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Some remarkable reactions of an open Ru₅ cluster *

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Abstract

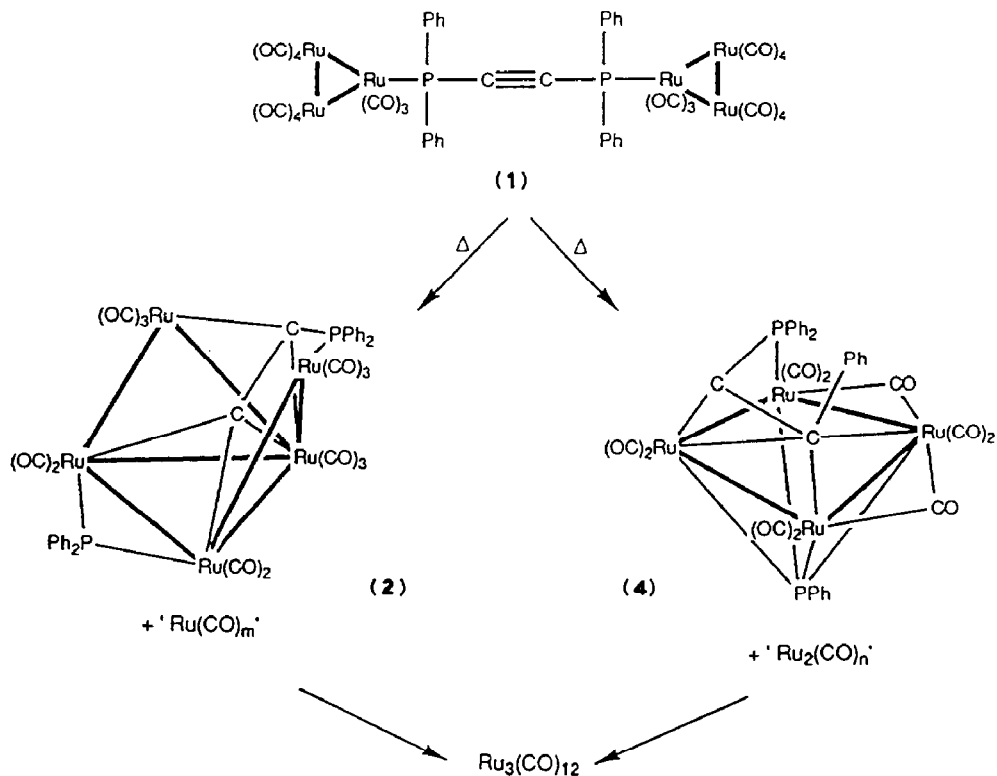
The current status of our studies of the chemistry of the complex Ru₅(μ₅-C₂PPh₂)(μ-PPh₂)(CO)₁₃, which contains an open Ru₅ cluster interacting with the diphenylphosphinoethynyl group, is summarised. Ready cleavage of the C–P bond occurs, to give a cluster-bound C₂ unit which undergoes a number of remarkable reactions and there are concomitant rearrangements of the metal core.

The chemistry of group 15 ligand derivatives of cluster carbonyls, particularly of ruthenium and osmium, shows that coordination activates the group 15 ligand towards C–H and C–P bond cleavage [1]. These reactions often generate unusual molecular species which are stabilised by coordination to the cluster framework. Studies of these reactions have shown that the ease of breaking the C–P bonds decreases in the order C(sp)–P > C(sp²)–P > C(sp³)–P, as found in the extensive comparative studies made by several groups [2,3], and elegantly systematised by Carty and coworkers [4].

As a result of the discovery of a method of synthesising group 15 ligand-substituted derivatives of Ru₃(CO)₁₂ and other cluster carbonyls selectively and in high yield under mild conditions [5], it has been possible to investigate the chemistry of selected examples of these complexes. In a rapidly increasing number of cases, subsequent reactions of these species occur, to give unusual and novel products.

