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Reactions of metalloalkynes 3. Facile synthesis of pentanuclear ruthenium clusters. X-ray structures of $[Ru_5(\mu_5\text{-}C{\equiv}C)(\eta\text{-}C_5H_4R)_2(dppm)(\mu_2\text{-}CO)_2(CO)_7]$ ($R = H, CH_3$)[1]

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Abstract

The reaction of the activated cluster compound, $Ru_3(CO)_{10}(dppm)$, **1**, with two ethyne-1,2-diyl compounds, $[\{Ru(CO)_2(\eta\text{-}C_5H_4R)\}_2(\mu\text{-}C{\equiv}C)]$, (**2a**, R = H; **2b**, $R = CH_3$) has resulted in a facile and high yielding synthesis of medium nuclearity cluster compounds, $[Ru_5(\mu_5\text{-}C{\equiv}C)(\eta\text{-}C_5H_4R)_2(dppm)(\mu_2\text{-}CO)_2(CO)_7]$, (**3a**, R = H; **3b**, $R = CH_3$). The core of these compounds incorporate an open and accessible carbide ligand bound to a relatively rare example of a spiked butterfly metal framework. Both of these clusters, **3**, have been characterised by X-ray crystallography. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Cluster; Carbide; Pentanuclear

1. Introduction

We are interested in the reactivity of metalloalkynes [1] in so far as their reactivity is similar or in fact different to the reactivity of simple organic alkynes. Our recent work [2] has indicated that the course of these reactions can sometimes be unpredictable.

The dimetalloalkynes, or ethyne-1,2-diyl [3–12] complexes are a special class of these complexes and their reactivity has been of particular interest [1] but little studied because of the paucity of methods for their preparation. These molecules contain the C_2 ligand that has inspired not just the scientific literature but also found vent in somewhat more conventional prose [13]. The ligand itself is quite pervasive but is often implicated in catalytic CO hydrogenation mechanisms [14]. Multinuclear homo- and heterometallic complexes containing the C_2 molecule offer the opportunity to study and observe the reactivity of such species.

The enhanced reactivity of $Ru_3(CO)_{10}(dppm)$ (dppm = 1,2-bis(diphenylphosphino)methane), **1**, over the ubiquitous $Ru_3(CO)_{12}$ is well known [15–26]. The phosphine containing cluster was found to smoothly add terminal alkynes [27] and this seemed a convenient starting point for the rational preparation of a medium nuclearity cluster.

2. Results and discussion

The reaction of an equimolar amount of **1** and $[\{Ru(CO)_2(\eta\text{-}C_5H_4R)\}_2(\mu\text{-}C{\equiv}C)]$, (**2a**, R = H; **2b**, $R = CH_3$), in refluxing tetrahydrofuran (THF) was carried out for a period of 48 h. Products were separated by preparative TLC giving a number of minor products that are yet to be characterised in both reactions and one major product, $[Ru_5(\mu_5\text{-}C{\equiv}C)(\eta\text{-}C_5H_4R)_2(dppm)(\mu_2\text{-}CO)_2(CO)_7]$, (**3a**, R = H; **3b**, R =

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[1] Dedicated to Professor Michael I. Bruce on the occasion of his 60th birthday and in recognition of his contribution to Organometallic chemistry. Happy birthday, Michael!

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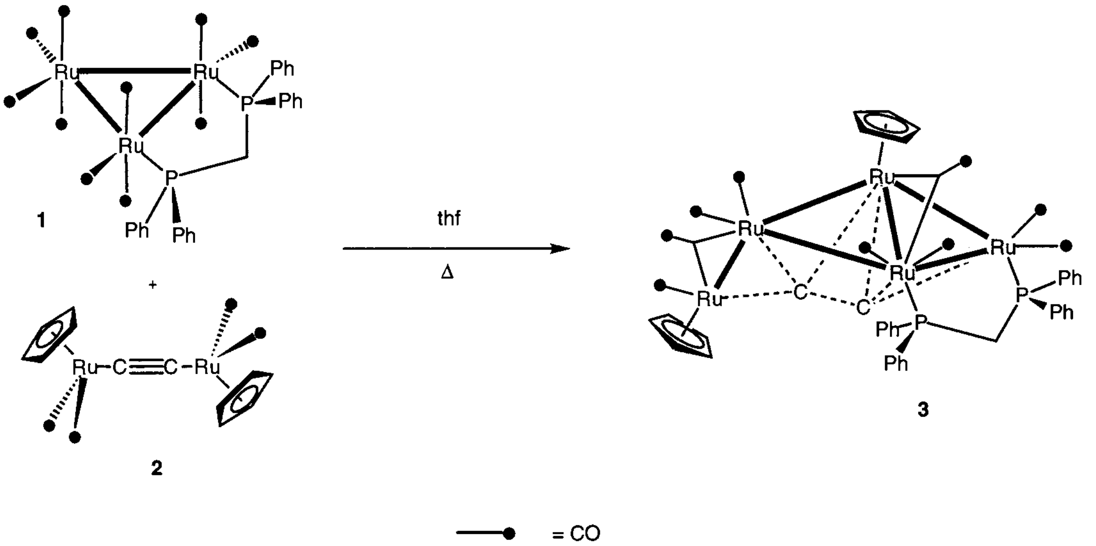


