

## CLUSTER CHEMISTRY

### XXXXII \*. SOME RUTHENIUM CARBONYL COMPLEXES OF *cis*-1,2-BIS(DIPHENYLPHOSPHINO)ETHENE. X-RAY STRUCTURE OF $\text{Ru}_2\{\mu\text{-C}_2\text{H}_2(\text{PPh}_2)_2\}(\text{CO})_6$

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(Received November 8th, 1985)

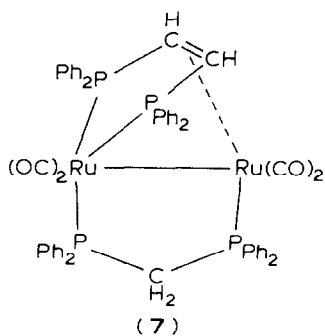
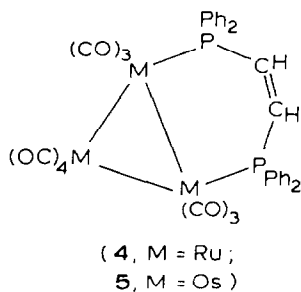
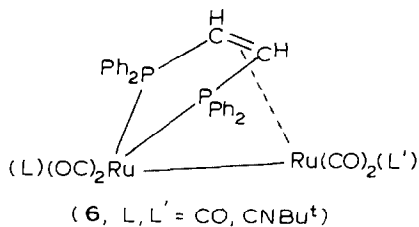
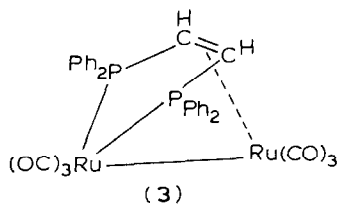
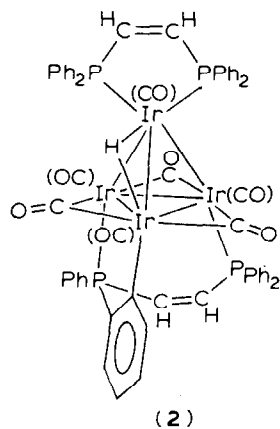
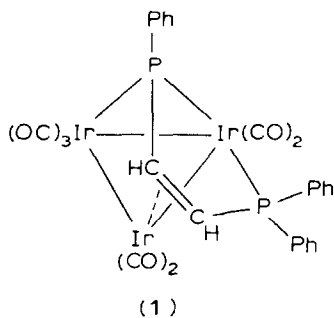
#### Summary

A reaction between  $\text{Ru}_3(\text{CO})_{12}$  and *cis*- $\text{PPh}_2\text{CH}=\text{CHPPh}_2$  (ebdp), catalysed by  $[\text{ppn}][\text{OAc}]$ , gave  $\text{Ru}_3(\mu\text{-ebdp})(\text{CO})_{10}$ , which readily eliminated  $\text{Ru}(\text{CO})_4$  on heating to form  $\text{Ru}_2(\mu\text{-ebdp})(\text{CO})_6$  in high yield. This complex has been fully characterised by an X-ray study, the ligand chelates one, nearly square-planar ruthenium, with the two phosphorus donors and bonds to the second, nearly trigonal bipyramidal ruthenium, via the C=C double bond. The Ru–Ru bond (2.8812(6) Å) is formally a 2e donor bond from the square planar Ru to the trigonal bipyramidal Ru. The complex  $\text{Ru}_2\{\mu\text{-C}_2\text{H}_2(\text{PPh}_2)_2\}(\text{CO})_6$  is monoclinic, space group  $P2_1/c$  with  $a$  12.242(3),  $b$  18.821(3),  $c$  13.613(2) Å,  $\beta$  90.69(1)° and  $Z = 4$ ; 5036 independent data with  $I > 3\sigma(I)$  were refined to  $R$  0.034,  $R'$  0.036. The reaction between  $\text{Os}_3(\text{CO})_{12}$  and ebdp gave only  $\text{Os}_3(\mu\text{-ebdp})(\text{CO})_{10}$ .

