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Coupling of acetylide and C_2 fragments during cluster condensation: pyrolysis of $[\{Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_8\}_2(\mu\text{-dppa})]$ [dppa = $C_2(PPh_2)_2$]

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Thermolysis of $[\{Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_8\}(\mu\text{-dppa})]$ [dppa = $C_2(PPh_2)_2$] gave two hexanuclear cluster complexes which were characterised as $[Ru_6(\mu_5\text{-}Bu^tCH{=}CHC_2PPh_2)(\mu_4\text{-}C_2Bu^t)(\mu\text{-}PPh_2)(CO)_{13}]$ and $[Ru_6(\mu_6\text{-}C_2CH{=}CHBu^t)(\mu_3\text{-}C_2Bu^t)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{12}]$ by X-ray crystallography, partial hydrogenation of the C_2Bu^t moiety being confirmed by ^1H NMR spectroscopy.

The chemistry of metal cluster carbonyls containing alkyne ligands has been well developed.[1,2] A characteristic reaction is coupling of a co-ordinated alkyne with a second or third molecule of alkyne, either the same or different. Related oligomerisation of 1,3-diynes and coupling of alkynes with 1,3-diynes has been reported by Carty and co-workers,[3,4] who have prepared carbon chains containing eight or twelve carbon atoms. However, as Lavigne and co-workers[5] have observed recently, such processes are not necessarily predictable.

Many complexes containing the acetylenic bis-tertiary phosphine $C_2(PPh_2)_2$ (dppa) bridging two metal carbonyl cluster moieties have now been reported. Examples include homodicluster complexes such as $[\{ML_n\}_2(\mu\text{-dppa})]$ [$ML_n = Re_3(\mu\text{-}H)_3(CO)_{11}$,[6] $Ru_3(CO)_{11}$,[7] $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_8$,[8] $Os_3(CO)_{11}$,[9,10] $NiOs_3(\mu\text{-}H)_3(CO)(\eta\text{-}C_5H_5)$[8] or $AuOs_4(\mu\text{-}H)(CO)_{12}$[10]] and heterodicluster derivatives, such as $[\{ML_n\}(\mu\text{-dppa})\{M'L'_m\}]$ [$ML_n = Ru_3(CO)_{11}$, $M'L'_m = Re_3(\mu\text{-}H)(CO)_{11}$,[6] $NiOs_3(\mu\text{-}H)_3(CO)_8(\eta\text{-}C_5H_5)$[8] or $Os_3(CO)_{11}$;[6] $ML_n = NiOs_3(\mu\text{-}H)_3(CO)_8(\eta\text{-}C_5H_5)$, $M'L'_m = Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_8$[8] or $NiRu_3(\mu\text{-}H)_3(CO)_8(\eta\text{-}C_5H_5)$[8]]. One reason for their synthesis is to examine the possibility of further interaction of the cluster nuclei with the C≡C triple bond, perhaps accompanied by cluster condensation to form higher nuclearity cluster cores. This has been achieved in several cases in reactions which have also taken advantage of the ready tendency of P–C(sp) bonds to cleave when acetylenic tertiary phosphines are co-ordinated to metal clusters.[11] For example, pyrolysis of $[\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})]$ affords $[Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}]$,[7] which on treatment with dimethyl disulfide gives a cluster containing the C_2 ligand, $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$.[12] Much chemistry of both these clusters has been reported and reviewed.[13] Similar studies of complexes derived from $Ph_2PC{\equiv}CC{\equiv}CPPh_2$ have shown that a variety of unusual cluster geometries can be obtained.[14]

We considered that the ready generation of a C_2 ligand from complexes containing the dppa ligand might be combined with the tendency of co-ordinated alkynes or alkynyl systems to give coupled species that would contain extended unsaturated carbon chains. Recently we described the synthesis of a cluster-bound butatrienylidene from $[Ru_5(\mu_5\text{-}C_2)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{11}]$ and $C_2(SiMe_3)_2$, probably by coupling of the C_2 ligand with an intermediate $:C{=}CH(SiMe_3)$ ligand on the cluster.[15]

Herein we describe some related results, in which we show that thermolysis of $[\{Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_8\}_2(\mu\text{-dppa})]$ **1**[16] affords two products, formed by cluster condensation with linking of C_2 or C_2PPh_2 fragments from the dppa ligand with a hydrogenated C_2Bu^t group.