Scheme 1. Summary of the reactions involved in the production of complexes **3**.

CH_3), in 74 and 55% yield, respectively. Complexes **3a** and **3b** were fully characterised by spectroscopic and X-ray crystallographic studies. The reactions are summarised in Scheme 1.

The solution IR spectra obtained for the compounds were similar and contained terminal ν(CO) bands and lower frequency bands assigned to the semi-bridging carbonyl groups. The proton NMR spectra contain resonances that are readily assigned to the two inequivalent methylene protons of the dppm ligand group in **3a** and **3b** with apparent coupling to the two inequivalent phosphorus atoms of the dppm ligand. The two inequivalent cyclopentadienyl groups give singlets at 4.66 and 4.97 ppm, respectively, in **3a**, and the CH_3 protons of the methylcyclopentadienyl ligand in **3b** are at 1.19 and 1.56 ppm, with eight separate resonances for the CH protons. The aromatic signals are in the usual region of the proton spectrum for both **3a** and **3b**.

The ^{13}C-NMR spectrum of the complexes **3** were similar, containing a double doublet for the methylene carbons and two signals for the inequivalent C_5H_5 groups in **3a**. All the carbons of the methyl cyclopentadienyl ligands in **3b** were inequivalent giving ten signals for the ring carbons and two for the methyl substituents at ca. 13 ppm. The quaternary ring carbons were assigned with the aid of DEPT experiments and were observed downfield of the methine carbons in the ring at 101.6 and 106.3 ppm.

The complexes both contain nine carbonyl groups and the majority of these can be assigned to signals observed in the spectrum. A number of these carbonyls would be expected to show coupling to the phosphorus atoms in the ^{13}C-NMR spectrum although it is unclear whether they would see both of these nuclei. The point of interest is the assignment of signals attributable to the carbide ligand. Two small signals were observed at δ 86.2 and 88.9 ppm in **3a** and it was tempting to assign these to the carbide ligand. However, DEPT NMR experiments showed that these were in fact due to a small percentage of an unidentified compound (ca. 1%) and were probably C_5H_5 signals of presumably an isomer of **3a**; there were no analogous signals in the spectrum of **3b**. The region downfield of the phenyl resonances shows 11 signals including one at δ 248.6 (**3a**) and 251.3 (**3b**) that have been tentatively assigned to one of the carbide carbons with the other probably at δ 211.8 (**3a**) and 211.9 ppm (**3b**). These signals appear to qualitatively have the longest relaxation times. In the relatively few examples of clusters containing the C_2 ligand, there appears to be no sensible correlation between chemical shift of that ligand, when observed, and structural and electronic properties.

Complexes **3** gave molecular ions in their FAB MS spectra with surprisingly little fragmentation observed for complex **3b**.

2.1. Solid-state structures of 3

The results of the r.t. X-ray structure determinations are presented (Figs. 1 and 2) with relevant interatomic parameters in Table 1. Details of the structure solutions and refinements are contained in Table 2

Suitable dark green/black specimens for X-ray diffraction were obtained from CH_2Cl_2/alcohol, which crystallised in the monoclinic space group $P2_1/c$ for **3a** and $P2/c$ for **3b**, with one complete molecule and the included (dichloromethane: two for **3a**, one-half for **3b**) solvent molecules comprising the asymmetric unit.

