Journal of Organometallic Chemistry, 255 (1983) 255–262
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CLUSTER CHEMISTRY

XXV *. SYNTHESIS AND STRUCTURE OF $Ru_4(\mu_4\text{-}\eta^2,P\text{-}HC{\equiv}CC_6H_4PPh_2)(CO)_{11}\cdot 0.5CH_2Cl_2$

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(Received May 4th, 1983)

Summary

The olefinic tertiary phospine complex $Ru_3(CO)_{10}(\mu\text{-}\eta^2,P\text{-}CH_2{=}CHC_6H_4PPh_2)$ is converted to the title μ_4-alkyne-Ru_4 cluster at 135°C; the latter is also formed from $H_2Ru_3(\mu_3\text{-}\eta^2,P\text{-}HC{\equiv}CC_6H_4PPh_2)(CO)_8$ and $Ru_3(CO)_{12}$. Crystals of the Ru_4 complex are monoclinic, space group $P2_1$, with a 8.700(3), b 17.611(3), c 11.926(2) Å, β 102.720(3)°, with $Z = 2$; 1702 data ($I > 2.5\ (\sigma)I$) were refined to $R = 0.026$, $R_w = 0.028$. The molecule contains a distorted octahedral Ru_4C_2 core, one carbon of which is attached to an o-$C_6H_4PPh_2$ moiety coordinated via P to a wing-tip Ru of the Ru_4 butterfly.

Introduction

We have recently described the synthesis of $Ru_3(CO)_{10}(\mu\text{-}\eta,P\text{-}CH_2{=}CHC_6H_4PPh_2)$ (**1**; Scheme) from $Ru_3(CO)_{12}$ and (2-vinylphenyl)diphenylphosphine (sp) in a radical-initiated reaction under mild conditions [1]. We also showed that at 40°C, a facile dehydrogenation of the vinyl moiety occurred, in which two hydrogens migrate to the metal cluster with concomitant formation of a μ_3-(2-ethynylphenyl)diphenylphosphine ligand, as shown by the crystal structure determination of the resulting complex $H_2Ru_3(CO)_8(\mu_3\text{-}HC{\equiv}CC_6H_4PPh_2)$ (**2**). We now find that if **1** is kept for 4 h at 135°C in an inert solvent, the initially red-coloured solution first lightens to yellow, and then progressively darkens, finally becoming purple-black. From this solution was isolated a tetranuclear complex (**3**), the characterisation and structure of which is the subject of this paper.

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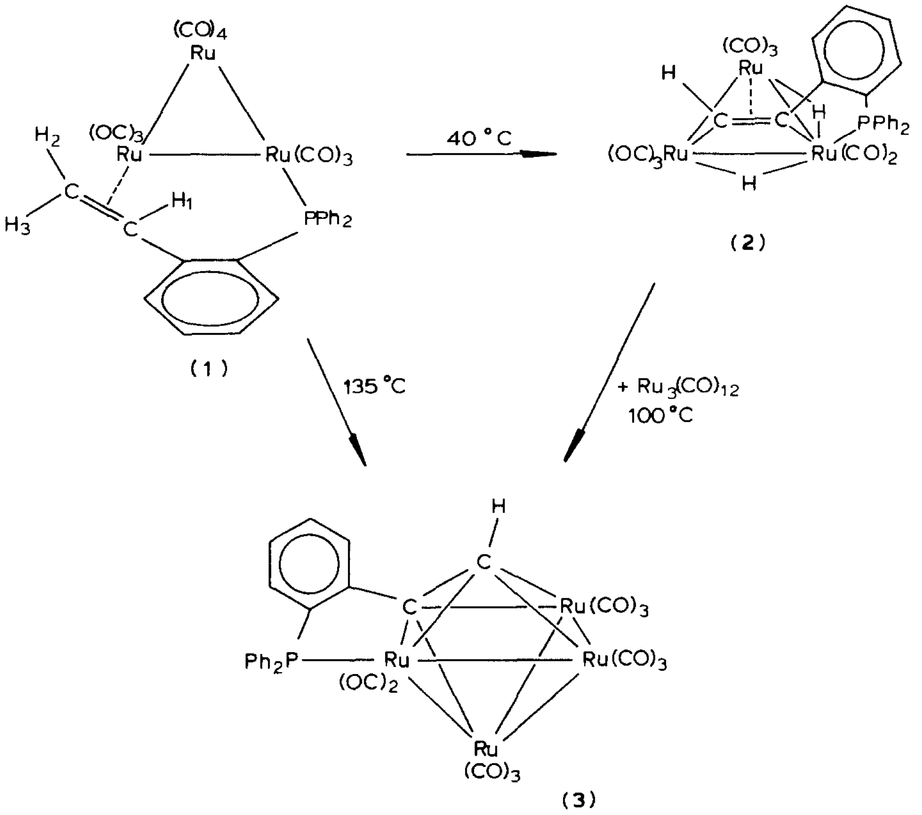
* For Part XXIV, see ref. 11.



