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XV *. FORMATION OF AN η^2-OLEFIN DERIVATIVE OF $Ru_3(CO)_{12}$, AND ITS CONVERSION TO AN η^2-ALKYNE-HYDRIDO COMPLEX: CRYSTAL AND MOLECULAR STRUCTURES OF $Ru_3(\mu\text{-}P,\eta^2\text{-}CH_2\!=\!CHC_6H_4PPh_2)(CO)_{10}$ AND $H_2Ru_3(\mu_3\text{-}P,\eta^2\text{-}HC\!\equiv\!CC_6H_4PPh_2)(CO)_8$

MICHAEL I. BRUCE *, BRIAN K. NICHOLSON and MICHAEL L. WILLIAMS

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001 (Australia)

Summary

In a radical-ion initiated reaction, $Ru_3(CO)_{12}$ reacts with $2\text{-}Ph_2PC_6H_4CH\!=\!CH_2$ (sp) to give $Ru_3(CO)_{10}$(sp) (**1**), containing the olefinic tertiary phosphine bridging two metal atoms. Gentle heating converts this complex to $H_2Ru_3(\mu_3\text{-}HCCC_6H_4PPh_2)(CO)_8$ (**2**), containing an acetylenic tertiary phosphine bridging all three metal atoms. Complex **1** is triclinic, space group $P\bar{1}$, a 9.336(3), b 12.598(4), c 13.781(5) Å, α 77.61(3), β 85.01(3), γ 79.10(3)°, $Z = 2$; complex **2** is also triclinic, space group $P\bar{1}$, a 11.653(6), b 16.284(6), c 17.284(8) Å, α 66.29(3), β 82.27(4), γ 88.86(4)°, $Z = 4$. The structures were refined to $R = 0.056$, $R_w = 0.059$ for 1984 data [for **1**] and to $R = 0.036$, $R_w = 0.041$ for 4293 data [for **2**].

Introduction

Several years ago, it was reported that the olefinic tertiary phosphine 2-styryl-diphenylphosphine ($2\text{-}Ph_2PC_6H_4CH\!=\!CH_2$, sp) reacted with $Ru_3(CO)_{12}$ in refluxing heptane, octane or nonane to give the mononuclear complexes $Ru(CO)(sp)_2$, $Ru(CO)_3(sp)$ or $Ru(CO)_2[Ph_2PC_6H_4CH(CH_2)_2CHC_6H_4PPh_2]$ according to the conditions [1]. A transient deep reddish-purple colouration was reported before the colour lightened to orange or yellow. Recently we described a method for obtaining substituted derivatives of $Ru_3(CO)_{12}$ under mild conditions [2], and we sought to establish the early course of the reaction leading to the mononuclear complexes mentioned above. Simple η^2-olefinic complexes from $Ru_3(CO)_{12}$ were also unknown, conversion to dehydrogenated derivatives occurring readily under the reaction conditions.

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* For Part XIV, see ref. 10.

Experimental

General experimental conditions were similar to those described in previous papers. Sodium diphenylketyl solution was prepared as previously described.

Preparation of $Ru_3(CO)_{10}(sp)$ (1)

A solution of $Na[Ph_2CO]$ was added dropwise to a mixture of $Ru_3(CO)_{12}$ (250 mg, 0.39 mmol) and sp (120 mg, 0.42 mmol) in THF (40 ml) until reaction was complete (TLC). About 30 drops were required, when the solution rapidly darkened in colour to deep red. Evaporation and recrystallisation (Et_2O/MeOH) afforded red crystals of $Ru_3(CO)_{10}(sp)$ (1) (250 mg, 74%), m.p. 113–114°C (Found: C, 42.21; H, 2.15%; $C_{30}H_{17}O_{10}PRu_3$ calcd.: C, 41.34; H, 1.97%). Infrared (cyclohexane): $\nu(CO)$ at 2094s, 2039s, 2026vs, 2015vs, 1999m, 1991w, 1976m, 1959w cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 2.51d, J_{13} 8.5 Hz, 1H, H(3); 3.24d, J_{12} 12.5 Hz, 1H, H(2); 4.90qu, 1H, H(1); 7.51m, 14H, aromatic.

