Synthesis and Crystal Structure of $[Ru_3Pt(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CBu^t)(CO)_7(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), a Butterfly Cluster containing an unusually Bonded Alkynyl Ligand: A Model for an Intermediate Molecular Geometry in a Cluster–Ligand Rearrangement

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Reaction of $[Ru_3Pt(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CBu^t)(CO)_9(L_2)]$ **1a** (L_2 = dppe) with $Ph_2PC{\equiv}CPPh_2$ affords the butterfly cluster $[Ru_3Pt(\mu\text{-}PPh_2)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CBu^t)(CO)_7(dppe)]$ **3**; the metal skeleton and $\mu_4\text{-}\eta^2$ alkynyl coordination mode in **3** represent a likely model for a transition geometry in the interconversion of **1** and its vinylidene tautomer $[Ru_3Pt\{\mu_4\text{-}\eta^2\text{-}C{=}C(H)Bu^t\}(CO)_9(L_2)]$ **2**.

The chemistry of multi-site bound unsaturated hydrocarbyl ligands in cluster compounds[1] continues to be of interest, in view of the relationship between these species and reactive intermediates in heterogeneous catalysis.[2] Changes in formal electron donating properties of unsaturated organic compounds upon chemical reduction require a flexibility in the geometry and coordinating ability of the cluster. Such flexibility of the metal skeleton is seen, for example, in butterfly clusters,[3] and hetero-platinum clusters,[4] and it provides a molecular model for the restructuring of metal surfaces during heterogeneous catalytic reactions.[5]

We have recently reported[6] that the (hydrido)alkynyl cluster $[Ru_3Pt(\mu\text{-}H)(\mu_4\text{-}\eta^2\text{-}C{\equiv}CBu^t)(CO)_9(L_2)]$ 1a (L_2 = dppe) undergoes a rearrangement to the vinylidene tautomer $[Ru_3Pt\{\mu_4\text{-}\eta^2\text{-}C{=}C(H)Bu^t\}(CO)_9(L_2)]$ 2a (L_2 = dppe). There are four important structural criteria involved in this reversible rearrangement: (*a*) the interconversion of a 62-electron spiked-triangular core and a 60-electron butterfly metal skeleton, (*b*) an intramolecular hydrogen migration from an Ru–Ru edge to form a new C–H bond, (*c*) the rotation of the C–C bond by *ca.* 60°, from a position perpendicular to an Ru–Ru edge to one such that it interacts in a π fashion with only one Ru atom, and (*d*) a motion of the diphosphine ligand such that the two P atoms become coplanar with the $PtRu_2$ triangle in **2**. These changes in the metal skeleton–ligand configuration are illustrated in Fig. 1.

We now report a new cluster whose metal skeleton–ligand configuration represents a model for a possible transition