An interesting derivative is that obtained by attaching an Ru₃ cluster to each end of the 1,2-bis(diphenylphosphino)ethyne ligand [C₂(PPh₂)₂, dppa] [6]. Expecting that mild heating of the resulting hexanuclear complex, {(OC)₁₁Ru₃}PPh₂C≡CPPh₂{Ru₃(CO)₁₁} (1) (Scheme 1), might induce (a) C–P bond cleavage and (b) interaction of the C≡C triple bond with the cluster framework, we heated a solution of 1 in toluene for 90 min; from the resulting black solution, the very dark

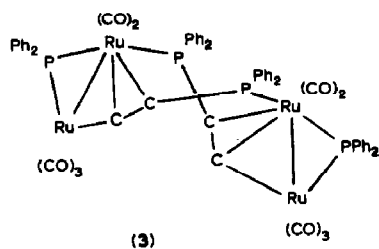
* Dedicated to Gordon Stone on the occasion of his 65th birthday, with best wishes. The author spent nine pleasant and stimulating years at Bristol.



Scheme 1.

brown-black pentanuclear cluster $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$ (**2**) was isolated in 85% yield [6]. In this condensation, the sixth metal atom is eliminated as ' $\text{Ru}(\text{CO})_4$ ', and recovered as $\text{Ru}_3(\text{CO})_{12}$. The molecular structure of **2** (Fig. 1) consists of a five-atom cluster arranged as three edge-fused triangles; the planes of the two outer ones are inclined at 27.6 and 45.7° to the central one. One edge is bridged by the PPh_2 group formed by cleavage of one of the $\text{C}(\text{sp})\text{-P}$ bonds in **1**; the remaining C_2PPh_2 ligand occupies the cavity formed by the metal atoms, the C_2 fragment being attached to four of them, while the PPh_2 group bridges C^β and the fifth Ru atom. The osmium analogue of **2** has been made in a similar manner by pyrolysis of $\{\text{Os}_3(\text{CO})_{11}\}_2\{\mu\text{-C}_2(\text{PPh}_2)_2\}$ (refluxing xylene, 2.5 h); it has essentially the same structure as that of **2** [7].

Complex **2** has been characterised independently by Daran and coworkers [8] among the products of the thermal reaction between $\text{Ru}_3(\text{CO})_{12}$ and dppa ; under these conditions (refluxing tetrahydrofuran), the tetranuclear complexes $\{\text{Ru}_2(\mu\text{-PPh}_2)(\mu\text{-C}_2\text{PPh}_2)(\text{CO})_5\}_2$ (**3**) and $\text{Ru}_4(\mu_4\text{-PPh})(\mu_4\text{-PhC}_2\text{PPh}_2)(\mu\text{-CO})_2(\text{CO})_8$ (**4**) were also obtained (see below) [9].



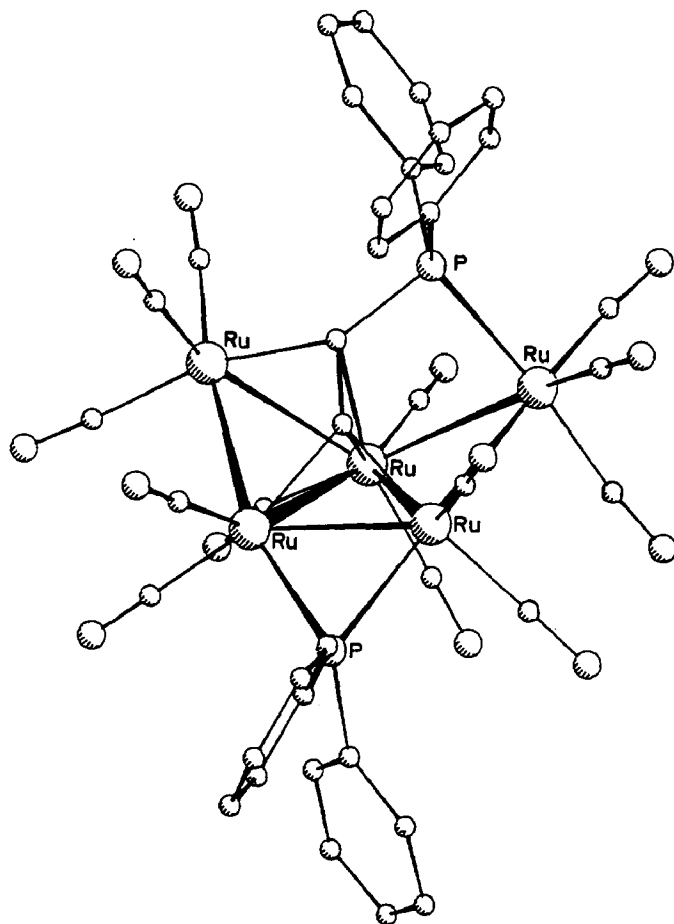


Fig. 1. Molecular structure of 2.