The facile substitution of CO by tertiary phosphines, phosphites or arsines has been achieved under electron transfer catalysis (ETC) conditions, using sodium diphenylketyl to initiate the reaction [1]. Similar results have been reported using  $[\text{ppn}][\text{OAc}]$  as catalyst [2]. As a result of these studies, ruthenium cluster carbonyl complexes containing a wide range of Group 15 donor ligands, including those with functional groups, are now available. We have recently described the synthesis, and further reactions of an open  $\text{Ru}_5$  complex derived from  $\{\text{Ru}_3(\text{CO})_{11}\}_2\{\mu\text{-}$

\* For Part XXXXI, see ref. 16.

$C_2(PPh_2)_2$  [3]; herein we report some studies on complexes derived from the related olefinic bis-tertiary phosphine, *cis*- $CH(PPh_2)=CH(PPh_2)$  (ebdp). To our knowledge, the only other cluster complexes containing this or related ligands are **1**, obtained from  $IrCl(CO)_2(NH_2C_6H_4Me-p)$  and the *trans* isomer of the olefinic phosphine with zinc under CO pressure, in which a dephenylated *cis* ligand bridges an  $Ir_3$  cluster, bonding via  $PPh$ ,  $PPh_2$  and  $C=C$  groups [4], and  $Ir_4(\mu\text{-ebdp})_2(CO)_8$  and its pyrolysis product **2**, in which oxidative cyclometallation of one of the phenyl groups has occurred [5].



The [ppn][OAc]-catalysed reaction between ebdp and  $\text{Ru}_3(\text{CO})_{12}$  in tetrahydrofuran gave two complexes, identified as the pale yellow binuclear  $\text{Ru}_2(\mu\text{-ebdp})(\text{CO})_6$  (**3**), and the ruby red cluster  $\text{Ru}_3(\mu\text{-ebdp})(\text{CO})_{10}$  (**4**). These complexes were characterised by microanalytical and spectroscopic methods, and in the case of **3**, by a single-crystal X-ray study (see below). The colour and relatively simple  $\nu(\text{CO})$  spectrum of **3** suggested that some fragmentation of the initial  $\text{Ru}_3(\text{CO})_{12}$  cluster had occurred, while the  $^1\text{H}$  NMR spectrum indicated coordination of the  $\text{CH}=\text{CH}$  moiety (multiplet at  $\delta$  3.22, AA'XX' pattern). In comparison, the olefinic protons of both the free ligand and **4**, in which it is only P-bonded, are found in the aromatic region. Complex **4** has a  $\nu(\text{CO})$  spectrum very similar to that of  $\text{Ru}_3(\mu\text{-dppe})(\text{CO})_{10}$ , which has been structurally characterised, and shows that the ebdp ligand bridges two metal atoms.

On heating in refluxing tetrahydrofuran for 1 h, the colour of a solution of **4** lightens to yellow-green, and TLC separation gave **3** and  $\text{Ru}_3(\text{CO})_{12}$ . The net reaction corresponds to a facile elimination of  $\text{Ru}(\text{CO})_4$  from **4**, but the reaction is not simple because rearrangement of the coordination of the ebdp ligand has occurred with both P atoms chelating one metal atom. Similar rearrangement of a  $\mu\text{-dppe}$  ligand to chelating has been reported for the isomerisation of  $\text{H}_4\text{Ru}_4(\text{CO})_{10}(\text{dppe})$  [6,7]; the related dppm complex contains a  $\mu\text{-dppm}$  ligand [8].

On the basis of the above observation, the most efficient synthesis of **3** was by heating  $\text{Ru}_3(\text{CO})_{12}$  with an excess of ebdp in refluxing tetrahydrofuran for 2.25 h. The reaction mixture first darkens, when **4** is present, then lightens to yellow-green. If an excess of ebdp is not present, some  $\text{Ru}_3(\text{CO})_{12}$  remains at the end of the reaction.

A similar reaction between  $\text{Os}_3(\text{CO})_{12}$  and ebdp, carried out in refluxing toluene, afforded a poor yield of orange  $\text{Os}_3(\mu\text{-ebdp})(\text{CO})_{10}$  (**5**). This has a  $\nu(\text{CO})$  spectrum which is similar to that of **4**, but shifted by up to  $10\text{ cm}^{-1}$  to higher energy; the  $\mu\text{-ebdp}$  structure shown is assigned to this compound. There was no conversion to the osmium analogue of **3** on longer heating.