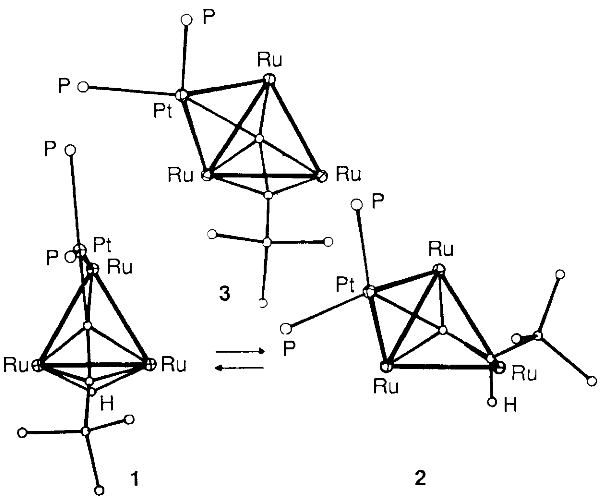

Fig. 1 Changes in metal skeleton–ligand configuration in cluster rearrangement

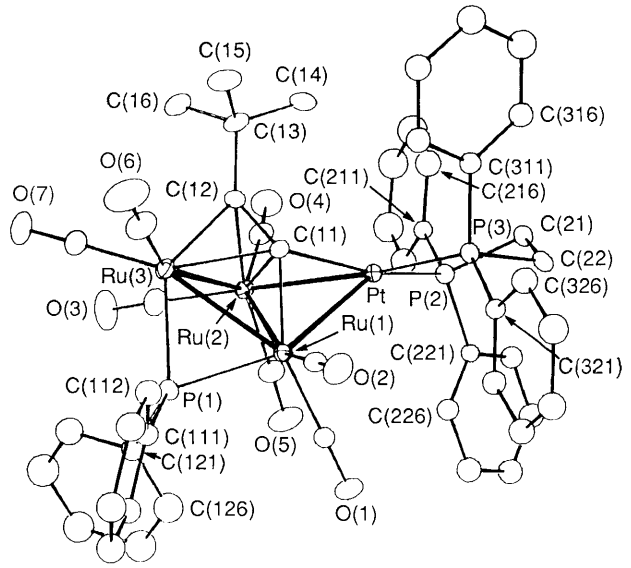

Fig. 2 Molecular structure and atomic labelling scheme for [Ru$_3$Pt(μ-PPh$_2$)(μ$_4$-η^2-C≡CBu^t)(CO)$_7$(dppe)] **3**, with thermal ellipsoids shown at the 20% probability level. Important bond lengths (Å) and bond angles (°) are: Pt–Ru(1) 2.770(1), Pt–Ru(2) 2.729(1), Ru(1)–Ru(2) 2.841(1), Ru(1)–Ru(3) 2.740(1), Ru(2)–Ru(3) 2.841(1), Pt–P(2) 2.267(3), Pt–P(3) 2.254(3), Ru(1)–P(1) 2.294(3), Ru(3)–P(1) 2.341(3), Pt–C(11) 2.095(9), Ru(1)–C(11) 2.061(9), Ru(2)–C(11) 2.161(9), Ru(3)–C(11) 2.269(9), Ru(2)–C(12) 2.292(9), Ru(3)–C(12) 2.102(9), C(11)–C(12) 1.356(13); P(2)–Pt–P(3) 85.4(1), Ru(1)–P(1)–Ru(3) 72.5(1), Pt–C(11)–C(12) 125.1(7), C(11)–C(12)–C(13) 138.2(9).

geometry between **1** and **2**. Reaction of Ph$_2$PC≡CPPh$_2$ with cluster **1a** affords two new phosphido species. The major[†] product has been characterised as [Ru$_3$Pt(μ-PPh$_2$)(μ$_4$-η^2-C≡CBu^t)(CO)$_7$(dppe)] **3** by an X-ray crystal structure[‡] determination and spectroscopic techniques.[§] The 60-electron cluster adopts a butterfly skeleton (Fig. 2) with a dihedral angle Pt–Ru(1)–Ru(2)–Ru(3) of 126.7(1)°. This is slightly wider than the corresponding angle of *ca.* 118° found in **2a**[6] and **2b**–**2d**.[7] The Pt–Ru distances are normal,[4] and a μ-PPh$_2$ group bridges the Ru(1)–Ru(3) vector.

The most interesting feature of **3** is the alkynyl bonding mode. A few examples of clusters containing μ$_4$-η^2-alkynyl ligands bonded to square or rhomboidal metal faces have been reported,[8] and the bonding to the spiked triangular metal skeleton has also been discussed.[6] To our knowledge the only structurally characterised *butterfly* cluster with such a ligand is the recently reported[9] [WOs$_3$(μ$_4$-η^2-C≡CPh)(CO)$_{11}$(η-C$_5$H$_5$)]. This has the alkynyl α-carbon bonded to *three* metal atoms, with one long, non-bonding, Os · · · C$_\alpha$ contact of 2.79(2) Å. The alkynyl ligands in [Mo$_2$Ru$_3$(μ$_4$-η^2-C≡CPh)$_2$(CO)$_{10}$(η-C$_5$H$_5$)$_2$] are similarly bonded to the two butterfly Mo$_2$Ru$_2$ faces.[10] In contrast, in cluster **3** the α-carbon C(11) is within bonding distance of *all four* metal atoms [M–C$_\alpha$ distances 2.061(9)–2.269(9) Å]. This bonding arrangement is shown clearly in Fig. 1.

Fig. 1 also illustrates the relationship between the metal skeletons and the C$_2$ ligand bonding mode in clusters **1**, **2** and **3**. The metal skeleton–ligand configuration in **3** is intermediate between that in **1** and **2**, and illustrates a likely reaction pathway in their interconversion. Structural criterion (*a*) is fulfilled in that a new Ru–Pt bond is formed from the spiked-triangle giving a butterfly arrangement. A small rotation of the alkynyl ligand, as required by structural criterion (*c*), is also observed, since the angle between the C–C vector and the bridged Ru–Ru bond is 91.3° in **1a**[6] and 99.8° in **3**.[¶] Such motion is related to the fluxional rotation of an alkynyl ligand about a trimetallic face, which has been observed by several authors.[11]

Table 1 Comparison of rate data for tautomerisation of complexes **1**

Starting complex[a]	K_{eq}[b]	$10^3 k_1$/min^{-1}	k_H/k_D[c]
1a (L$_2$ = dppe)	9	3.3	0.56
1b (L$_2$ = dppb)	9	0.5	0.53
1c (L$_2$ = dppp)	40	9.9	
1d (L$_2$ = dppet)	31	8.3	

[a] dppe = bis(diphenylphosphino)ethane, dppb = (2*S*,3*S*)-bis(diphenylphosphino)butane (chiraphos), dppp = 1,3-bis(diphenylphosphino)propane, dppet = *cis*-1,2-bis(diphenylphosphino)ethene. [b] K_{eq} for **1** ⇌ **2** at 29.5(±1) °C. [c] k_H/k_D determined using [μ-^{2}H]-**1**; D incorporation > 95% according to NMR integration.