The high yield preparation of 2 provided an opportunity to study the chemistry of a pentanuclear complex in detail, both in respect of the core rearrangements and also of the expected reactivity of the C_2 moiety which nestles in the cavity formed by four metal atoms. The PPh_2 group attached to both the C_2 fragment and the fifth metal atom serves to prevent the facile closure of the skeleton to the more stable square pyramidal array, as found for pentanuclear μ_4-C_2R complexes (see below).

Part of the inherent interest in pentanuclear complexes relates to the wide range of skeletal rearrangements that are not only possible but are actually observed. This contrasts with the limited range available for M_4 clusters, and with the relative stability of the octahedral and trigonal prismatic geometries for M_6 clusters, which seem to preclude ready rearrangements to other shapes. Figure 2 illustrates some of the M_5 clusters that are related by cleavage of one $M-M$ bond at a time. A recent statistical study [10] suggested that the M_5 clusters occupy a position in which the bonding is intermediate between localised ($M_{\leq 4}$) and delocalised ($M_{\geq 6}$).

Most of the previous studies of the chemistry of pentanuclear ruthenium complexes commenced with $Ru_5C(CO)_{15}$ (5), which contains a square pyramidal Ru_5

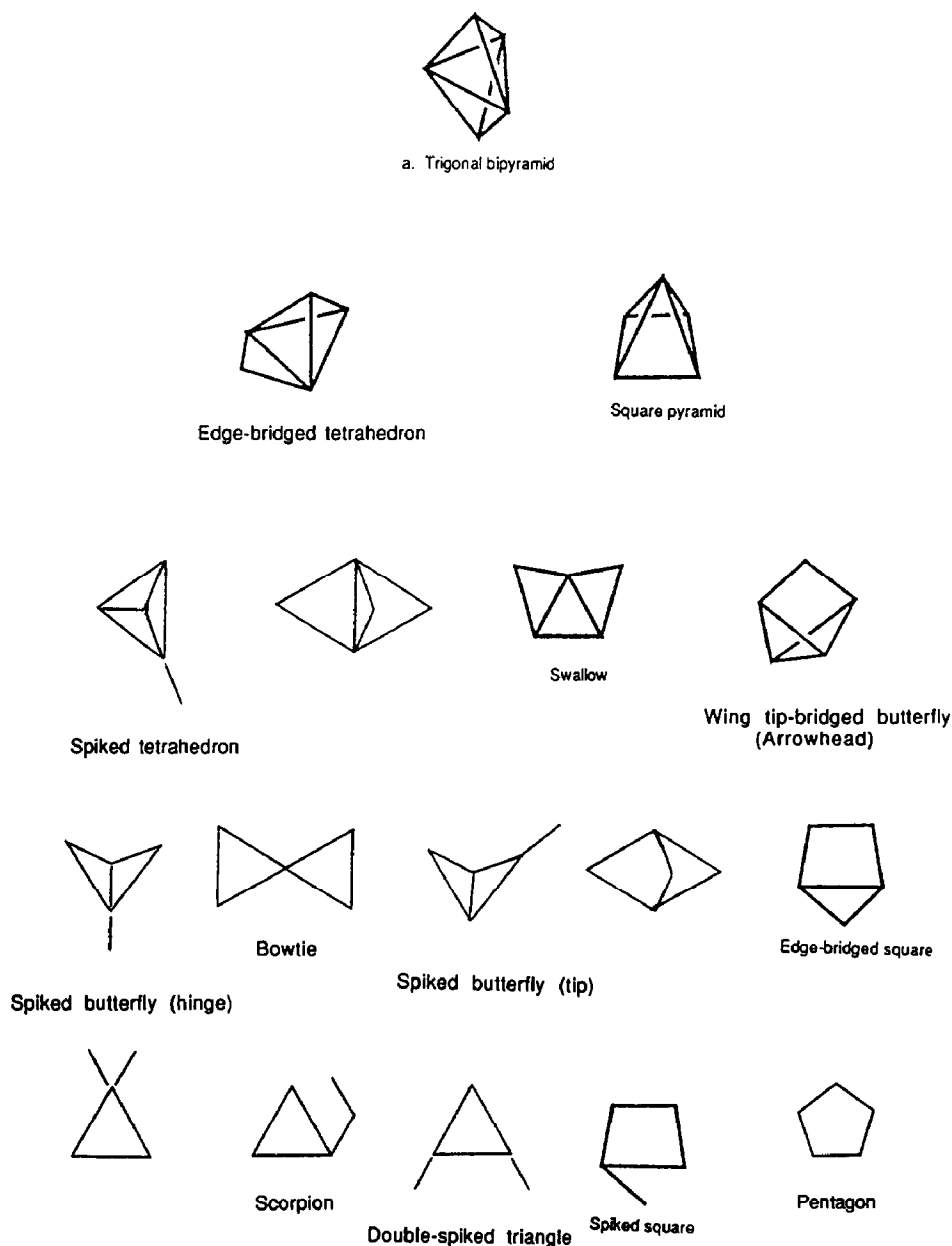
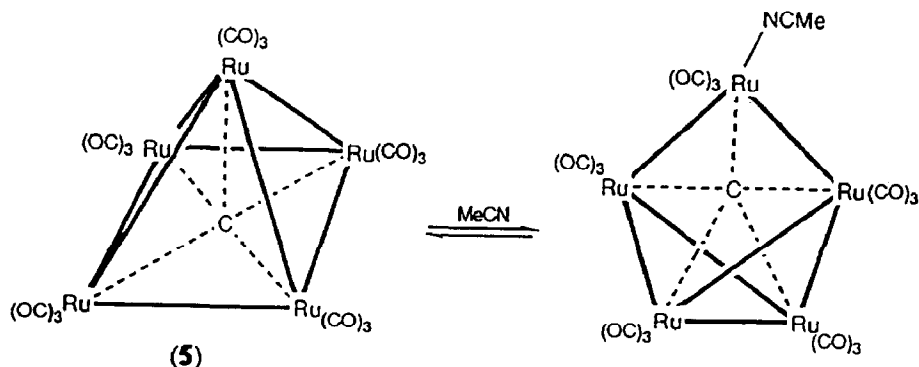


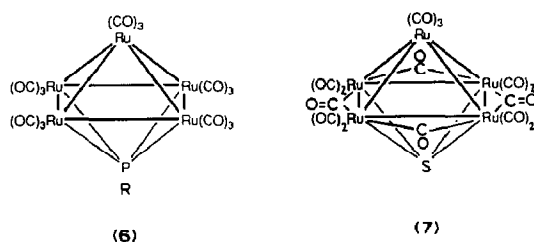
Fig. 2. Possible core geometries for M_5 clusters. Each structure contains one less M–M bond than those in the row above it.

core containing a C atom in the square face [11], the related species $Ru_5(\mu_4-PR)(CO)_{15}$ (6) [12] and $Ru_5(\mu_4-S)(CO)_{14}$ (7) [13]. A characteristic reaction of the carbido cluster 5 is opening of the square pyramidal skeleton to the 'arrowhead' (or 'bridged butterfly') configuration, a reaction often observed when ligands are added to this cluster (Scheme 2). Of particular interest in the present context are the results obtained with derivatives of the phosphinoalkynes $Ph_2C\equiv CR$ ($R = Pr^i, Ph$) [14]. Although a complete survey of this chemistry is not appropriate here, the formation and subsequent reactions of complexes such as $Ru_5(\mu_4-C_2R)(\mu-PPh_2)(CO)_{13}$ ($R =$



Scheme 2.