Complex **1** undergoes CO-substitution reactions on heating for long periods with  $\text{CNBu}^t$  or dppm in refluxing cyclohexane to give off-white  $\text{Ru}_2(\text{CO})_5(\text{CNBu}^t)(\text{ebdp})$  (**6**) and pale yellow  $\text{Ru}_2(\text{CO})_4(\text{dppm})(\text{ebdp})$  (**7**), respectively. The spectral properties of these complexes are not sufficient to determine the molecular structures of these complexes, and it is not possible to determine to which ruthenium atom in **6** the isocyanide ligand is attached. The well-known propensity for dppm to bridge two metal atoms leads us to suggest that a similar mode of attachment occurs in **7**, but we have not been able to obtain any X-ray quality crystals.

### *Molecular structure of 3*

A molecule of **3** is shown in Fig. 1, and details of the environment of each metal atom are given in Table 2. The complex is binuclear, with the ebdp ligand bridging the two metal atoms, and is bonded to one ruthenium by the two phosphorus atoms, and to the second by the olefinic  $\text{C}=\text{C}$  double bond. Three carbonyl groups on each ruthenium complete the coordination. Ru(1) thus achieves the 18e configuration from  $(3\text{CO} + 2\text{P})$ , whereas Ru(2) receives only eight electrons from  $(3\text{CO} + \text{C}=\text{C})$ . The Ru(1)–Ru(2) interaction is therefore considered to be an Ru(1)  $\rightarrow$  Ru(2) donor bond; its length (2.8812(6) Å) is considerably greater than those found in  $\text{Ru}_2(\text{CO})_6\{\text{C}_4(\text{CO}_2\text{Me})_4\}$  [9],  $\text{Ru}_2(\text{CO})_6\{\text{C}_4(\text{CH}_2\text{OH})_4\}$  and  $\text{Ru}_2(\text{CO})_6\{\text{C}_4\text{Et}_2(\text{C}_2-$

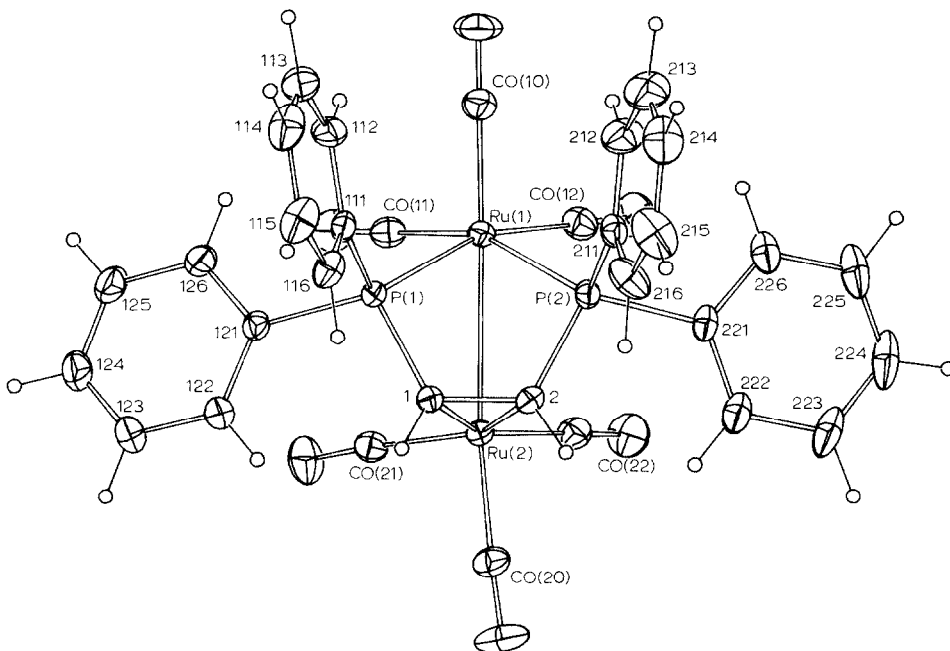


Fig. 1. A single molecule of  $\text{Ru}_2(\mu\text{-ebdp})(\text{CO})_6$  (**3**), showing atom numbering system, and 20% thermal ellipsoids for the non-hydrogen atoms. Hydrogen atoms have an arbitrary radius of 0.1 Å.