After heating cluster **1** in refluxing toluene for 25 min (Scheme 1), separation by preparative TLC on silica gel gave two products, **2** and **3**, each obtained as black crystals.† Mass spectra showed that these were isomeric (both had M^+ at m/z 1530, which fragmented by loss of up to 13 CO groups). Their structures were determined by single crystal X-ray studies which, in conjunction with their ^1H NMR spectra, showed that they had the formulations $[Ru_6(\mu_5\text{-}Bu^tCH{=}CHC_2PPh_2)(\mu_4\text{-}C_2Bu^t)(\mu\text{-}PPh_2)(CO)_{13}]$ **2** and $[Ru_6(\mu_6\text{-}C_2CH{=}CHBu^t)(\mu_3\text{-}C_2Bu^t)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{12}]$ **3**.‡ Plots of the molecular

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† A solution of cluster **1** (80 mg, 0.05 mmol) in toluene (40 cm^3) was heated at reflux for 25 min. Separation by preparative TLC (silica gel, acetone–hexane 3:7) gave a grey-black band [R_f 0.83, containing **2** (9 mg, 12%) and a dark red-brown band (R_f 0.70) containing **3** (16 mg, 21%)]. Both complexes gave black prismatic crystals from CH_2Cl_2–MeOH which had correct elemental analyses (Found for **2**: C, 39.95; H, 2.65. Found for **3**: C, 39.35; H, 2.75. $C_{51}H_{40}O_{13}P_2Ru_6$ requires C, 40.05; H, 2.65%).

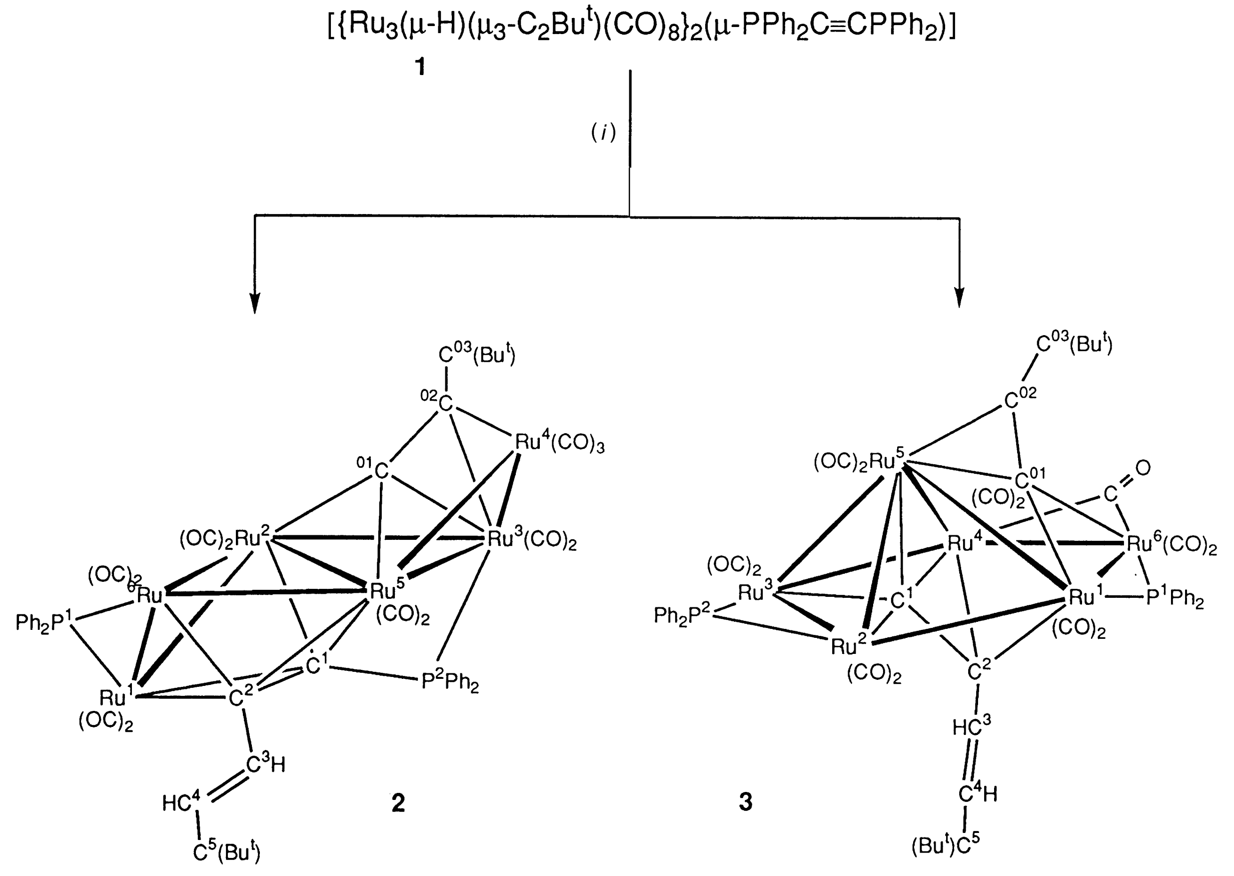
For **2**. IR (cyclohexane): ν(CO) 2074m, 2032w, 2013vs, 2001m, 1994w, 1981vw, 1967vw, 1961w, 1954vw, 1944vw cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.50 (s, 9 H, CMe_3), 1.29 (s, 9 H, CMe_3), 4.92 [d, $J(HH) = 15.15$, 1 H, CH], 5.55 [d, $J(HH) = 15.15$ Hz, 1 H, CH], 7.32–8.34 (m, 20 H, Ph). FAB mass spectrum: m/z 1530, M^+; 1502–1166, $[M - nCO]^+$ ($n = 1$–13).