A recent survey of medium nuclearity clusters reports that the spiked butterfly arrangement of the ruthenium core adopted by the complexes has only been seen twice for 103 structurally characterised M_5 Ru and Os clus-

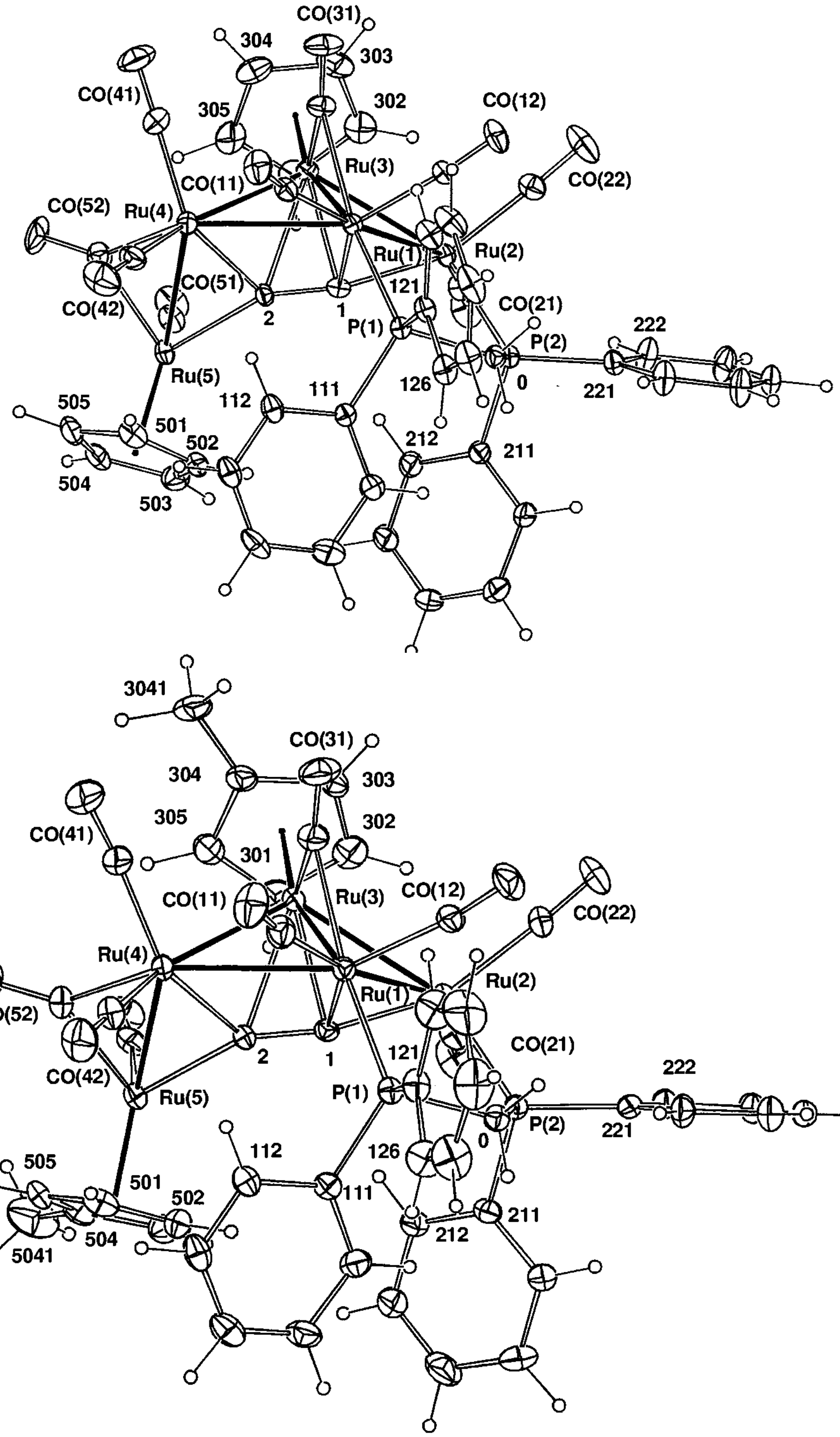


Fig. 1. Molecular structures of **3a** (above) and **3b** (below): 20% probability ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