$\text{H}_4\text{OH})_2\}$  [10] (2.734(2), 2.753(2) and 2.743(3), and 2.717(1) Å, respectively) but it is comparable with that in  $\text{Ru}_3(\text{CO})_{12}$  (2.852 Å) [11].

The Ru(1)–P(1) and Ru(1)–P(2) distances (2.366(1) and 2.376(1) Å) are within the usual range found for  $\text{Ru}^0\text{–P}$  bonds; the Ru(2)–C(1) and Ru(2)–C(2) distances (2.170(3) and 2.167(3) Å) are likewise unexceptional, while the C(1)–C(2) bond (1.445(5) Å) is similar to that found in (**1**) (1.435(16) Å) [4]. The coordination about Ru(1) approaches square-pyramidal (angles C(10)–Ru(1)–C(11), –C(12), –P(1) and –P(2) are 98.0(2), 95.3(2), 101.5(1)° and 102.6(2)°, respectively), while that about Ru(2) is distorted trigonal-bipyramidal (angles C(20)–Ru(2)–C(21), –C(22) and to C(1)–C(2) mid-point are 94.0(2), 93.3(2) and 93.6(2)°, respectively; angles C(21)–Ru(2)–C(22), C(21)–Ru(2)–(C(1)–C(2) mid-point) and C(22)–Ru(2)–(C(1)–C(2) mid-point) are 99.2(2), 125.7(1) and 133.7(1)°, respectively). The C(10)–Ru(1)–Ru(2) and C(20)–Ru(2)–Ru(1) angles are 166.8(1) and 168.7(1)°, respectively, suggesting that the maximum orbital overlap in the Ru–Ru donor bond occurs outside the line connecting the metal atoms, near the point where the C(10)–Ru(1) and C(20)–Ru(2) vectors intersect. Interestingly, a similar pairing of trigonal bipyramidal and pyramidal geometries has been found recently in the dianion  $[\text{Ru}_2(\text{CO})_8]^{2-}$ ; in this case, the Ru–Ru separation is 2.936(1) Å [12].

In conclusion, we note that the formation of **3** is another example of the profound rearrangement which occurs on coordinating olefinic tertiary phosphines to  $\text{Ru}_3(\text{CO})_{12}$ . In the present case, formation of the trinuclear complex **4** is followed by rapid thermal degradation of the cluster to **3** and  $\text{Ru}_3(\text{CO})_{12}$  in a reaction that must involve migration of one of the P atoms from one metal to that adjacent to it,

already bearing the second P-donor group, with concomitant coordination of the olefinic moiety. We have previously noted the high but different reactivity of the coordinated olefinic group in  $\text{Ru}_3(\text{CO})_{10}(\text{sp})$  ( $\text{sp} = 2\text{-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$ ), which is rapidly dehydrogenated at temperatures as low as  $40^\circ\text{C}$  to give a cluster-bonded alkynylphosphine ligand in  $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-}\eta^2, P\text{-HC}\equiv\text{CC}_6\text{H}_4\text{PPh}_2)(\text{CO})_8$  [13].