Pyrolysis of $Ru_3(CO)_{10}(sp)$

A solution of $Ru_3(CO)_{10}(sp)$ (100 mg, 0.12 mmol) was heated in refluxing cyclohexane (20 ml) for 30 min, after which time the reaction was adjudged complete (the disappearance of the $\nu(CO)$ band at 2094 cm^{-1} was monitored). Evaporation and preparative TLC (silica gel, cyclohexane) gave three products: (i) $Ru_3(CO)_{12}$ (4 mg, 5%); (ii) an unidentified yellow solid (6 mg), m.p. 103–108°C (dec), with $\nu(CO)$ at 2069s, 2048(sh), 2037s, 2004s, 1991vs, 1982s cm^{-1}; (iii) yellow $H_2Ru_3(CO)_8(2$-$HCCC_6H_4PPh_2)$ (2) (61 mg, 65%), from Et_2O/EtOH, darkened > 150°C, m.p. 184–188°C (Found: C, 41.26; H, 1.90%, M = 817; $C_{28}H_{17}O_8PRu_3$ calcd.: C, 41.23; H, 2.10%; M = 817). Infrared (cyclohexane): $\nu(CO)$ at 2099w, 2085s, 2062(sh), 2053vs, 2043s, 2029w, 2014vs, 2008s, 1999m, 1995w, 1989m cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) −17.72s(br), 2H, RuHRu; 7.31m, 14H, aromatic; 10.14s, 1H, CCH. Three purple products were also present in trace amounts only.

Crystal structure determinations of complexes 1 and 2

Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo-K_α X-rays. Cell dimensions were derived using 25 high angle reflections.

Crystal data. (1) $C_{30}H_{17}O_{10}PRu_3$, M = 871.6, triclinic, space group $P\bar{1}$, a 9.336(3), b 12.598(4), c 13.781(5) Å, α 77.61(3), β 85.01(3), γ 79.10(3)°, U 1552 Å^3, D_m 1.86(2), D_c 1.87 g cm^{-3} for $Z = 2$, $F(000) = 848$, λ(Mo-K_α) 0.7107 Å, μ(Mo-K_α) 14.9 cm^{-1}. Crystal form: deep-red irregular prism, 0.12 × 0.10 × 0.08 mm; Data: 2981 unique reflections collected in the range 1.5° < θ < 21°, with 1984 having $I > 2.5\sigma(I)$ being used in the refinement. Absorption corrections were not applied.

(2) $C_{28}H_{17}O_8PRu_3$, M = 815.6, triclinic, space group $P\bar{1}$, a 11.653(6), b 16.284(6), c 17.284(8) Å, α 66.29(3), β 82.27(4), γ 88.86(4)°, U 2973 Å^3, D_m 1.82, D_c 1.82 g cm^{-3} for $Z = 4$, $F(000) = 1584$, λ(Mo-K_α) 0.7107 Å, μ(Mo-K_α) 15.4 cm^{-1}. Crystal form: yellow triangular wedge, 0.38 × 0.23 × 0.16 mm. Data: 5205 unique reflections were collected in the range 1.5 < θ < 20° with 4293 having $I > 2.5\sigma(I)$ used in the refinement after correction for absorption.

Structure solutions and refinements. The structures of both 1 and 2 were solved by direct methods to give the positions of the Ru atoms. Subsequent refinement and

TABLE 1

FINAL POSITIONAL PARAMETERS FOR $[Ru_3(CO)_{10}(Ph_2PC_6H_4CH=CH_2-2)]$ (1)