ters[28]; significantly both these examples contain the C_2 ligand. The most relevant of these structure determinations to the present work is that of $[Ru_5(\mu_5\text{-}CC)(\eta\text{-}PPh_2)_2(CO)_{11}(py)_2]$ [29], **4**. The geometry of the Ru_5 C_2 core (Fig. 2) for complexes **3** is similar in most respects to that of complex **4** and the analogous bond lengths and angles are collected in Table 1 for direct comparison. The metal cores in **3** are comprised of a rather flattened butterfly (dihedral angles between the planes bounded by Ru(2)–Ru(3)–Ru(1) and Ru(4)–Ru(3)–Ru(1) are 143.18(4) (**3a**), 140.77(4) (**3b**) and 147.42(4)° (**4**)), with the extra ruthenium atom occupying a wingtip position on the butterfly. The Ru–Ru separations are comparable between the three structures with the hinge distance being the shortest, but the longest between Ru(1) and Ru(4) in **3** and associated with the 'spike', Ru(4)–Ru(5), in **4**. The C_2 ligand in the complexes **3** is bound to all five ruthenium atoms but C(2) does not bond to Ru(1) (Ru(1)–C(2) 2.702(3), **3a**; 2.756(7), **3b** Å), this being essentially the only difference in connectivity between the cores of **3** and **4**; the analogous distance in **4** is also rather long.

The C_2 ligand contributes six electrons to the 78 c.v.e complex with Ru(1), Ru(3) and Ru(5) achieving a formal 18-electron count and the remaining metal atoms have 17-electron counts. A consideration of the bonding distances and geometries of the central cores in the complexes **3** suggests a structure consistent with that depicted in **I**.

The remaining electron density is supplied to the cluster by two pentahapto cyclopentadienyl ligands attached to Ru(3) and Ru(5), presumably persisting from the ethyne-1,2-diyl starting material. The dppm ligand has remained intact and is bound through its phosphorus atoms to Ru(1) and Ru(2) with distances similar to that expected for bidentate coordination. The remaining ligands defining the connectivity are two semi-bridging carbonyl groups, one bridging the hinge and the other the spike and seven terminal CO ligands. The bond lengths and angles of these supporting ligands are unexceptional.

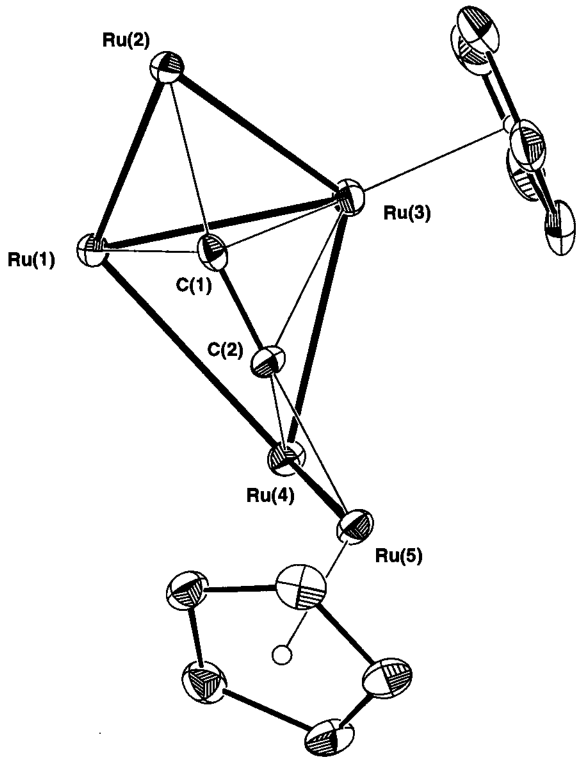


Fig. 2. Central core geometries of complex **3a**.

Table 1
Selected bond distances (Å) and angles (°) for $[Ru_5(\mu_5\text{-}C{\equiv}C)(\eta\text{-}C_5H_4R)_2(dppm)(\mu_2\text{-}CO)_2(CO)_7]$, **3a**, **3b** and $[Ru_5(\mu_5\text{-}C{\equiv}C)(\eta\text{-}PPh_2)_2(CO)_{11}(py)_2]$, **4**