[†] The red-brown crystalline minor product is tentatively formulated as [Ru$_3$Pt{μ$_n$-η^2-C=C(H)Bu^t}(μ-PPh$_2$)$_2$(CO)$_7$(dppe)]; FAB mass spectrum, *m*/*z* 1545, C$_{63}$H$_{54}$O$_7$P$_4$ ^{195}Pt^{102}Ru$_3$ = 1547; NMR (25 °C, CDCl$_3$) ^{1}H: δ 0.31 (s, 9H, Bu^t), 2.72–2.24 (m, 4H, CH$_2$), 5.04 [dd, 1H, C=C(*H*), *J*(P–H) 3.2, 2.9 Hz] and 7.96–7.00 (m, 40H, Ph); ^{31}P: δ 56.8 [d, 1P, *J*(P–P) 15, *J*(Pt–P) 2997 Hz], 64.3 [dt, 1P, *J*(P–P) 20, 15, *J*(Pt–P) 3534 Hz] and 217.9 [d, 2P, *J*(P–P) 20, *J*(Pt–P) 97 Hz].

[‡] *Crystal data* for **3**: C$_{51}$H$_{43}$O$_7$P$_3$PtRu$_3$, *M* = 1359.11, monoclinic, *P*2$_1$/*n*, *Z* = 4, *a* = 14.091(2), *b* = 16.392(4), *c* = 21.902(3) Å, β = 97.92(1)°, *U* = 5010(2) Å^3, D_c = 1.801 g cm^{-1}, *F*(000) = 2640, μ(Mo-Kα) = 38.26 cm^{-1}. The structure was solved by direct methods and refined by full-matrix least-squares using 4456 observed, absorption-corrected, data [$F_o > 2.5\sigma(F_o)$]. A total of 6541 unique data were measured on an Enraf–Nonius CAD4-F diffractometer with graphite-monochromated Mo-Kα X-radiation (λ = 0.71609 Å) using θ/2θ scans. The final *R*(R_w) values were 0.031(0.038) for 346 parameters, and [$\sigma^2(F_o)$]$^{-1}$ weights. Hydrogen atoms were incorporated at fixed positions with C–H = 1.0 Å, except for aryl hydrogens on the phenyl ring C(211)–C(216), which was disordered over two sites (occupancies 0.55 : 0.45). Only the major orientation is shown in Fig. 1. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

[§] *NMR data* for **3** (25 °C, CDCl$_3$) ^{1}H: δ 1.22 (s, 9H, Bu^t), 2.44–1.80 (m, 4H, CH$_2$) and 8.45–6.41 (m, 30H, Ph); ^{31}P: δ 53.1 [d, P(2), *J*(P–P) 15, *J*(Pt–P) 3084 Hz], 58.0 [dd, P(3), *J*(P–P) 15.19, *J*(Pt–P) 3430 Hz], 250.4 [d, P(1), *J*(P–P) 19, *J*(Pt–P) 109 Hz]. Resonances for P(2) and P(3) assigned on basis of Pt–P distances and ^1J(Pt–P).

[¶] Note that there is structural evidence for some flexibility in the μ$_4$-η^2 coordination of alkynyl ligands to a spiked triangular metal framework, see ref. 6.

More interestingly, structural criterion (*d*) is also fulfilled, since the coordination geometry about the Pt atom in cluster **3** (even ignoring the Pt–C bond) deviates significantly from planarity. The twist angle between the normals to the Pt–P(2)–P(3) and Pt–Ru(1)–Ru(2) planes is 38.2°, while the coordination geometry about the Pt centres in **1a** and **2** (ignoring the Pt–C bond in the latter) closely approximates to planarity. A low energy to rotational motion of the PtL$_2$ unit in **1** is also evidenced by the fluxional exchange between the inequivalent ^{31}P environments on the NMR timescale.[6]

In order to probe possible effects of diphosphine ligand motion, we have investigated the rearrangement of **1** to **2** using several bis(diphenylphosphino) ligands L$_2$. All processes follow first-order kinetics and the rate of tautomerisation varies by about an order of magnitude. Data are summarised in Table 1. Differences in the electron donating properties of the diphosphine ligands are probably not important, since the IR spectra, in the ν(CO) region, of the thermodynamically more stable vinylidene clusters **2** are identical within 1 or 2 cm^{-1}. It is more likely that the flexibility of the diphosphine backbone plays an important role, since extensive motion of metals and ligands is required to accomplish the interconversion of **1** and **2**. The order of increasing forward rates (k_1) is: **1b** (L$_2$ = dppb) < **1a** (L$_2$ = dppe) < **1c** (L$_2$ = dppp), which follows intuitive expectations of diphosphine flexibility, while the fast rate observed for **1d** (L$_2$ = dppet) is probably a consequence of the fixed planar geometry required by the sp^2 hybridisation at the backbone carbons. Any significant change in conformation of the Pt–P–C–C–P ring in the PtL$_2$ unit along the reaction coordinate is thus unlikely, and the faster rate may arise from a relative raising in energy of **1d**. The inverse kinetic deuterium isotope effect observed for **1a** and **1b**, using the (μ-D) derivatives, implies that there is substantial C–H (vinylidene) bonding in the transition state,[12] and from the structure of **3** we suggest that the new Pt–Ru bond is formed early along the reaction coordinate.

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