Atom	x	y	z
Ru(1)	2487(1)	2727(1)	6971(1)
Ru(2)	616(1)	1127(1)	7236(1)
Ru(3)	2696(1)	1342(1)	5576(1)
P	1565(4)	3514(3)	8347(3)
C(11)	4117(18)	1706(13)	7615(13)
C(12)	855(19)	3701(13)	6288(13)
C(13)	3777(22)	3671(17)	6401(14)
C(21)	1961(18)	295(15)	8205(14)
C(22)	− 843(21)	2024(16)	6371(16)
C(23)	451(18)	−153(16)	6778(16)
C(31)	3866(19)	174(14)	6453(14)
C(32)	1316(22)	2499(17)	4757(15)
C(33)	2558(20)	392(15)	4736(15)
C(34)	4337(24)	1977(18)	4935(16)
O(11)	5126(13)	1138(11)	7969(12)
O(12)	− 117(14)	4304(9)	5937(9)
O(13)	4584(17)	4258(12)	6002(11)
O(21)	2637(13)	− 224(12)	8862(10)
O(22)	− 1820(15)	2538(10)	5883(13)
O(23)	315(15)	− 912(10)	6506(11)
O(31)	4555(14)	− 586(10)	6916(9)
O(32)	563(20)	3052(13)	4222(12)
O(33)	2576(16)	− 273(12)	4241(11)
O(34)	5264(18)	2391(15)	4529(13)
C(1)	− 533(15)	1830(12)	8526(13)
C(2)	− 1181(18)	922(16)	8396(16)
C(42)	− 1243(16)	2971(13)	8369(12)
C(43)	− 2785(17)	3322(17)	8222(15)
C(44)	− 3414(18)	4418(17)	8046(17)
C(45)	− 2657(18)	5207(15)	8072(15)
C(46)	− 1155(17)	4911(14)	8247(13)
C(41)	− 421(15)	3860(14)	8344(12)
C(52)	2123(11)	5588(8)	7441(6)
C(53)	2613(11)	6568(8)	7383(6)
C(54)	3116(11)	6796(8)	8215(6)
C(55)	3129(11)	6044(8)	9106(6)
C(56)	2638(11)	5064(8)	9165(6)
C(51)	2135(11)	4837(8)	8332(6)
C(62)	868(8)	2791(8)	10365(7)
C(63)	1175(8)	2249(8)	11326(7)
C(64)	2572(8)	1702(8)	11542(7)
C(65)	3662(8)	1698(8)	10798(7)
C(66)	3354(8)	2240(8)	9838(7)
C(61)	1957(8)	2787(8)	9622(7)

fourier difference cycles revealed all other non-hydrogen atoms. For each structure least-squares refinement was blocked full-matrix, with anisotropic temperature factors for the ruthenium, phosphorus and oxygen and for the carbonyl and styryl carbon atoms. The unsubstituted phenyl rings were included as rigid groups with

TABLE 2

SELECTED BOND LENGTHS AND ANGLES FOR $[Ru_3(CO)_{10}(Ph_2PC_6H_4CH=CH_2-2)]$ (1)

Bond lengths (Å)

Ru(1)–Ru(2)	2.855(2)	C(1)–C(42)	1.44(2)
Ru(1)–Ru(3)	2.834(2)	C(41)–C(42)	1.46(3)
Ru(2)–Ru(3)	2.871(2)	C(42)–C(43)	1.44(2)
Ru(1)–P	2.348(5)	C(43)–C(44)	1.37(3)
Ru(2)–C(1)	2.25(2)	C(44)–C(45)	1.33(3)
Ru(2)–C(2)	2.23(2)	C(45)–C(46)	1.41(2)
C(1)–C(2)	1.44(3)	C(41)–C(46)	1.36(2)
P–C(41)	1.82(1)		
P–C(51)	1.84(1)		
P–C(61)	1.83(1)		

Ru–CO range from 1.86(2)–1.94(2) (average 1.91)

C–O range from 1.10(2)–1.18(3) (average 1.15)

Bond angles (°)

Ru(1)–Ru(2)–Ru(3)	59.3(1)	C(1)–C(42)–C(41)	121.4(13)
Ru(2)–Ru(1)–Ru(3)	60.6(1)	C(42)–C(41)–P	118.3(11)
Ru(1)–Ru(3)–Ru(2)	60.1(1)	C(42)–C(41)–C(46)	118.9(13)
Ru(1)–Ru(2)–C(1)	88.7(4)	Ru(1)–P–C(41)	110.1(6)
Ru(1)–Ru(2)–C(2)	126.2(6)	Ru(1)–P–C(51)	113.9(3)
Ru(3)–Ru(2)–C(1)	147.6(4)	Ru(1)–P–C(61)	121.6(4)
Ru(3)–Ru(2)–C(2)	172.9(6)	Ru(2)–Ru(1)–P	97.4(1)
Ru(2)–C(1)–C(2)	70.3(10)	Ru(3)–Ru(1)–P	157.9(1)
Ru(2)–C(1)–C(42)	119.9(11)	C(2)–Ru(2)–C(1)	37.5(7)
Ru(2)–C(2)–C(1)	72.2(10)	C(42)–C(1)–C(2)	125.5(14)
		C(43)–C(42)–C(1)	123.3(16)
		C(41)–C(42)–C(43)	115.4(15)

Dihedral angles (°)