	3a	**3b**	**4** [29]
Bond lengths (Å)			
Ru(1)–Ru(2)	2.775(1)	2.782(2)	2.8418(5)
Ru(1)–Ru(3)	2.738(1)	2.746(1)	2.7184(6)
Ru(1)–Ru(4)	2.972(1)	2.969(1)	2.8425(5)
Ru(2)–Ru(3)	2.838(1)	2.835(1)	2.8112(5)
Ru(3)–Ru(4)	2.833(1)	2.857(1)	2.8850(6)
Ru(4)–Ru(5)	2.777(1)	2.786(1)	2.9357(5)
Ru(1)–C(1)	2.184(8)	2.183(6)	2.165(3)
Ru(1)–C(2)	2.702(8)	2.756(7)	2.434(3)
Ru(2)–C(1)	1.982(7)	1.964(7)	1.955(4)
Ru(3)–C(1)	2.165(6)	2.183(6)	2.210(4)
Ru(3)–C(2)	2.337(7)	2.351(7)	2.309(4)
Ru(4)–C(2)	2.134(7)	2.109(7)	2.123(3)
Ru(5)–C(2)	2.066(8)	2.050(7)	2.192(4)
Ru(1)–P(1)	2.321(2)	2.326(2)	—
Ru(2)–P(2)	2.286(2)	2.277(2)	—
C(1)–C(2)	1.29(1)	1.308(9)	1.301(5)
Bond angles (°)			
Ru(1)–Ru(4)–Ru(5)	106.26(3)	107.85(3)	100.87(1)
Ru(3)–Ru(4)–Ru(5)	90.96(3)	90.33(4)	90.45(1)
Ru(2)–C(1)–Ru(3)	86.2(3)	86.1(2)	85.8(2)
Ru(2)–C(1)–Ru(1)	83.4(2)	84.0(2)	85.9(1)
Ru(4)–C(2)–Ru(5)	82.7(3)	84.1(2)	85.7(2)
Ru(2)–C(1)–C(2)	166.1(5)	164.1(5)	162.6(3)
Ru(4)–C(2)–C(1)	125.1(6)	123.2(5)	135.5(3)
Ru(5)–C(2)–C(1)	152.0(6)	152.2(5)	138.7(3)
Ru(3)–C(2)–Ru(4)	78.5(2)	79.4(2)	—
Ru(3)–C(2)–Ru(5)	130.5(3)	130.7(3)	—

2.2. Formation of the complexes

The reactions of $Ru_3(CO)_{10}(dppm)$, **1**, are often characterised by an abundance of products as a result of the enhanced reactivity of this substituted cluster. In the absence of a facile interaction with a provided substrate, **1** will cannibalise its bidentate phosphine ligand extruding benzene after orthometallating one of its other phosphine phenyl substituents resulting in the formation of **5**.

This enhanced reactivity of **1** over $Ru_3(CO)_{12}$ results from steric strain induced at the unsubstituted Ru atom in **1** by the presence of the dppm ligand bridging a Ru–Ru bond. This has the ultimate effect of labilising an equatorial carbonyl on the unsubstituted Ru atom and allowing ready substitution at this position. Possible structures, **II** and **III**, have been proposed as intermediates at which nucleophilic substitution can occur at a vacant coordination site in the former and rapid associative substitution occurs at the 17-electron $Ru(CO)_4$ moiety in the latter. Scheme 2 depicts the probable course of the reaction between **1** and the ethyne-1,2-diyls, **2**. In the posited intermediate **IV** one of the $Ru(\eta\text{-}C_5H_5)$ fragments interacts with one of the dppm substituted Ru atoms to form the hinge bond found in **3a** and incorporating the originally unsubstituted Ru atom from **1** into the butterfly core ultimately giving complexes **3**.

3. Conclusion

The reaction of $Ru_3(CO)_{10}$(dppm) with ruthenium ethyne-1,2-diyl complexes has allowed us to present the rational synthesis of medium nuclearity cluster compounds. These clusters contain a carbide ligand attached to five metals with a high degree of accessibility and with the absence of bridging ligands likely to complicate the reactions of the central C_2 ligand. We are currently investigating the reactivity of these complexes.

4. Experimental

4.1. General conditions

Manipulation of oxygen- and moisture-sensitive compounds was performed under an atmosphere of high purity argon using standard Schlenk techniques or in a dry box (Miller Howe).

IR spectra were recorded using a Bio-Rad FTS 45 or 40 FTIR spectrometer. ^{1}H- and ^{13}C-NMR spectra were acquired using Varian Gemini 200 or Bruker ARX 500 spectrometers. ^{31}P-NMR spectra were acquired using a Bruker ARX 500 spectrometer. ^{1}H- and ^{13}C-NMR spectra were referenced with respect to incompletely deuterated solvent signals. ^{31}P-NMR spectra are reported relative to external 85% H_3PO_4 (0.0 ppm) and are proton decoupled.