For **3**. IR (cyclohexane): ν(CO) 2055w, 2031vs, 2004m, 1993s, 1968vw, 1957vw, 1935vw, 1896vw (br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.45 (s, 9 H, CMe_3), 1.22 (s, 9 H, CMe_3), 5.20 [d, $J(HH) = 15.3$, 1 H, CH], 5.43 [d, $J(HH) = 15.3$ Hz, 1 H, CH], 7.34–8.10 (m, 20 H, Ph). FAB mass spectrum: m/z 1530, M^+; 1502–1166, $[M - nCO]^+$ ($n = 1$–13).

‡ Unique room-temperature four-circle diffractometer data sets (2θ–θ scan mode; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å; $T \approx 295$ K), N independent absorption-corrected data, $N_o[I > 3\sigma(I)]$ deemed 'observed' and used in the large-block least-squares refinement (anisotropic thermal parameter forms for non-hydrogen atoms); $(x, y, z, U_{iso})_H$ included constrained at estimated values. Conventional R, R' on $|F|$ quoted [statistical weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$]; neutral atom complex scattering factors, XTAL 92[17] program system.

For **2** $[Ru_6(\mu_5\text{-}Bu^tCH{=}CHC_2PPh_2)(\mu_4\text{-}C_2Bu^t)(\mu\text{-}PPh_2)(CO)_{13}]$, $C_{51}H_{40}O_{13}P_2Ru_6$, $M = 1529.2$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 21.35(1)$, $b = 20.392(10)$, $c = 26.927(4)$ Å, $\beta = 110.53(4)°$, $U = 10\,978$ Å^3, D_c ($Z = 8$) = 1.85 g cm^{-3}, $F(000) = 5952$, $\mu_{Mo} = 17.3$ cm^{-1}, specimen: 0.50 × 0.56 × 0.28 mm, $A^*_{min,max} = 1.35$, 1.63 (Gaussian correction), $2\theta_{max} = 50°$, $N = 19\,265$, $N_o = 13\,137$; $R = 0.040$, $R' = 0.040$, $(\Delta/\sigma)_{max,mean} = 0.1$, 0.004, $|\Delta\rho|_{max} = 0.9$ e Å^{-3}. Comment: the *tert*-butyl groups of the two independent molecules are rotationally disordered. Location of associated hydrogen atoms assigns C(n3)–C(n4) as the double bond in each.

For **3** $[Ru_6(\mu_6\text{-}C_2CH{=}CHBu^t)(\mu_3\text{-}C_2Bu^t)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{12}]\cdot CH_2Cl_2$, $C_{51}H_{40}O_{13}P_2Ru_6\cdot CH_2Cl_2$, $M = 1614.2$, monoclinic, space group $P2_1/c$, $a = 18.604(1)$, $b = 14.761(3)$, $c = 21.03(2)$ Å, $\beta = 91.78(5)°$, $U = 5772$ Å^3, D_c ($Z = 4$) = 1.86 g cm^{-3}, $F(000) = 3144$, $\mu_{Mo} = 17.4$ cm^{-1}, specimen: 0.27 × 0.26 × 0.80 mm, $A^*_{min,max} = 1.45$, 1.72, $2\theta_{max} = 60°$, $N = 16\,778$, $N_o = 9607$, $R = 0.046$, $R' = 0.046$, $(\Delta/\sigma)_{max,mean} = 0.1$, 0.004,


$[\{Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_8\}_2(\mu\text{-}PPh_2C{\equiv}CPPh_2)]$

1

2

3

Scheme 1 (*i*) Toluene, reflux, 25 min

structures are given in Figs. 1 and 2, respectively, the captions of which contain significant bond parameters not otherwise referred to below. Both contained Ru_6 clusters, though with different geometries; the asymmetric unit of **2** contains two similar molecules, the geometry of molecule 1 being quoted as representative.