Ru(1)–Ru(2)–Ru(3)/C(1)–C(2)–C(42)	72.0
Ru(1)–Ru(2)–Ru(3)/C(41)···C(46)	66.5
C(1)–C(2)–C(42)/C(41)···C(46)	9.7

isotropic thermal parameters and all aromatic hydrogen atoms were included in calculated positions with a common thermal parameter. All calculations were carried out using SHELX 76. Final residuals were:

(1) $R = 0.056$, $R_w = 0.059$, where $w = 1.00\left[\sigma^2(F_0) + 0.0007F_0^2\right]^{-1}$;

(2) $R = 0.036$, $R_w = 0.041$ where $w = 1.00\left[\sigma^2(F_0) + 0.0017F_0^2\right]^{-1}$.

Tables 1 and 2 contain final positional parameters, selected bond lengths and angles, and least squares planes and dihedral angles for complex **1**; Tables 3 and 4 contain similar data for complex **2**. Tables of structure factors, thermal parameters and full lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England, and may be obtained on request from the Director. All such requests should contain the full literature citation for this paper.

TABLE 3

FINAL POSITIONAL PARAMETERS FOR $[H_2Ru_3(\mu_3\text{-}HCCC_6H_4PPh_2)(CO)_8]$ (2)

| Atom	Molecule 1			Atom	Molecule 2		
	x	y	z		x	y	z
Ru(11)	5128(1)	4480(1)	3273(1)	Ru(21)	574(1)	9526(1)	3145(1)
Ru(12)	5067(1)	4219(1)	1731(1)	Ru(22)	1340(1)	9283(1)	1605(1)
Ru(13)	4239(1)	2788(1)	3195(1)	Ru(23)	1589(1)	7834(1)	3079(1)
P(1)	6483(1)	5654(1)	2715(1)	P(2)	−666(1)	10675(1)	2613(1)
C(11)	5985(6)	3102(5)	2707(5)	C(21)	62(6)	8159(5)	2536(5)
C(12)	6374(5)	3918(4)	2656(4)	C(22)	−362(5)	8965(4)	2505(5)
C(111)	3907(6)	5096(5)	3682(4)	C(211)	−432(7)	9010(5)	4180(5)
C(112)	5757(7)	3972(5)	4307(5)	C(212)	1580(6)	10140(5)	3569(5)
C(121)	3553(7)	4462(5)	1412(5)	C(221)	1415(7)	8592(6)	950(6)
C(122)	5894(7)	5262(7)	857(6)	C(222)	2984(8)	9526(5)	1327(5)
C(123)	5488(8)	3542(7)	1084(6)	C(223)	809(6)	10322(6)	704(6)
C(131)	4196(8)	1973(7)	2654(7)	C(231)	1132(7)	6945(6)	4200(7)
C(132)	4240(7)	1884(6)	4312(7)	C(232)	3222(8)	7995(5)	3194(5)
C(133)	2565(8)	2939(6)	3284(5)	C(233)	1837(7)	6968(6)	2586(6)
O(111)	3217(6)	5492(4)	3896(4)	O(211)	−1038(6)	8659(4)	4794(4)
O(112)	6147(6)	3620(4)	4927(4)	O(212)	2105(5)	10536(4)	3800(4)
O(121)	2645(6)	4629(5)	1242(4)	O(221)	1515(6)	8158(5)	563(5)
O(122)	6379(6)	5860(5)	308(4)	O(222)	3944(5)	9673(4)	1187(4)
O(123)	5778(7)	3140(5)	688(5)	O(223)	561(5)	10917(4)	135(4)
O(131)	4206(7)	1481(6)	2338(6)	O(231)	866(6)	6418(5)	4877(5)
O(132)	4218(6)	1346(5)	4984(5)	O(232)	4138(6)	8119(5)	3231(4)
O(133)	1629(6)	13059(5)	3305(5)	O(233)	1947(6)	6458(5)	2289(5)
C(142)	7794(4)	5674(3)	3944(3)	C(241)	−1435(4)	11084(3)	3365(3)
C(143)	8168(4)	6030(3)	4483(3)	C(242)	−2454(4)	10636(3)	3869(3)
C(144)	7740(4)	6837(3)	4480(3)	C(243)	−3017(4)	10913(3)	4482(3)
C(145)	6937(4)	7289(3)	3938(3)	C(244)	−2562(4)	11638(3)	4593(3)
C(146)	6563(4)	6933(3)	3400(3)	C(245)	−1543(4)	12086(3)	4089(3)
C(141)	6991(4)	6126(3)	3402(3)	C(246)	−979(4)	11809(3)	3476(3)
C(151)	7769(5)	5175(4)	2355(4)	C(251)	−1748(5)	10196(4)	2232(4)
C(152)	8858(6)	5581(5)	2127(4)	C(252)	−2798(6)	10580(5)	2000(5)
C(153)	9785(7)	5146(6)	1866(5)	C(253)	−3531(6)	10173(6)	1700(6)
C(154)	9563(7)	4334(6)	1833(5)	C(254)	−3242(6)	9397(6)	1624(6)
C(155)	8495(6)	3928(5)	2056(5)	C(255)	−2204(6)	8992(5)	1845(5)
C(156)	7550(5)	4340(4)	2337(4)	C(256)	−1443(5)	9401(4)	2180(4)
C(162)	6992(3)	7200(3)	1167(3)	C(261)	−71(3)	11696(2)	1717(2)
C(163)	6686(3)	7922(3)	460(3)	C(262)	−750(3)	12225(2)	1107(2)
C(164)	5521(3)	8091(3)	380(3)	C(263)	−274(3)	13011(2)	439(2)
C(165)	4661(3)	7538(3)	1006(3)	C(264)	880(3)	13267(2)	379(2)
C(166)	4966(3)	6816(3)	1712(3)	C(265)	1559(3)	12738(2)	989(2)
C(161)	6132(3)	6647(3)	1793(3)	C(266)	1084(3)	11952(2)	1657(2)