TABLE 1  
NON-HYDROGEN ATOM COORDINATES

Atom	x	y	z
Ru(1)	0.20948(2)	0.10156(2)	0.08250(2)
Ru(2)	0.18000(2)	0.24595(2)	0.14729(2)
C(10)	0.2428(3)	0.0021(2)	0.0691(3)
O(10)	0.2611(3)	-0.0560(2)	0.0572(3)
C(11)	0.2808(3)	0.1347(2)	-0.0335(3)
O(11)	0.3227(3)	0.1536(2)	-0.1024(2)
C(12)	0.0702(3)	0.0966(2)	0.0135(3)
O(12)	-0.0089(3)	0.0925(2)	-0.0284(3)
C(20)	0.1549(3)	0.3322(2)	0.2140(3)
O(20)	0.1359(3)	0.3835(2)	0.2540(3)
C(21)	0.2723(3)	0.2889(2)	0.0501(3)
O(21)	0.3283(3)	0.3176(2)	-0.0022(2)
C(22)	0.0423(3)	0.2500(2)	0.0771(3)
O(22)	-0.0380(3)	0.2542(2)	0.0345(3)
P(1)	0.35731(7)	0.14111(5)	0.18177(7)
C(111)	0.4374(3)	0.0763(2)	0.2532(3)
C(112)	0.4661(4)	0.0112(2)	0.2131(3)
C(113)	0.5327(4)	-0.0344(2)	0.2673(4)
C(114)	0.5693(4)	-0.0171(3)	0.3580(4)
C(115)	0.5423(4)	0.0470(3)	0.3978(3)
C(116)	0.4758(3)	0.0936(2)	0.3457(3)
C(121)	0.4697(3)	0.1907(2)	0.1267(3)
C(122)	0.5026(3)	0.2567(2)	0.1624(3)
C(123)	0.5876(4)	0.2923(3)	0.1199(4)
C(124)	0.6408(4)	0.2639(3)	0.0417(5)
C(125)	0.6108(4)	0.1997(3)	0.0055(4)
C(126)	0.5257(4)	0.1618(2)	0.0486(3)
C(1)	0.2890(3)	0.2020(2)	0.2585(2)
C(2)	0.1771(3)	0.1862(2)	0.2833(3)
P(2)	0.12095(7)	0.10609(5)	0.23672(7)
C(211)	0.1390(3)	0.0344(2)	0.3270(3)
C(212)	0.1415(4)	0.0506(3)	0.4251(3)
C(213)	0.1491(5)	-0.0024(3)	0.4957(4)
C(214)	0.1545(4)	-0.0716(3)	0.4676(4)
C(215)	0.1524(5)	-0.0888(3)	0.3699(4)
C(216)	0.1447(4)	-0.0359(3)	0.2994(4)
C(221)	-0.0275(3)	0.1155(2)	0.2385(3)
C(222)	-0.0912(3)	0.0594(3)	0.2066(3)
C(223)	-0.2032(4)	0.0643(3)	0.2069(4)
C(224)	-0.2527(3)	0.1242(4)	0.2382(4)
C(225)	-0.1917(4)	0.1808(3)	0.2717(4)
C(226)	-0.0777(3)	0.1760(3)	0.2719(3)

TABLE 2

RUTHENIUM ENVIRONMENT (The first column in the matrix is the ruthenium–ligand distance (Å); the other entries are the angles (degrees) subtended at the ruthenium by the atoms at the head of the relevant row and column. Geometries at the central ligand atoms are given similarly)

Ru(1)	<i>r</i>	P(1)	P(2)	C(10)	C(11)	C(12)		
Ru(2)	2.8812(6)	68.04(3)	68.62(3)	166.8(1)	90.3(1)	94.7(1)		
P(1)	2.366(1)		80.67(4)	101.5(1)	90.9(1)	162.6(1)		
P(2)	2.376(1)			102.6(1)	158.9(1)	91.3(1)		
C(10)	1.926(4)				98.0(2)	95.3(2)		
C(11)	1.918(4)					91.3(2)		
C(12)	1.939(4)							
Ru(2)	<i>r</i>	P(1)	P(2)	C(1) <sup>a</sup>	C(2) <sup>a</sup>	C(20)	C(21)	C(22)
Ru(1)	2.8812(6)	47.70(2)	47.67(2)	77.02(9)	77.03(9)	168.7(1)	96.2(1)	89.9(1)
P(1)	2.967(1)		62.00(3)	36.23(9)	62.56(9)	128.3(1)	87.3(1)	137.6(1)
P(2)	2.993(1)			61.96(10)	35.85(10)	121.3(1)	142.6(1)	91.3(1)
C(1)	2.170(3)				38.9(1)	95.4(2)	106.2(1)	152.5(1)
C(2)	2.167(3)					91.8(2)	145.1(1)	114.9(2)
C(20)	1.886(4)						94.0(2)	93.3(2)
C(21)	1.928(4)							99.2(2)
C(22)	1.929(4)							
P(1)	<i>r</i>	Ru(2)	C(1) <sup>a</sup>	C(111)	C(121)			
Ru(1)	2.366(1)	64.26(3)	100.2(1)	119.6(1)	120.0(1)			
Ru(2)	2.967(1)		46.5(1)	155.6(1)	98.5(1)			
C(1)	1.768(4)			111.8(2)	106.0(2)			
C(111)	1.836(4)				99.0(2)			
C(121)	1.830(4)							
P(2)	<i>r</i>	Ru(2)	C(2) <sup>a</sup>	C(211)	C(221)			
Ru(1)	2.376(1)	63.71(3)	99.7(1)	120.8(1)	118.6(1)			
Ru(2)	2.993(1)		45.8(1)	153.0(1)	99.5(1)			
C(2)	1.772(4)			110.0(2)	107.1(2)			
C(211)	1.837(4)				100.0(2)			
C(221)	1.827(3)							