Complex **2** contains a non-planar core comprised of four fused triangles (or two edge-fused butterflies) [Ru–Ru separations 2.6693(9)–2.905(2) Å; the shortest bond is the diagonal of the Ru(2,3,5,6) rhomboid, while Ru(1)–Ru(6), bridged by P(1), is also short, at 2.6952(9) Å] which supports a ligand formed by formal cleavage of one P–C(sp) bond in the original dppa ligand, followed by coupling of the resulting C_2PPh_2 fragment with one of the C_2Bu^t groups. The resulting C_4 ligand has also picked up the two cluster hydrides to give a Bu^tCH-CHC_2PPh_2 ligand. The PPh_2 group bridges the Ru(1)–Ru(6) edge [Ru(1,6)–P(1) 2.252, 2.299(2) Å]. The second C_2Bu^t ligand is now attached to four Ru atoms in a manner similar to that found in $[Ru_3Pt(\mu_4\text{-}C_2Bu^t)(\mu\text{-}PPh_2)(CO)_7(dppe)]$.[18] Here, C(01) is σ-bonded to Ru(2,3,5) [2.019–2.105(7) Å] with Ru(4)–C(02) at 2.077(6) Å. The C(1)–C(2) fragment is attached to Ru(1,2,5,6) [Ru(2)–C(1) 2.149(6), Ru(6)–C(2) 2.202(7) Å; Ru(1,5)–C(1) 2.327, 2.315(6); Ru(1,5)–C(2) 2.241(6), 2.342(7) Å] to form a distorted octahedral system similar to those already found in simpler μ_4-alkyne derivatives of Ru_4 clusters. In this case, the two alkyne substituents are P(2), which bridges to Ru(3), and the *trans*-$Bu^tCH{=}CH$ group. The presence of the latter, no longer co-ordinated to the cluster, suggests that it has been displaced from its original cluster by the C_2PPh_2 group when condensation occurs.

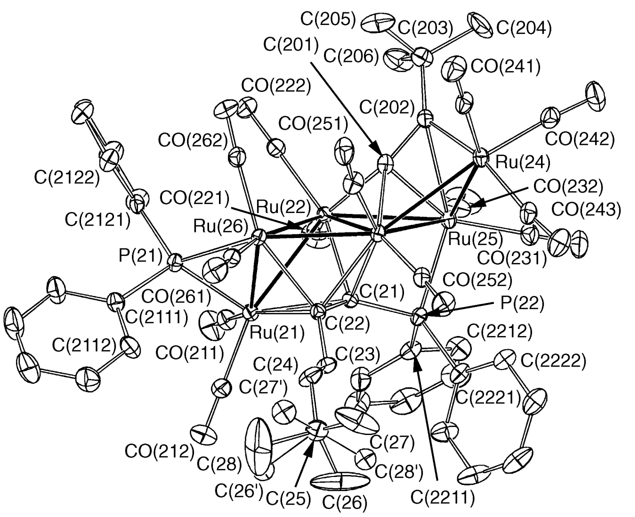


Fig. 1 Plot of molecule 2 of $[Ru_6(\mu_5\text{-}Bu^tCH{=}CHC_2PPh_2)(\mu_4\text{-}C_2Bu^t)(\mu\text{-}PPh_2)(CO)_{13}]$ **2** showing the atom numbering scheme. In this and subsequent figures, non-hydrogen atoms are shown with 20% thermal envelopes; hydrogen atoms have arbitrary radii of 0.1 Å. Significant bond lengths (Å) and angles (°) (for molecule 1): Ru(1)–Ru(2) 2.815(1), Ru(1)–Ru(6) 2.6952(9), Ru(2)–Ru(3) 2.820(1), Ru(2)–Ru(5) 2.6693(9), Ru(2)–Ru(6) 2.865(1), Ru(3)–Ru(4) 2.759(1), Ru(3)–Ru(5) 2.829(1), Ru(4)–Ru(5) 2.905(2), Ru(1)–P(1) 2.252(2), Ru(6)–P(1) 2.299(2), Ru(3)–P(2) 2.308(2), Ru(1)–C(2) 2.241(6), Ru(6)–C(2) 2.202(7), Ru(2)–C(1) 2.149(6), Ru(5)–C(1) 2.315(6), Ru(2)–C(01) 2.019(6), Ru(3)–C(01) 2.093(7), Ru(5)–C(01) 2.105(7), Ru(3)–C(02) 2.465(7), Ru(4)–C(02) 2.077(6), C(1)–C(2) 1.44(1), C(01)–C(02) 1.37(1), C(2)–C(3) 1.49(1), C(3)–C(4) 1.28(1), C(4)–C(5) 1.51(1); Ru(1)–P(1)–Ru(6) 72.62(7), Ru(3)–P(2)–C(1) 93.5(2), P(2)–C(1)–C(2) 139.4(5), C(2)–C(3)–C(4) 127.1(8), C(3)–C(4)–C(5) 131.3(9), C(01)–C(02)–C(03) 130.0(6)

