987(9)	3030(5)	94(3)
C(9)	−610(11)	11914(10)	1325(5)	102(3)
C(10)	−1052(13)	13067(13)	1754(6)	135(4)
C(11)	2510(14)	11747(13)	806(6)	133(4)
C(12)	2529(17)	12583(16)	1187(8)	174(6)
C(13)	5815(9)	9666(8)	1547(4)	81(2)
O(1)	5501(4)	7969(4)	2234(2)	48(2)
C(22)	7442(5)	6989(5)	3556(2)	74(2)
C(23)	8871	6526	3792	91(2)
C(24)	9157	6544	4470	93(3)
C(25)	8015	7024	4913	90(2)
C(26)	6587	7486	4678	68(2)
C(21)	6300	7469	3999	52(1)
C(32)	3533(4)	6784(3)	4620(2)	58(1)
C(33)	2733	6639	5180	71(2)
C(34)	1902	7787	5514	82(2)
C(35)	1791	9079	5289	84(2)
C(36)	2551	9224	4729	68(2)
C(31)	3422	8076	4395	48(1)
C(42)	5082(4)	10488(5)	3608(3)	81(2)
C(43)	4736	11877	3477	110(3)
C(44)	3336	12781	3258	106(3)
C(45)	2283	12295	3170	92(2)
C(46)	2629	10905	3302	69(2)
C(41)	4029	10002	3521	55(1)

4. Experimental details

The general preparative techniques [25] and the synthesis of **1** [10] have been described previously.

4.1. Preparation of 3 and 4

A solution of 80 mg (0.096 mmol) of **1** in 30 ml of toluene was treated with 120 μl (about 90 mg, about 1.1 mmol) of hexyne-3 and the mixture was heated under reflux. After 2 h, all of **1** and the intermediate **2** has disappeared (IR monitoring). The solvent was removed *in vacuo* and the residue taken up in a minimum amount of CH_2Cl_2. Preparative TLC on silica gel plates (Merck, silica gel 60, 0.2 mm, F_{254}) with CH_2Cl_2–hexane (1:3) yielded, from the first fraction (red-purple), 10 mg (11%) **3**, m.p. 192°C. After a small yellow fraction (not identified), the third fraction (yellow) contained 8 mg (9%) **4**, m.p. 172°C.

3: Anal. Found: C, 45.57; H, 3.48. $C_{38}H_{37}O_7PRu_3$ (939.9) calcd.: C, 48.56; H, 3.97%. FD-MS: mol. peak 939. **4**: Anal. Found: C, 47.62; H, 3.24, $C_{39}H_{33}O_9PRu_3$ (979.9) calcd.: C, 47.81; H, 3.39%. FD-MS: mol. peak 979.

4.2. Structure determination [26*]

Crystals of **4** (0.4 mm × 0.2 mm × 0.2 mm) were obtained from hexane–CH_2Cl_2 (3:1) at −30°C. They belong to the space group $P\bar{1}$: $a = 1017.3(2)$, $b = 1080.1(2)$, $c = 2003.3(4)$ pm, $\alpha = 86.09(3)°$, $\beta = 89.63(3)°$, $\gamma = 64.97(3)°$, $Z = 2$, $V = 1.9892(7)$ nm^3, $d_{calcd.} = 1.63$ gcm^{-3}, $\mu = 11.9$ cm^{-1}. 7671 independent reflections with $I \geq 3\ \sigma\ (I)$ were collected with a Nonius CAD 4 diffractometer using Mo-Kα radiation and the $\omega/2\theta$ technique at $2\theta = 2$–$60°$ and for the indices $\pm h$, $+k$, $\pm l$. The structure was solved by direct methods and refined anisotropically with the SHELX program system [27]. No absorption correction was applied, the phenyl rings were treated as rigid bodies, and all hydrogen atoms were included with a common temperature factor and a fixed C–H distance of 96 pm. The final unweighted R value was 0.052 for 308 variables. The difference electron density maxima were $+1.1$ and $-1.5 \cdot 10^{-6}$ e pm^{-3}. The drawing was produced with the SCHAKAL program [28]. Table 3 lists the atomic coordinates.

Acknowledgment

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