SCHEME 1

Experimental

Pyrolysis of $Ru_3(CO)_{10}(\mu\text{-}\eta^2,P\text{-}CH_2{=}CHC_6H_4PPh_2)$ *(1)*

A solution of complex **1** (100 mg, 0.115 mmol) in petroleum spirit (boiling range 120–160°C, 35 ml) was stirred at 135°C (bath temperature) for 4 h. The red solution first lightened to yellow, and then the colour deepened to black-purple. After cooling, and filtering to remove some ruthenium metal, solvent was removed under reduced pressure. The residue was separated by preparative TLC (Kieselgel GF_{254} (Type 60); 95/5 cyclohexane/diethylether) into five fractions: Band 1 (R_f 0.57) contained a trace of unidentified yellow material, ν(CO) (cyclohexane) 2069s, 2048w(sh), 2037s, 2004s, 1991vs, 1928s cm^{-1}; Band 2 (R_f 0.43) contained yellow $H_2Ru_3(CO)_8(\mu_3\text{-}\eta^2,P\text{-}HC{\equiv}CC_6H_4PPh_2)$ (**2**) (trace, identified by IR); Band 3 (R_f 0.34), purple, not identified, trace only; Band 4 (R_f 0.26), contained the major product, isolated as purple crystals, dec. > 200°C, from CH_2Cl_2/isopentane, and identified as $Ru_4(\mu_4\text{-}\eta^2,P\text{-}HC{\equiv}CC_6H_4PPh_2)(CO)_{11} \cdot 0.5CH_2Cl_2$ (**3**) (20 mg, 17%) by an X-ray study. Found: C, 35.76; H, 1.22; $C_{31}H_{15}O_{11}PRu_4 \cdot 0.5CH_2Cl_2$ calcd.: C, 36.34; H, 1.55%. Infrared (cyclohexane): ν(CO) at 2078m, 2060(sh), 2040s, 2026vs, 2004w, 1993m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 7.40, m, 14H, $PPh_2 + C_6H_4$; 9.57, s, 1H, $\equiv CH$; Band 5 (R_f 0.10), purple, not identified, trace only.

Pyrolysis of $H_2Ru_3(CO)_8(\mu_3\text{-}\eta^2,P\text{-}HC{\equiv}CC_6H_4PPh_2) + Ru_3(CO)_{12}$

A mixture of complex **2** (100 mg, 0.123 mmol) and $Ru_3(CO)_{12}$ (78 mg, 0.123 mmol) was kept at 100°C in heptane (30 ml) for 48 h. During this time the solution became turbid, and the colour changed from orange to purple. Evaporation and separation by preparative TLC (light petroleum) afforded five bands: Band 1 (R_f 0.86), $Ru_3(CO)_{12}$ (45 mg, 58%), identified by IR; Band 2 (R_f 0.61), red, unidentified (trace); Band 3 (R_f 0.34), complex **2** (60 mg, 60%), identified by IR; Band 4 (R_f 0.28), purple, not identified; Band 5 (R_f 0.10), complex **3** (20 mg, 16%), identified by IR.

Crystallography

A crystal of dimensions 0.05 × 0.13 × 1.09 mm was mounted on a glass fibre and coated with cyanoacrylate super glue. Lattice parameters at 27°C were determined by a least-squares fit to the setting angles of 25 independent reflections, measured and refined by scans performed on an Enraf–Nonius CAD4 four-circle diffractometer employing graphite monochromated Mo-K_α radiation.

Crystal Data: $C_{31}H_{15}O_{11}PRu_4 \cdot 0.5CH_2Cl_2$, formula weight 1041.17, monoclinic, space group $P2_1$, a 8.700(3), b 17.611(3), c 11.926(2) Å; β 102.720(3)°; D_c 2.022 g cm^{-3}; $U = 1782.41$; $Z = 2$; μ(Mo-K_α) 18.90 cm^{-1}; λ(Mo-K_α) 0.7107 Å; $F(000)$ 1782 electrons.