<sup>a</sup> C(1)–C(2), 1.445(5) Å. Ru(2)–C(1)–P(1), C(2), 97.2(1), 70.4(2). Ru(2)–C(2)–P(2), C(1), 98.4(2), 70.7(2). P(1)–C(1)–C(2), 117.5(3); P(2)–C(2)–C(1), 117.1(3)°.

TABLE 3

## CARBONYL GEOMETRIES

Carbonyl	<i>r</i> (C–O) (Å)	Ru–C–O (°)
10	1.129(6)	177.1(4)
11	1.132(5)	179.3(4)
12	1.121(5)	178.0(4)
20	1.135(5)	177.5(4)
21	1.131(5)	175.2(3)
22	1.138(5)	178.0(4)

## Experimental

All reactions were carried out under a nitrogen atmosphere, but no special precautions were taken to exclude oxygen during work-up; all complexes described below were unaffected by air in the solid state. The ligand ebdp was obtained from Strem Chemicals, Danvers, Mass., and was used as received.

### Reactions of *cis*-CH(PPh<sub>2</sub>)=CH(PPh<sub>2</sub>) (ebdp)

(a) *With Ru<sub>3</sub>(CO)<sub>12</sub> in the presence of [ppn][OAc].* [ppn][OAc] (5 mg) was added to a solution of Ru<sub>3</sub>(CO)<sub>12</sub> (100 mg, 0.156 mmol) and ebdp (313 mg, 0.78 mmol) in thf (30 ml) and the mixture was stirred for 1 h. The solution was evaporated and separated (preparative TLC, developed with light petroleum/acetone 70/30) to give two fractions: band 1 (*R<sub>f</sub>* 0.5), pale yellow, was crystallised (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) to give clear pale yellow crystals of Ru<sub>2</sub>(μ-ebdp)(CO)<sub>6</sub> (**3**) (42 mg, 23%), m.p. 180–182°C (dec). (Found: C, 49.88; H, 2.99; C<sub>32</sub>H<sub>22</sub>O<sub>6</sub>P<sub>2</sub>Ru<sub>2</sub> calcd.: C, 50.14; H, 2.89%). IR (cyclohexane): ν(CO) 2070s, 2032s, 2014s, 1989s, 1974s, 1964vs cm<sup>-1</sup>; <sup>1</sup>H NMR: δ (CDCl<sub>3</sub>) 7.97–6.90, m, 20H, Ph; 3.22, AA'XX' pattern, 2H, C<sub>2</sub>H<sub>2</sub>; <sup>13</sup>C NMR: δ (CDCl<sub>3</sub>) 203.2–195.6, m, CO; 142.5–127.7, m, Ph; 17.4, m, C<sub>2</sub>H<sub>4</sub>. Band 2 (*R<sub>f</sub>* 0.2), red, was crystallised (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) to give ruby red crystals of Ru<sub>3</sub>(μ-ebdp)(CO)<sub>10</sub> (**4**) (65 mg, 43%) m.p. 140–141°C (dec). (Found: C, 44.07; H, 2.18; C<sub>36</sub>H<sub>22</sub>O<sub>10</sub>P<sub>2</sub>Ru<sub>3</sub> calcd.: C, 44.13; H, 2.26%). IR (cyclohexane): ν(CO) 2085m, 2038s, 2018m, 2009vs, 1986w, 1975m, 1945w cm<sup>-1</sup> (cf. Ru<sub>3</sub>(μ-dppe)(CO)<sub>10</sub> 2083m, 2016vs, 2002s, 1986w, 1960w cm<sup>-1</sup>). <sup>1</sup>H NMR: δ (CDCl<sub>3</sub>) 7.37–8.00, m, Ph and C<sub>2</sub>H<sub>2</sub>.