Results

A reaction between $Ru_3(CO)_{12}$ and sp in tetrahydrofuran at room temperature was initiated by dropwise addition of a solution of sodium diphenylketyl, and the solution rapidly darkened in colour to deep red. Crystallisation of the reaction

TABLE 4

SELECTED BOND LENGTHS AND ANGLES FOR $[H_2Ru_3(\mu_3\text{-HCCC}_6H_4PPh_2)(CO)_8]$ (2)

Bond lengths (Å)	Molecule 1	Molecule 2
Ru(1)–Ru(2)	2.874(1)	2.871(1)
Ru(2)–Ru(3)	2.731(1)	2.736(1)
Ru(1)–Ru(3)	3.021(1)	3.016(1)
Ru(1)–C(2)	2.098(7)	2.104(9)
Ru(2)–C(2)	2.262(7)	2.278(6)
Ru(2)–C(1)	2.289(7)	2.293(6)
Ru(3)–C(1)	2.085(6)	2.083(7)
Ru(1)–P	2.303(2)	2.301(2)
C(2)–C(56)	1.478(8)	1.498(9)
P–C(41)	1.816(6)	1.816(6)
P–C(51)	1.826(7)	1.818(8)
P–C(61)	1.844(4)	1.825(3)
Bond angles (°)		
Ru(1)–Ru(2)–Ru(3)	65.2(1)	65.0(1)
Ru(1)–Ru(3)–Ru(2)	59.7(1)	59.6(1)
Ru(2)–Ru(1)–Ru(3)	55.1(1)	55.3(1)
Ru(1)–C(2)–Ru(2)	82.4(2)	81.8(2)
Ru(3)–C(1)–Ru(2)	77.1(2)	77.2(2)
Ru(3)–C(1)–C(2)	114.5(5)	113.5(6)
Ru(1)–C(2)–C(1)	111.4(4)	112.4(5)
Ru(1)–C(2)–C(56)	119.9(6)	118.7(6)
C(1)–C(2)–C(56)	128.2(7)	128.4(8)
Dihedral angles (°)		
Ru(1)–Ru(2)–Ru(3)/C(1)–C(2)–C(56)	115.1	115.9
Ru(1)–Ru(2)–Ru(3)/C(51)···C(56)	112.6	112.5
C(1)–C(2)–C(56)/C(51)···C(56)	4.5	4.1