Intensity data were collected in the range $1.3° < \theta < 22°$ using an $\omega - \frac{n}{3}\,\theta$ scan, where n (= 6) was optimized by profile analysis of a typical reflection. The ω scan angles and horizontal counter apertures employed were $(1.05 + 0.35 \tan\theta)°$ and $(2.40 + 0.5 \tan\theta)$ mm, respectively. Three standard reflections, monitored after every 25 min of data collection, indicated that by completion of the data collection no decomposition had occurred. Data reduction and application of Lorentz and polarization corrections were performed using programme SUSCAD [2]. Of the 1798 reflections collected, 1702 with $I > 2.5\sigma(I)$ were considered observed and used in the calculations.

Structure solution and refinement

Three of the four ruthenium atom positions were found using the direct method routine SOLV of the SHELXTL [2] programme. Earlier attempts at solving the structure using the TANG procedure of SHELX76 [2] gave correct images for the ruthenium cluster, but incorrectly located in the cell and displaced from the phosphine group. All other non-hydrogen atoms were located in the Fourier difference maps of successive blocked-cascade least-squares refinements. The remaining electron density at this stage was modelled as dichloromethane with the carbon disordered over three sites. All hydrogen atoms were included at calculated positions (C–H, 0.97 Å) with group temperature factors. The phenyl entities were refined initially as rigid groups (C–C, 1.395 Å). In the final blocked-cascade least-squares calculations all non-hydrogen atoms were independent and modelled anisotropically. The refinement converged with the residuals $R = 0.026$ and $R_w = 0.028$. The weighting scheme employed converged at $w = 1.00/(\sigma^2F_0 + 0.0012F_0^2)$. The largest peak remaining in the final difference map (height 1.0 eÅ^{-3}) was associated with the disordered dichloromethane molecule.

TABLE 1

ATOM COORDINATES ($\times 10^4$) AND TEMPERATURE FACTORS ($A \times 10^3$) FOR **3**

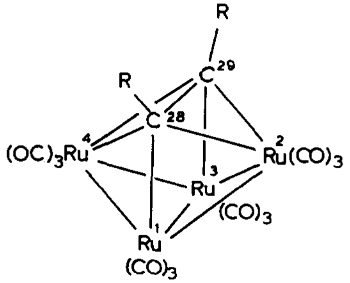
Atom	x	y	z	U^a
Ru(1)	1683(1)	4957	6323(1)	29(1)
Ru(2)	2829(1)	3546(1)	5986(1)	27(1)
Ru(3)	327(1)	4072(1)	4377(1)	25(1)
Ru(4)	1877(1)	5404(1)	4127(1)	24(1)
P(1)	2125(2)	5175(1)	2275(2)	29(1)
C(1)	3504(9)	4393(4)	2441(8)	33(3)
C(2)	3731(8)	3989(4)	3514(9)	34(3)
C(3)	4814(8)	3398(5)	3715(8)	31(3)
C(4)	5675(9)	3226(4)	2895(7)	31(3)
C(5)	5453(9)	3615(5)	1869(8)	35(3)
C(6)	4415(10)	4213(5)	1639(8)	38(3)
C(7)	2946(9)	5905(5)	1541(8)	38(3)
C(8)	4593(10)	6103(6)	1927(10)	52(4)
C(9)	5268(11)	6643(6)	1350(11)	58(4)
C(10)	4369(12)	7068(6)	518(10)	63(4)
C(11)	2817(13)	6853(7)	73(9)	67(4)
C(12)	2100(11)	6322(7)	638(10)	67(5)
C(13)	374(9)	4865(4)	1226(7)	32(3)
C(14)	−1037	5250	1144	73
C(15)	−2373	5020	334	69
C(16)	−2272	4417	−408	79
C(17)	−897(11)	4041(6)	−375(9)	54(4)
C(18)	428(10)	4268(5)	504(9)	42(3)
C(19)	−88(9)	3456(5)	3038(8)	38(3)
C(20)	−804(9)	3386(4)	5145(8)	32(3)
C(21)	−1448(9)	4731(5)	3932(8)	38(3)
C(22)	1973(11)	3296(5)	7240(8)	42(4)
C(23)	2955(11)	4947(6)	7876(9)	52(4)
C(24)	−322(12)	4799(6)	6759(9)	50(4)
C(25)	4929(11)	3367(5)	6795(9)	40(4)
C(26)	2558(9)	2573(5)	5266(8)	36(3)
C(27)	249(9)	6116(4)	3654(8)	36(3)
C(28)	2808(8)	4243(4)	4382(7)	25(3)
C(29)	3477(9)	4688(4)	5404(8)	30(3)
C(30)	1433(10)	6018(5)	6301(8)	36(4)
C(31)	3349(9)	6205(5)	4356(8)	36(3)
C(32)	2019	1586	1859	111(4)
C(33)	5670	7140	−1790	111(6)
C(34)	1920	1750	2710	111(6)
C(35)	2027(405)	1898(238)	1908(326)	111(6)
O(1)	−407(8)	3063(4)	2260(6)	65(3)
O(2)	−1486(7)	2983(4)	5572(7)	63(3)
O(3)	−2572(8)	5094(4)	3740(8)	77(3)
O(4)	1294(9)	6671(4)	6390(7)	67(3)
O(5)	3721(8)	4954(7)	8769(6)	85(4)
O(6)	−1533(9)	4716(6)	6970(8)	89(4)
O(7)	6218(7)	3248(4)	7320(6)	62(3)
O(8)	1505	3117	8069	57
O(9)	2326(7)	2018(4)	4790(6)	56(3)
O(10)	−686(7)	6573(4)	3391(7)	59(3)
O(11)	4221(8)	6703(4)	4517(7)	62(3)
Cl(1)	1963(4)	2130(2)	676(4)	94(2)
Cl(2)	4067(5)	1238(3)	2442(4)	120(2)