$|\Delta\rho|_{max} = 1.1$ e $Å^{-3}$. Comment: C(3,4) are disordered over two sets of sites; their occupancies were set at 0.5 and that of the solvent at 1 after trial refinement.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/468.

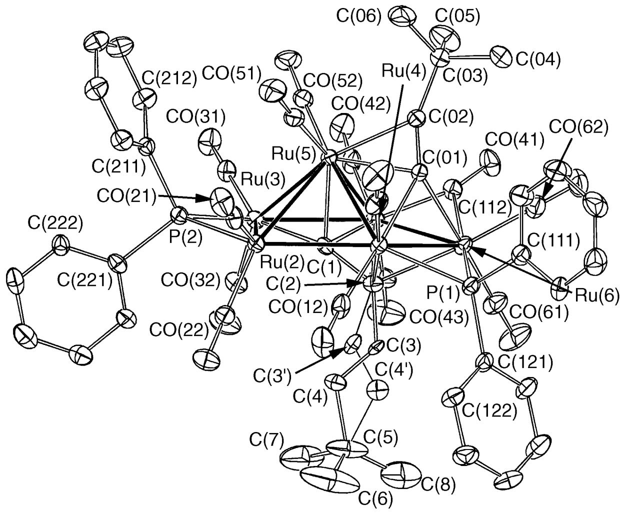


Fig. 2 Plot of a molecule of $[Ru_6(\mu_6\text{-}C_2CH{=}CHBu^t)(\mu_3\text{-}C_2Bu^t)(\mu\text{-}PPh_2)_2(\mu\text{-}CO)(CO)_{12}]$ **3** showing the atom numbering scheme. Significant bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.890(1), Ru(1) · · · Ru(4) 3.880(2), Ru(1)–Ru(5) 2.8468(7), Ru(1)–Ru(6) 2.779(3), Ru(2)–Ru(3) 2.775(2), Ru(2)–Ru(5) 2.786(2), Ru(3)–Ru(4) 2.798(2), Ru(4)–Ru(5) 2.848(2), Ru(4)–Ru(6) 2.8053(9), Ru(1)–P(1) 2.329(2), Ru(6)–P(1) 2.312(2), Ru(2)–P(2) 2.275(2), Ru(3)–P(2) 2.291(3), Ru(1)–C(1) 2.413(6), Ru(2)–C(1) 2.136(6), Ru(3)–C(1) 2.127(6), Ru(4)–C(1) 2.204(6), Ru(5)–C(1) 2.100(6), Ru(1)–C(2) 2.340(6), Ru(4)–C(2) 2.238(6), Ru(6)–C(2) 2.260(6), Ru(1)–C(01) 2.168(6), Ru(5)–C(01), 2.211(6), Ru(6)–C(01), 2.210(6), Ru(5)–C(02) 2.269(6), C(1)–C(2) 1.426(8), C(01)–C(02) 1.245(8); Ru(1)–P(1)–Ru(6) 73.58(8), Ru(2)–P(2)–Ru(3) 74.83(5), C(01)–C(02)–C(03) 155.4(6)