mixture afforded red $Ru_3(CO)_{10}(sp)$ in 74% yield, readily identified as **1** (Scheme 1) by analytical and spectroscopic techniques, with the final stereochemical details being supplied by a single-crystal X-ray diffraction study. In the ^1H NMR spectrum, the presence of an η^2-complexed $CH_2\!\!=\!\!CH$ fragment was shown by three equal
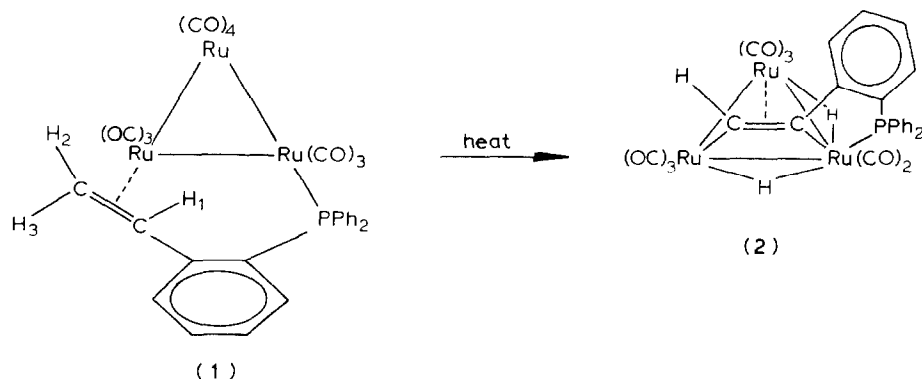
SCHEME 1

intensity resonances at δ 2.51d, 3.24d and 4.90q ppm, assigned to H(3), H(2) and H(1), respectively. These resonances have similar chemical shifts to those found in Ru(CO)₃(sp) (δ 1.62, 2.45 and 3.96 ppm) [1], but are quite distinct from those of a non-complexed vinyl group, which appear at lower fields. There are no resonances from metal-bonded protons.

Short heating in refluxing cyclohexane smoothly converted **1** to a yellow complex **2**, together with small amounts of $Ru_3(CO)_{12}$ and a second yellow product, which has not presently been identified. The major product analyses for $Ru_3(CO)_8(sp)$, corresponding to a loss of two CO groups from **1**. The ${}^1H$ NMR contains a characteristic low-field signal at δ 10.14, assigned to a CCH group (cf. similar low field resonances in $Os_3(\mu_3-\eta^2-HCCH)(\mu-CO)(CO)_9$ at δ 9.67, and in $H_2Os_3(\mu_3-HC-CMe)(CO)_9$ at δ 7.30 ppm [3]), together with a broad high-field singlet of relative intensity 2H at δ − 17.7 ppm. These data suggest that the formation of this complex occurs by migration of two hydrogen atoms from the vinyl group to the Ru_3 cluster, with concomitant bridging of the three metal atoms by the alkyne unit so formed (Scheme 1). The structure thus corresponds to **2**, and again the precise stereochemistry was confirmed by X-ray crystallography.

Crystal structures of 1 and 2

The crystal of **1** consists of discrete molecules, and there are no intermolecular contacts shorter than Van der Waals separations. The molecule (Fig. 1) consists of an Ru_3 cluster containing an unaltered sp ligand bridging the Ru(1)–Ru(2) bond, the P and C=C groups occupying adjacent equatorial sites. The CH=CH₂ group is displaced from the phenyl ring plane by 9.7°, and the plane C(42)–C(1)–C(2) is inclined at 72° to the Ru_3 plane. The C=C vector is nearly parallel to the Ru_3 plane and displaced by 0.2 Å from it; the P atom lies in the Ru_3 plane. The Ru(2)–C(1)
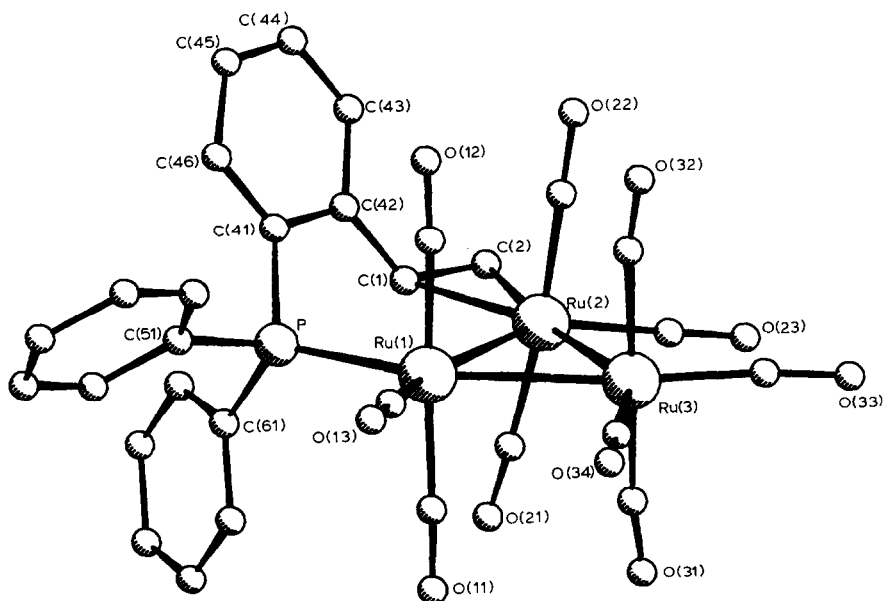