Table 2
Summary of diffraction data for the complexes

Complex	3a	3b
Formula	$C_{46}H_{32}O_9P_2Ru_5\cdot 2CH_2Cl_2$	$C_{48}H_{36}O_9P_2Ru_5\cdot 0.5CH_2Cl_2$
Mr	1465.9	1366.6
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (C^5_{2h}, No. 14)	$P2/c$ (C^4_{2h}, No. 13)
a (Å)	11.465(4)	11.631(3)
b (Å)	28.224(11)	17.620(9)
c (Å)	16.975(5)	24.268(8)
β (°)	110.50(3)	93.53(2)
V (Å^3)	3145(3)	4964(3)
Z	4	4
D_{calc} (g cm^{-3})	1.89_2	1.82_8
μ_{Mo} (cm^{-1})	17.6	16.6
F(000)	2856	2668
Crystal size (mm)	0.23 × 0.08 × 0.36	0.34 × 0.57 × 0.15
A^* (min, max)	1.14, 1.44	1.28, 1.73
$2\theta_{max}$ (°)	50	50
N	8707	8729
N_0	6614	6907
R	0.046	0.044
R_w	0.045	0.061

MS spectra were obtained on a VG AutoSpec spectrometer employing a fast atom bombardment (FAB) ionisation source in all samples unless otherwise specified.

Elemental analysis were performed by Chemical and Micro Analytical Services, Melbourne, Australia.

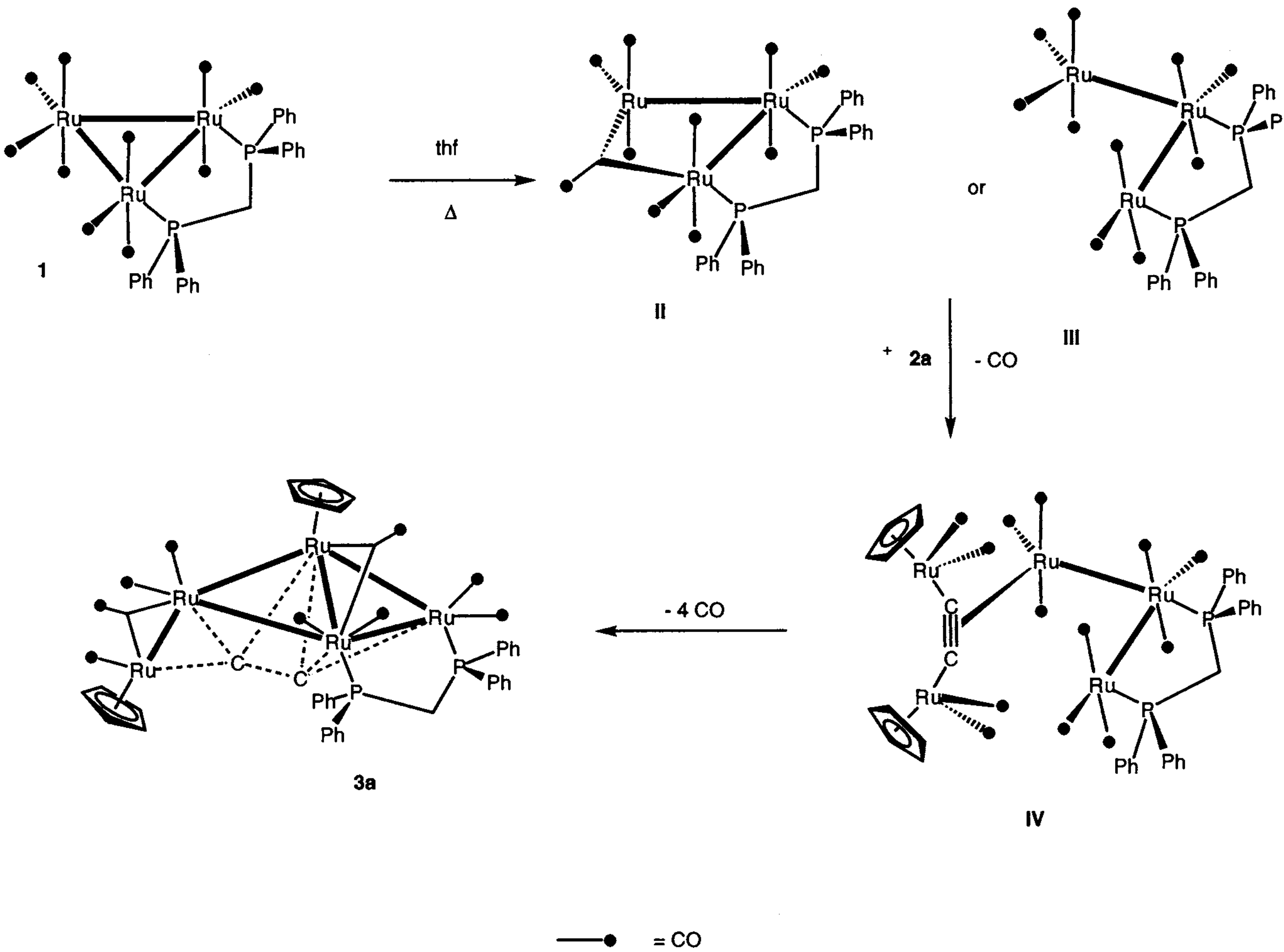
THF was dried over sodium metal and distilled from potassium benzophenone ketyl under an atmosphere of argon. *n*-Hexane and toluene were dried over sodium metal and distilled from sodium benzophenone ketyl under an atmosphere of argon.