(b) *With Ru<sub>3</sub>(CO)<sub>12</sub> in refluxing tetrahydrofuran.* A mixture of Ru<sub>3</sub>(CO)<sub>12</sub> (300 mg, 0.469 mmol) and ebdp (300 mg, 0.749 mmol) was stirred in refluxing thf (30 ml) for 2.25 h. The solution first darkened to deep red, and then changed to yellow-green. This solution was evaporated and chromatographed (preparative TLC, light petroleum/acetone 90/10) to give two bands: band 1, yellow, was crystallised (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) to give yellow crystals of Ru<sub>2</sub>(μ-ebdp)(CO)<sub>6</sub> (**3**) (475 mg, 88%) identified from its IR ν(CO) spectrum; band 2, orange (trace) Ru<sub>3</sub>(μ-dppm)(CO)<sub>10</sub>, identified from its IR ν(CO) spectrum, and probably originating in a small amount of dppm present in the unsaturated ligand, and from which the latter is made.

(c) *With Os<sub>3</sub>(CO)<sub>12</sub> in refluxing toluene.* A mixture of Os<sub>3</sub>(CO)<sub>12</sub> (100 mg, 0.11 mmol) and ebdp (44 mg, 0.11 mmol) was stirred in refluxing toluene (20 ml) for 2.5 h during which time the colour changed from yellow to orange. The solution was evaporated and the residue separated (preparative TLC, light petroleum/acetone 90/10) to give three bands and an orange base line. Band 1 (*R<sub>f</sub>* 0.45), yellow Os<sub>3</sub>(CO)<sub>12</sub> (40 mg, 40%) (IR); band 3 (*R<sub>f</sub>* 0.20), yellow, was crystallised (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) to give orange crystals of Os<sub>3</sub>(μ-ebdp)(CO)<sub>10</sub> (**5**) (32 mg, 23%) m.p. > 200°C. (Found: C, 34.70; H, 1.66; C<sub>36</sub>H<sub>22</sub>O<sub>10</sub>Os<sub>3</sub>P<sub>2</sub> calcd.: C, 34.67; H, 1.78%). IR (cyclohexane): ν(CO) 2098m, 2048s, 2014vs, 1994w, 1979w, 1967m, 1939w cm<sup>-1</sup>. (cf. Os<sub>3</sub>(μ-dppm)(CO)<sub>10</sub> 2098m, 2033m, 2019s, 2010vs, 1986m, 1968m, 1958s, 1947w, 1922vw cm<sup>-1</sup>). <sup>1</sup>H NMR: δ (CDCl<sub>3</sub>) 7.37–8.01, m, Ph and C<sub>2</sub>H<sub>2</sub>. The other bands were not characterised.

### Pyrolysis of Ru<sub>3</sub>(μ-ebdp)(CO)<sub>10</sub> (**4**)

A solution of Ru<sub>3</sub>(μ-ebdp)(CO)<sub>10</sub> (50 mg, 0.051 mmol) in thf (10 ml) was refluxed for 1 h during which time the colour changed from red to yellow-green (the

reaction was monitored by TLC). Evaporation and separation by preparative TLC (light petroleum/acetone 90/10) gave two major bands. Band 1 ( $R_f$  0.8),  $\text{Ru}_3(\text{CO})_{12}$  (6 mg, 19%) (IR); band 2 ( $R_f$  0.4), was crystallised ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ ) to give  $\text{Ru}_2(\mu\text{-ebdp})(\text{CO})_6$  (**3**) (30 mg, 51%) (IR).

#### Reactions of $\text{Ru}_2(\mu\text{-ebdp})(\text{CO})_6$ (**3**)

(a) *With CNBu'*. A mixture of  $\text{Ru}_2(\mu\text{-ebdp})(\text{CO})_6$  (100 mg, 0.130 mmol) and  $\text{CNBu}'$  (11 mg, 0.132 mmol) was stirred in refluxing cyclohexane (20 ml) for 44 h when the reaction was adjudged complete (the disappearance of the  $\nu(\text{CO})$  band of **3** at  $2070\text{ cm}^{-1}$  was monitored). The solution was evaporated and the residue recrystallised ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ ) to give  $\text{Ru}_2(\text{CO})_5(\text{CNBu}')(\text{ebdp})$  (**6**) (100 mg, 93%) as an off-white powder, m.p.  $110\text{--}115^\circ\text{C}$ . (Found: C, 52.74; H, 3.88; N, 1.78;  $\text{C}_{36}\text{H}_{33}\text{NO}_5\text{P}_2\text{Ru}_2$  calcd.: C, 52.49; H, 4.04; N, 1.70%). IR (cyclohexane)  $\nu(\text{CN})$   $2164\text{m}$ ;  $\nu(\text{CO})$   $2035\text{s}$ ,  $2007\text{s}$ ,  $1969\text{s}$ ,  $1955\text{s}$ ,  $1948\text{s cm}^{-1}$ .