[a] Equivalent isotopic U defined as one third of orthogonalised U tensor, except for the values marked with an asterisk.

Final least-squares positional parameters and temperature factors for complex **3** are given in Table 1. The dichloromethane and hydrogen atom coordinates, together with a complete table of bond lengths, have been deposited *. All the above calculations were performed using the scattering factors for the respective neutral atoms as tabulated in the International Tables for X-ray crystallography [3].

Results and discussion

Complex **1** is smoothly converted into the related μ_4-alkyne derivative **3** on heating for a short time in an inert solvent at 135°C. Complex **3**, which was characterised by an X-ray structural study, exhibits a characteristic singlet resonance at δ 9.57 for the C*H* proton of the alkynyl unit. A parallel can thus be drawn between the reactions of $Ru_3(CO)_{12}$ with $Ph_2PC_6H_4CH{=}CH_2$ on the one hand, and with $PhCH{=}CH_2$ recently reported [4], on the other; the intermediates **1** and **2** earlier described by us undoubtedly have their (undetected) counterparts in the latter reaction.



(4)

The unit cell of **3** contains two molecules of the complex, together with a disordered molecule of dichloromethane; there are no unusually short intermolecular contacts. A plot of a molecule of **3** is shown in Fig. 1. The structural study reveals few unusual features, apart from the anchoring of the alkyne unit to the Ru_4 butterfly via the $Ph_2PC_6H_4$ group. There are two other complexes containing the Ru_4C_2 core previously reported, namely $Ru_4(\mu_4\text{-}C_2R_2)(CO)_{12}$ (**4**, R = Me [5] and Ph [6]), although complexes of this type have long been known from the reactions between alkynes and ruthenium carbonyls [7]. More recently, two heteronuclear examples of this type of complex have been described, namely $FeRu_3(\mu_4\text{-}C_2Ph_2)(CO)_{12}$ [8] and $RuCo_3(\mu_4\text{-}HC_2Bu^t)(\mu\text{-}PPh_2)(CO)_9$ [9].

Selected bond lengths and angles for **3** are given in Tables 2 and 3, and where appropriate, corresponding values for the other Ru_4 complexes are also listed. As found previously, the Ru–Ru bonds in the Ru_4 butterfly embrace a set of four, the wing edges, between 2.722(1)–2.770(1) Å, and a longer 'hinge' bond of 2.823(1) Å, which is significantly shorter than that found in complex **4** (R = Me). The major difference between **3** and complexes **4** is the presence of the tertiary phosphine

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* These data are available on request from the Director of the Cambridge Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England. Any request should be accompanied by the full literature citation for this paper.