4.2. Starting materials

The compounds $[Ru_3(CO)_{10}(dppm)]$ [30] and $[\{Ru(CO)_2(\eta\text{-}C_5H_4R)\}_2(\mu\text{-}C{\equiv}C)]$ [31] were prepared according to literature procedures.

4.3. Preparation of $[Ru_5(\mu_5\text{-}C{\equiv}C)(\eta\text{-}C_5H_5)_2(dppm)(\mu_2\text{-}CO)_2(CO)_7]$ (3a)

To a solution of **1** (0.100 g, 0.103 mmol) in THF (20 ml) solid $[\{Ru(CO)_2(\eta\text{-}C_5H_5)\}_2(\mu_2\text{-}C{\equiv}C)]$, **2**, (0.050 g, 0.107 mmol) was added and the resulting solution stirred at r.t. for 1 h and then heated under reflux for 12 h. The solvent was removed in vacuo and the green/black residue was chromatographed on silica TLC plates. Seven bands were developed; the major green/black band (R_f 0.33) was collected and crystallised from CH_2Cl_2/MeOH giving deep green/black crystals of **3a** (0.150g, 74%), in two crops. Anal. Calc. for $C_{46}H_{32}O_9P_2Ru_5\cdot 2CH_2Cl_2$: C, 39.32; H, 2.47. Found: C, 39.20; H, 2.18%. IR (CH_2Cl_2): ν(CO) 2006 m, 1988 vs, 1951 s, 1933 sh, 1833 vw, 1763 w cm^{-1}. ^{1}H-NMR (CD_2Cl_2) δ 3.42 (m, 1H, $P_xCH_AH_BP_y$), 3.94 (m, 1H, $P_xCH_AH_BP_y$), 4.66 (s, 5H, C_5H_5), 4.97 (s, 5H, C_5H_5), 6.3–8.3 (m, 20H, *Ph*PCH_2). $^{13}C\{^1H\}$-NMR (CD_2Cl_2) 47.6 (dd, $J_{cp} = 23$, 27 Hz; $P_xCH_2P_y$); 84.4 (s, C_5H_5); 87.8 (s, C_5H_5); 128.7–137.0 (m, *Ph*PCH_2); 183.9 (s, CO); 184.7 (s, CO); 200.1 (d, $J_{cp} = 9$ Hz, CO); 201.2 (s, CO); 207.3 (d, $J_{cp} = 7$ Hz, CO); 208.6 (s, CO); 209.4 (d, $J_{cp} = 38$ Hz, CO); 211.5 (d, $J_{cp} = 15$ Hz, CO); 211.8 (s, *C*C); 212.7 (d, $J_{cp} = 17$ Hz, CO); 248.6 (s, *C*C). $^{31}P\{^1H\}$-NMR (C_6D_6) δ 32.5 (d, $^2J_{PP} = 42$ Hz *P*CH_2P), 37.6 (d, $^2J_{PP} = 42$ Hz PCH_2*P*). FAB MS (NOBA/CH_2Cl_2) m/z 1296, [M$^+$]; 1031–807, [M-nCO]$^+$ $n = 1$–9.