Fig. 1. PLUTO plot of $Ru_3(CO)_{10}(Ph_2PC_6H_4CH=CH_2-2)$ (**1**), showing atom numbering scheme.
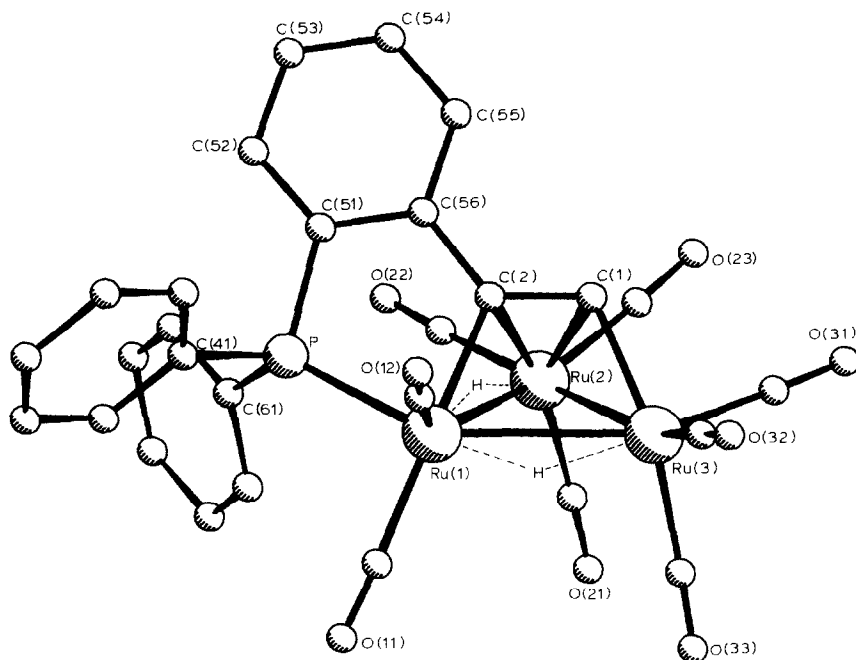
Fig. 2. PLUTO plot of $H_2Ru_3(\mu_3\text{-}HCCC_6H_4PPh_2)(CO)_8$ (2), showing atom numbering scheme.

and Ru(2)–C(2) bond lengths are equal within the precision of the experiment, at 2.24 Å (average), while the C(1)–C(2) bond (1.44(3) Å) is, as expected, intermediate in length between normal C–C single and C=C double bonds.

The asymmetric unit in **2** contains two independent molecules, but these do not differ significantly so the following discussion is based on bond parameters averaged over both molecules. In this complex (Fig. 2), the vinyl group of the sp ligand has been dehydrogenated to an ethynyl group which is now attached to all three metal atoms by means of σ-type interactions of C(1) and C(2) with Ru(3) and Ru(1), respectively, and a π-type interaction of C(1)–C(2) with Ru(2). The C_2 unit is thus attached in the familiar $(2\sigma + \pi)$, or $\mu_3\text{-}\eta^2$, mode. The Ru–C σ bonds are 2.085(6), 2.098(7) Å, while the distances of C(1) and C(2) from Ru(2) (2.262, 2.289(7) Å), are longer, and close to those of the η^2-vinyl-Ru group in **1**. The phosphorus atom occupies an equatorial site, but is displaced by 0.80 Å out of the Ru_3 plane. The C(1)–C(2) vector still lies effectively within the phenyl ring plane which is now inclined at 113° to the Ru_3 core; the displacements of C(1) and C(2) from the C_6 ring plane are 0.16 and 0.11 Å, respectively. The C(1)–C(2) vector is almost parallel (5.1°) to the Ru(1)–Ru(3) edge.