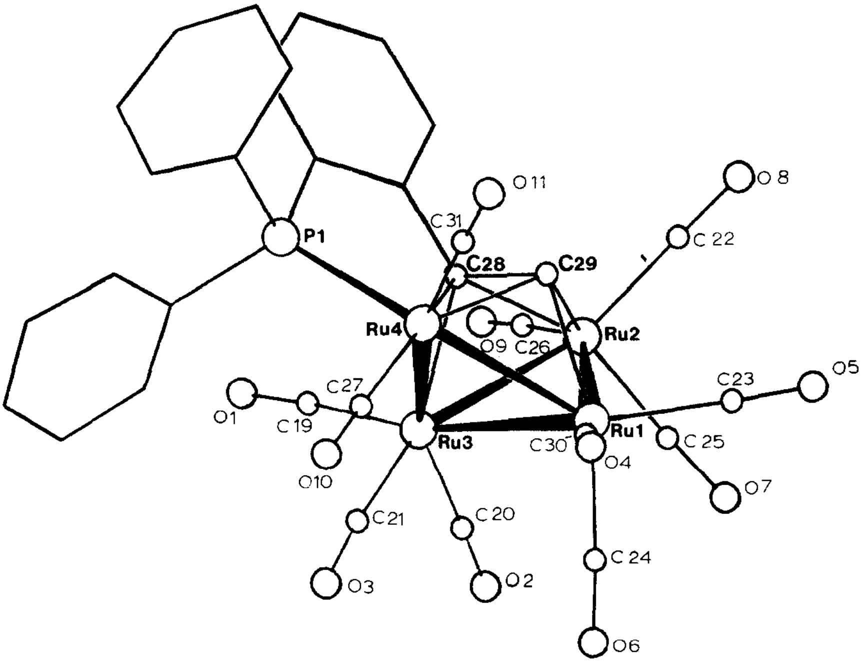

Fig. 1. PLUTO plot of the molecular structure of $Ru_4(\mu_4\text{-}\eta^2,P\text{-}HC{\equiv}CC_6H_4PPh_2)(CO)_{11}$ (3) showing atom numbering scheme.

TABLE 2

SELECTED BOND DISTANCES (Å) IN 3 AND RELATED COMPLEXES

Bond	3	4 (R = Me) [a]	4 (R = Ph) [b]
Ru(1)-Ru(2)	2.735(1)	2.728(1)	2.74(1)
Ru(1)-Ru(3)	2.823(1)	2.880(1)	2.85(1)
Ru(1)-Ru(4)	2.770(1)	2.710(1)	2.71(1)
Ru(2)-Ru(3)	2.722(1)	2.710(1)	2.71(1)
Ru(3)-Ru(4)	2.749(1)	2.728(1)	2.74(1)
Ru(1)-C(29)	2.144(9)	2.16(1)	2.16(1)
Ru(2)-C(29)	2.235(8)	2.24(1)	2.25(1)
Ru(4)-C(29)	2.212(8)	2.27(1)	2.24(1)
Ru(2)-C(28)	2.266(8)	2.27(1)	2.26(1)
Ru(3)-C(28)	2.174(7)	2.16(1)	2.16(1)
Ru(4)-C(28)	2.190(7)	2.24(1)	2.24(1)
C(28)-C(29)	1.455(11)	1.45(1)	1.46(2)
Ru(4)-P(1)	2.297(3)		
P(1)-C(1)	1.805(8)		
P(1)-C(7)	1.787(10)		
P(1)-C(13)	1.826(7)		
C(2)-C(28)	1.508(13)		
Ru-CO (mean)	1.898 [range 1.860-1.942(11)]		
C-O (mean)	1.145 [range 1.115-1.189(12)]		

[a] Ref. 5. [b] Ref. 6.