Scheme 2. Probable reaction course between **1** and **2**.

4.4. Preparation of [$Ru_5(\mu_5\text{-}C{\equiv}C)(\eta\text{-}C_5H_4CH_3)_2(dppm)(\mu_2\text{-}CO)_2(CO)_7$] (3b)

To a solution of **1** (0.100 g, 0.103 mmol) in THF (20 ml) solid [{$Ru(CO)_2(\eta\text{-}C_5H_4Me)\}_2(\mu_2\text{-}C{\equiv}C)$], **2b**, (0.053 g, 0.106 mmol) was added and the resulting solution stirred at r.t. for 1 h and then heated under reflux for 12 h. The solvent was removed in vacuo and the green/black residue was chromatographed on silica TLC plates. Seven bands were developed, the major green/black band (R_f 0.33) was collected and crystallised from CH_2Cl_2/MeOH giving deep green/black crystals of **3b** (0.150g, 55%), in two crops. Anal. Calc. for $C_{48}H_{36}O_9P_2Ru_5\cdot 2CH_2Cl_2$: C, 40.18; H, 2.70. Found: C, 39.72; H, 2.63%. IR (CH_2Cl_2): ν(CO) 2004 m, 1986 vs, 1948 s, 1928 sh, 1830 vw, 1762 w cm^{-1}. ^{1}H-NMR (CD_2Cl_2) δ 1.19 (s, 3H, C_5H_4Me); 1.56 (s, 3H, C_5H_4Me); 2.78 (m, 1H, $P_xCH_AH_BP_y$); 3.36 (m, 2H, $P_xCH_AH_BP_y$ and C_5H_4Me), 3.02 (m, 1H, C_5H_4Me); 3.61 (m, 1H, C_5H_4Me); 3.91 (m, 1H, C_5H_4Me); 4.09 (m, 2H, C_5H_4Me); 4.62 (m, 1H, C_5H_4Me); 4.70 (m, 1H, C_5H_4Me) 5.7–7.6 (m, 20H, PhPCH$_2$). ^{13}C{^{1}H}-NMR (CD_2Cl_2) 12.8 (s, $C_5H_4CH_3$) 13.2 (s, $C_5H_4CH_3$) 47.9 (dd, $J_{cp} = 23$, 27 Hz; $P_xCH_2P_y$); 81.2, 82.4, 83.7, 83.8, 85.3, 87.1, 89.7, 91.2 (s, 2 × $C_5H_4CH_3$); 101.6, 106.3 (s, CCH_3); 128.95–137.2 (m, PhPCH$_2$); 184.7 (s, CO); 185.3 (d, $J_{cp} = 5$ Hz, CO); 200.5 (d, $J_{cp} = 9.6$ Hz, CO); 201.3 (br s, CO); 207.6 (d, $J_{cp} = 7$ Hz, CO); 209.3 (s, CO); 210.8 (d, $J_{cp} = 37$ Hz, CO); 211.9 (s, CC); 212.0 (d, $J_{cp} = 15$ Hz, CO); 213.1 (d, $J_{cp} = 17$ Hz, CO) 251.3 (s, CC). ^{31}P{^{1}H}-NMR (C_6D_6) δ 31.0 (d, $^2J_{PP} = 40$ Hz PCH$_2$P), 35.8 (d, $^2J_{PP} = 40$ Hz PCH$_2P$). FAB MS (NOBA/CH_2Cl_2) m/z 1325, [M$^+$].

4.5. Structure determinations of 3

Unique r.t. diffractometer data sets were measured ($2\theta/\theta$ scan mode, $2\theta_{max}$ 50°; monochromatic Mo–K$_\alpha$ radiation, $\lambda = 0.71073$ Å; $T \sim 295$ K), yielding N independent reflections, N_0 of these with $I > 2\sigma(I)$ considered 'observed' and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ being constrained at estimated values. Conventional residuals R, R_w on $|F|$ are quoted at convergence, statistical weights being derivative of $\sigma^2(I)=\sigma^2(I_{\rm diff})+0.0004\sigma^4(I_{\rm diff})$. Neutral atom complex scattering factors were employed. Computation used the XTAL3.4 program system implemented by S.R. Hall.

The solvent molecules in **3a** were constrained to unit populations after initial refinement and were refined as half weighted in **3b**.

Acknowledgements

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