In **1**, the Ru–Ru bonds range between 2.834–2.871(2) Å; in **2** there is one short bond, at 2.731(1) Å, one of medium length, at 2.874(1) Å, and a long bond, at 3.021(1) Å. The latter is bridged by the alkyne (C_2) group, while the other two are bridged by only one carbon. The hydrogen atoms were not located in the structural study, but their chemical shift, and the Ru–Ru separations, suggest that they bridge Ru(1)–Ru(2) and Ru(1)–Ru(3). The single high field resonance, considerably broadened, indicates that they equilibrate rapidly on the NMR timescale. These locations

are also consistent with the positions of the CO groups, which are splayed out to form the usual cavities which are occupied by the hydrogens.

The Ru–P separations in **1** and **2** are 2.348(5) and 2.303(2) Å, respectively, and call for no special comment.

Discussion

Reactions of olefins with $Ru_3(CO)_{12}$ are reported to proceed in refluxing inert solvents to afford complexes containing μ_3-alkynyl, μ_2-vinyl, μ_3-allenyl or μ_3-allylic hydrido-carbonyls [4]. We have used the opportunity presented by our finding of the radical-catalysed substitution reactions of $Ru_3(CO)_{12}$ to prepare the first η^2-olefinic derivative of $Ru_3(CO)_{12}$. The olefinic tertiary phosphine sp readily affords **1** at room temperature within minutes, two CO groups being displaced from *cis* equatorial positions on adjacent metal atoms by the chelate ligand. Possible mechanisms for this reaction have been discussed previously [2]. No evidence was obtained for the formation of either of the *P*-bonded or η^2-bonded isomers of a putative intermediate $Ru_3(CO)_{11}(sp)$.

As expected on the basis of the results obtained earlier with simple monoolefins, **1** undergoes ready migration of hydrogen from the η^2-olefin to the metal cluster, with concomitant loss of CO and structural rearrangement to give the μ_3-η^2-alkyne complex **2**. In several previous instances, reactions of $Ru_3(CO)_{12}$ with olefins has given similar complexes. For example, ethylene (1 atm) is reported to react with $Ru_3(CO)_{12}$ to give complexes **3a** and **4a** [5], although a more recent paper [6] described only **4a**, together with mononuclear $Ru(CO)_4(\eta\text{-}C_2H_4)$ and complexes containing oligomers of the olefin. At higher temperatures and pressures, complex mixtures containing Ru_4 and Ru_6 clusters are obtained [7]. The trinuclear osmium analogues **3b** and **4b** have been obtained from reactions between $Os_3(CO)_{12}$ and ethylene [8].

(a , M = Ru ;
b, M = Os)

(5)
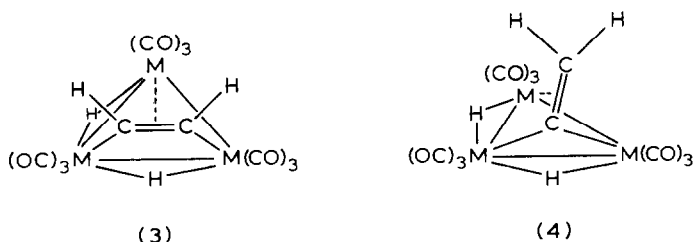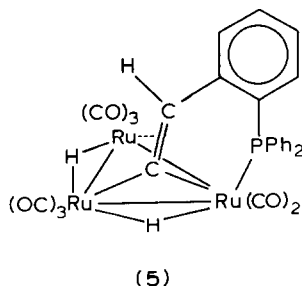
Our observations provide evidence for the generally-held assumption of the intermediacy of an $(\eta^2\text{-olefin})M_3(CO)_{11}$ complex in these reactions. However, we note that an osmium analogue, $Os_3(CO)_{11}(\eta\text{-}C_2H_4)$, obtained under relatively mild conditions from ethylene and $Os_3(CO)_{11}(NCMe)$, is readily transformed on heating to the μ_3-vinylidene complex **4b** [9], suggesting that these are the preferred isomers. However, the constraints imposed by the presence of the chelating phosphine evidently preclude the formation of complexes such as **5**.

Complexes **1** and **2** must also be intermediates in the production of the several mononuclear complexes observed by earlier workers, and we are presently investigating the further transformations that these complexes undergo on more vigorous heating.

Acknowledgements

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