TABLE 3

SELECTED BOND ANGLES (DEGREES) IN 3

Ru(1)–Ru(2)–Ru(3)	62.3	Ru(1)–Ru(3)–Ru(2)	59.1
Ru(1)–Ru(3)–Ru(4)	59.6	Ru(1)–Ru(4)–Ru(3)	61.5
Ru(2)–Ru(1)–Ru(3)	58.6	Ru(2)–Ru(1)–Ru(4)	91.1
Ru(3)–Ru(1)–Ru(4)	58.9		
Ru(1)–Ru(4)–P(1)	153.4(1)	Ru(3)–Ru(4)–P(1)	96.1(1)
Ru(1)–Ru(2)–C(28)	72.4(2)	Ru(1)–Ru(2)–C(29)	49.9(2)
Ru(1)–Ru(3)–C(28)	71.8(2)	Ru(1)–Ru(4)–C(28)	72.7(2)
Ru(1)–Ru(4)–C(29)	49.4(2)	Ru(2)–Ru(1)–C(29)	52.9(2)
Ru(2)–Ru(3)–C(28)	53.7(2)	Ru(3)–Ru(1)–C(29)	71.2(2)
Ru(3)–Ru(2)–C(29)	50.7(2)	Ru(3)–Ru(2)–C(29)	72.1(2)
Ru(3)–Ru(4)–C(28)	50.7(2)	Ru(3)–Ru(4)–C(29)	71.9(2)
Ru(4)–Ru(1)–C(29)	51.6(2)	Ru(4)–Ru(3)–C(28)	51.2(2)
Ru(1)–C(29)–Ru(2)	77.3(3)	Ru(1)–C(29)–Ru(2)	65.2(2)
Ru(1)–C(29)–Ru(4)	78.9(3)	Ru(2)–C(28)–Ru(3)	61.6(2)
Ru(2)–C(28)–Ru(4)	123.7(4)	Ru(2)–C(29)–Ru(4)	124.2(3)
Ru(3)–C(28)–Ru(4)	78.1(2)		
Ru(1)–C(29)–C(28)	110.2(5)	Ru(2)–C(28)–C(29)	70.0(5)
Ru(2)–C(29)–C(28)	72.3(4)	Ru(3)–C(28)–C(29)	114.7(5)
Ru(4)–C(28)–C(29)	71.5(4)	Ru(4)–C(29)–C(28)	69.9(4)
P(1)–Ru(4)–C(27)	93.0(3)	P(1)–Ru(4)–C(28)	82.0(2)
P(1)–Ru(4)–C(29)	112.5(2)	P(1)–Ru(4)–C(31)	93.8(3)
C(28)–Ru(2)–C(29)	37.7(3)	C(28)–Ru(4)–C(29)	38.6(3)
Ru–C–O (mean)	176.5 [range 174.1–178.5(7)]		

ligand attached to Ru(4), which significantly lengthens the Ru(1)–Ru(4) bond *trans* to P (to 2.770(1) Å), and to a lesser extent, the one *cis* to the phosphorus ligand (Ru(3)–Ru(4), 2.749(1) Å). The alkyne C(28)–C(29) bond (1.455(11) Å) has lengthened appreciably from the normal value associated with a C≡C triple bond, as a result of the interaction with the four metal atoms. The Ru(4)–P(1) separation is 2.297(3) Å, not significantly different from those found earlier in **2** (2.302(2) Å) [1]. The Ru(4)–P(1)–C(1)–C(2)–C(28) chelate ring is planar, and distorts the regular symmetry of the Ru_4C_2 cluster so that C(28) is slightly nearer to Ru(4), and further from Ru(2), than is C(29). The C(2)–C(28) separation (1.508(13) Å) is consistent with there being a normal single bond from the phenyl ring to the cluster (alkyne) carbon atom. The C(2)–C(28)–C(29) angle (123.1(10)°) may be compared with the similar Me–C–C angle of 123.8(2)° found in **4** (R = Me).

The formation of **3** from **1** requires the formal addition of an $Ru(CO)_3$ group to generate the Ru_4 cluster, with concomitant loss of H_2. Significantly, we find that simple heating of the μ-alkyne complex **2** alone at higher temperatures does not give any **3**, but the new complex is formed on heating a mixture of **2** and $Ru_3(CO)_{12}$. We note that $Ru_3(CO)_{12}$ was isolated from the reaction which afforded **2**, and the intermediate yellow solution (see Experimental) contains both **2** and $Ru_3(CO)_{12}$. We recall that the earliest account of reactions between $Ru_3(CO)_{12}$ and sp described the formation of mononuclear complexes containing sp or modified sp ligands [8]. None of these complexes have been detected among the products of the reactions which have afforded **2** or **3**, and these reactions are obviously more complex than appears at first sight. Indeed, the variety of reactions that we are finding in this system further highlights the complexity of cluster chemistry, and of attempts to use these reactions to model changes that occur on metal surfaces. The present example illustrates the use of a tertiary phosphine moiety to anchor a reactive hydrocarbon to a metal cluster fragment; at higher temperatures, it would be expected that cleavage of P–C bonds might occur, with formation of complexes containing the μ-PPh_2 group, for example. The results of experiments designed to test this idea, which allow further elaboration of the alkynyl moiety, will be described elsewhere.

Acknowledgements

We thank Dr. M.A. Bennett (Australian National University, Canberra) for a generous gift of the ligand sp, Professor B.R. Penfold and Dr. W.T. Robinson (School of Chemistry, University of Canterbury) for computing facilities (SHELXTL), and the University of Adelaide for study leave (MRS). Thanks are also due to the Australian Research Grants Scheme for grants (to MIB and MRS) in partial support of this work. MLW was the holder of a Commonwealth Postgraduate Research Award.

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