The Ru_6 core in **3** is best described as a pentagonal pyramid [Ru–Ru(basal) 2.775(2)–2.890(1) Å; Ru(ap)–Ru(basal) 2.786(2)–2.848(2) Å], into one Ru(ap)–Ru(basal) of which a C_2Bu^t group is inserted. This C_2Bu^t group is attached to only three Ru atoms [Ru(1,5,6)] of the Ru_4 butterfly so formed. All six Ru atoms are attached to the $Bu^tCH{=}CHC_2$ ligand in a manner similar to that found for the related ligand in $[Ru_6(\mu_5\text{-}C_2C{\equiv}CBu^t)(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_{13}]$, obtained by pyrolysis of $[Ru_3(CO)_{11}\{PPh_2(C{\equiv}CC{\equiv}CBu^t)\}]$.[19] Notable in both is the Ru(5)–C(1) interaction [2.100(6) Å here] which has led to the alkylated carbide description for this ligand. Also present in **3** are two μ-PPh_2 ligands [bridging Ru(2)–Ru(3) and Ru(1)–Ru(6)]. One CO ligand semi-bridges Ru(4)–Ru(6), co-ordination being completed by two terminal CO ligands attached to each Ru atom.

We have not observed any interconversion of these two complexes, so cannot say whether they are formed sequentially or in competitive reactions. It appears that the hydrogens originally present on the acetylide clusters have migrated to the same C_2Bu^t group in **2**; in **3**, they were not located, but the absence of long Ru–Ru vectors which might be bridged by them, and the unusual geometry about C(4)–C(5), suggests that in **3** as well, the H atoms have migrated to the organic ligand. This is confirmed by the ^1H NMR spectrum, which the CH resonances are found at δ 5.20 and 5.43; there is no high-field resonance typical of a cluster-bound H atom.

While it is not possible to determine the mode of formation of these clusters, we might speculate that **2** is formed by cleavage of one P–C(sp) bond in dppa on oxidative addition to an Ru–Ru bond in one Ru_3 moiety, followed by aggegation of the two clusters to give an open Ru_6 array. Further reaction results in formation of **3** by cleavage of the second P–C bond, with concomitant stronger attachment of C(1) to Ru(1–4) (as found in many examples of condensation or reactions of acetylide on C_2 clusters).[13] Formation of a new Ru–Ru bond results in the core of **3** being more condensed than that found in **2**. It is notable that no CO groups are eliminated in the conversion of **2** to **3**.

Acknowledgements

We thank the Australian Research Council for support of this work and Johnson Matthey Technology, Reading, for a generous loan of $RuCl_3\cdot nH_2O$.

References

1 E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev.*, 1983, **83**, 203.
2 P. R. Raithby and M. J. Rosales, *Adv. Inorg. Chem. Radiochem.*, 1985, **29**, 169.
3 J. F. Corrigan, S. Doherty, N. J. Taylor and A. J. Carty, *Organometallics*, 1992, **11**, 3160.
4 J. F. Corrigan, N. J. Taylor and A. J. Carty, *Organometallics*, 1994, **13**, 3778.
5 S. Rivomanana, C. Mongin and G. Lavigne, *Organometallics*, 1996, **15**, 1195.
6 C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1993, **447**, 91.
7 M. I. Bruce, M. L. Williams, J. M. Patrick and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 1229.
8 E. Sappa, *J. Organomet. Chem.*, 1988, **352**, 327.
9 M. I. Bruce, J.-C. Daran, E. Cabrera and M. L. Williams, *J. Organomet. Chem.*, 1987, **319**, 239.
10 A. J. Amoroso, B. F. G. Johnson, J. Lewis, A. D. Massey, P. R. Raithby and W. T. Wong, *J. Organomet. Chem.*, 1992, **440**, 219.
11 A. J. Carty, *Pure Appl. Chem.*, 1982, **54**, 113.
12 C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *J. Chem. Soc., Chem. Commun.*, 1992, 26.
13 M. I. Bruce, *J. Organomet. Chem.*, 1990, **394**, 365; *Coord. Chem. Rev.*, in the press.
14 C. J. Adams, M. I. Bruce, E. Horn, B. W. Skelton, E. R. T. Tiekink and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1993, 3299.
15 C. J. Adams, M. I. Bruce, B. W. Skelton and A. H. White, *Chem. Commun.*, 1996, 2661.
16 M. I. Bruce, P. A. Humphrey, B. W. Skelton and A. H. White, unpublished work.
17 *XTAL 92 Reference Manual*, eds. S. R. Hall, H. D. Flack and J. M. Stuart, Universities of Western Australia, Geneva and Maryland, 1992.
18 L. J. Farrugia, N. MacDonald and R. D. Peacock, *J. Chem. Soc., Chem. Commun.*, 1991, 163.
19 P. E. Blenkiron, N. J. Taylor and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 1995, 327.

Received 21*st January* 1997; *Communication* 7/00479F