(b) *With dppm*. A mixture of  $\text{Ru}_2(\mu\text{-ebdp})(\text{CO})_6$  (100 mg, 0.130 mmol) and dppm (50 mg, 0.130 mmol) was stirred in refluxing cyclohexane ( $20\text{ cm}^3$ ) for 74 h when the reaction was adjudged complete (the disappearance of the  $\nu(\text{CO})$  band at  $2070\text{ cm}^{-1}$  was monitored). The solution was dried and the residue recrystallised ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ ) to give fine pale yellow crystals of  $\text{Ru}_2(\text{CO})_4(\text{dppm})(\text{ebdp})$  (**7**) (115 mg, 81%), m.p.  $>250^\circ\text{C}$ . (Found: C, 59.94; H, 3.91;  $\text{C}_{55}\text{H}_{44}\text{O}_4\text{P}_4\text{Ru}_2$  calcd.: C, 60.33; H, 4.05%). IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$   $2052\text{vs}$ ,  $1996\text{m}$ ,  $1979\text{s}$ ,  $1959\text{w}$ ,  $1905\text{m cm}^{-1}$ .  $^1\text{H NMR}$ :  $\delta$  ( $\text{CDCl}_3$ ) 6.78–8.12, m, 40H, Ph; 2.5–4.0, m, 4H,  $\text{CH}_2$  and  $\text{C}_2\text{H}_2$ .

#### Crystallography

*Crystal data.*  $\text{C}_{32}\text{H}_{22}\text{O}_6\text{P}_2\text{Ru}_2$ , mol. weight = 766.6, Monoclinic, space group  $P2_1/c$  ( $C_{2h}^5$ , No. 14),  $a$  12.242(3),  $b$  18.821(3),  $c$  13.613(2) Å,  $\beta = 90.69(1)^\circ$ ,  $U$  3136.2(9) Å<sup>3</sup>,  $D_m$  1.60(1),  $D_c$  ( $Z = 4$ ) 1.62 g cm<sup>-3</sup>,  $F(000)$  1520. Monochromatic  $\text{Mo-K}\alpha$  radiation,  $\lambda$  0.71069 Å,  $\mu$  18.8 cm<sup>-1</sup>. Specimen:  $0.27 \times 0.28 \times 0.25$  mm.  $A_{\text{min,max}}^*$  (Gaussian absorption correction): 1.42, 1.55.  $T$  295 K.

*Structure determination.* A unique data set was measured to  $2\theta_{\text{max}} 55^\circ$ , using a Syntex P1 four-circle diffractometer in conventional  $2\theta/\theta$  scan mode. 7235 independent reflections were obtained, 5036 with  $I > 3\sigma(I)$  being considered 'observed' and used in the basically  $9 \times 9$  block diagonal least-squares refinement after solution of the structure by direct methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; ( $x, y, z, U_{\text{iso}}$ )<sub>H</sub> were included constrained at idealized values. For the olefinic hydrogen atoms, however, ( $x, y, z$ ) observed from difference maps are given. Residuals at convergence,  $R, R'$  on  $|F|$ , were 0.034, 0.036, reflection weights being  $(\sigma^2(I_0) + 0.0003\sigma^4(I_0))^{-1}$ . Neutral complex scattering factors were used [14]; computing was carried out with the XTAL 83 program system [15], implemented by S.R. Hall on a Perkin-Elmer 3240 computer. Results are given in the Figures and Tables; atom labelling is also shown in the Figure. Material deposited comprises structure factor amplitudes, thermal parameters, hydrogen atom parameters, ligand geometries and planes.

#### Acknowledgements

We thank the Australian Research Grants Scheme for financial support of this work; MLW was the holder of a Commonwealth Post-Graduate Research Award.



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