Pr^i , Ph) (**8**, Scheme 3) [15] are related to our own studies. In particular, the readily reversible addition of CO to **8** to give **9** contrasts with the stability of **2** (see below).

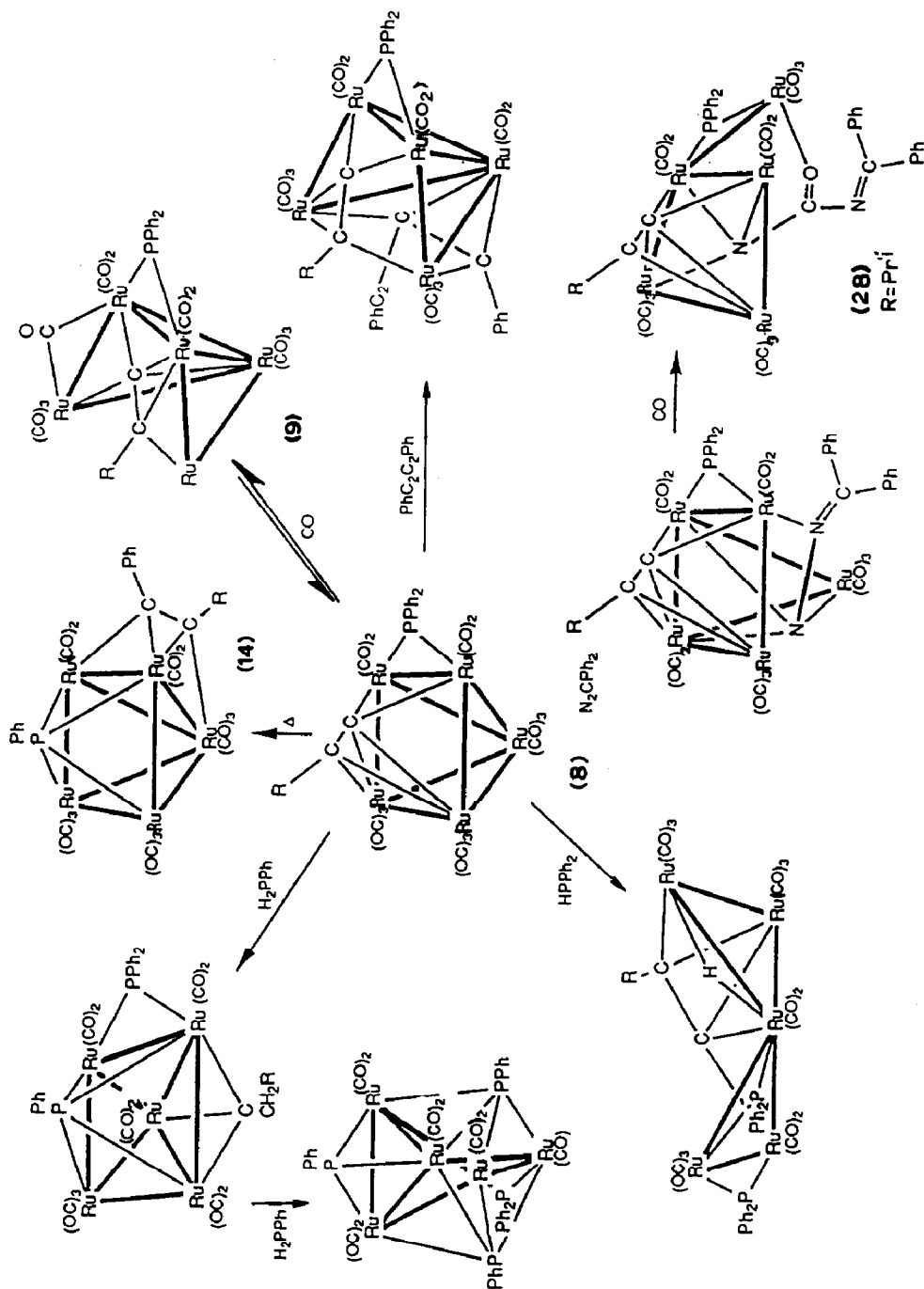


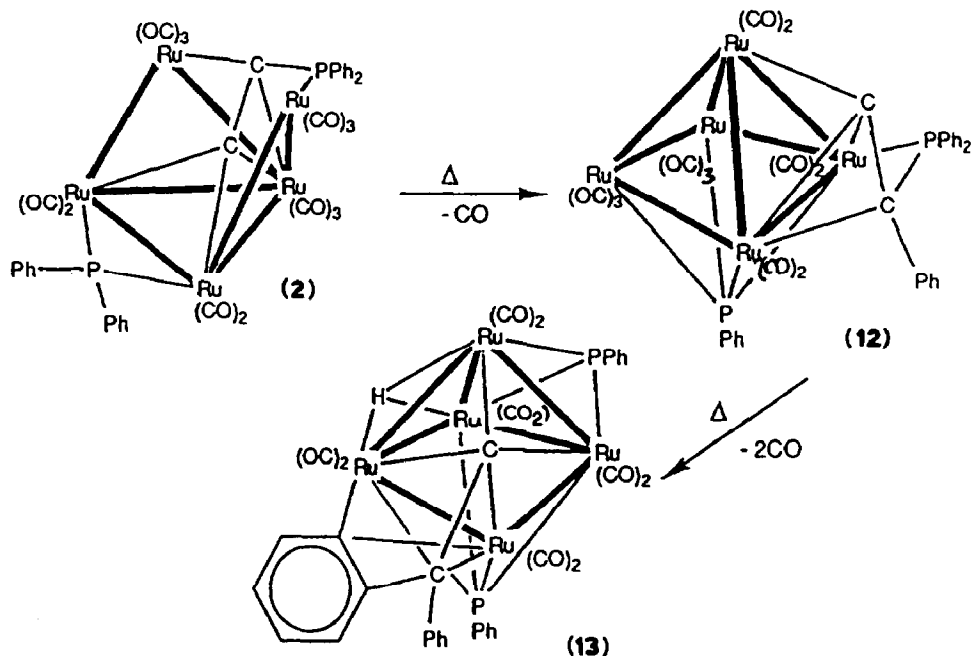
Pyrolysis. In addition to the tetranuclear complex mentioned above, we have also isolated small amounts of the complexes $\text{Ru}_4(\mu_4\text{-C}_2)(\mu\text{-PPh}_2)_2(\text{CO})_{12}$ (**10**), $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{15}$ (**11t**), $\text{Ru}_5(\mu_4\text{-PPh})(\mu_3\text{-CCPh}(\text{PPh}_2))(\text{CO})_{12}$ (**12**) and $\text{Ru}_5(\mu\text{-H})(\mu_4\text{-PPh})(\mu_3\text{-PPh})(\mu_4\text{-CCPh}(\text{C}_6\text{H}_4))(\text{CO})_{10}$ (**13**) in large scale (ca. 2 g) preparations of **2**; minor products, which have not yet been fully characterised, include $\text{Ru}_5(\text{CO})_{13}(\text{dppa}^*)$ and $\text{Ru}_8(\text{CO})_{17}(\text{dppa}^*)$.

It appears that **4** forms by the condensation of **1** in the presence of small amounts of CO. Its formation involves the cleavage of a $\text{C}(sp)\text{-P}$ bond and migration of a phenyl group from PPh_2 to C^α of the C_2PPh_2 ligand, together with elimination of one Ru atom; the PPh group caps one face of the Ru_4 core which has a distorted rhomboidal geometry. The phosphino-alkyne caps the opposite face. A similar migration of phenyl from P to C occurs on pyrolysis of (**8**, R = Ph), which gives $\text{Ru}_5(\mu_4\text{-PPh})(\mu_5\text{-PhC}_2\text{Ph})(\text{CO})_{13}$ (**14**; Scheme 3) [15].

Pyrolysis of **2** in refluxing toluene for 2.5 h afforded sequentially $\text{Ru}_5(\mu_4\text{-PPh})(\mu_3\text{-CCPh}(\text{PPh}_2))(\text{CO})_{12}$ (**12**) and $\text{Ru}_5(\mu\text{-H})(\mu_4\text{-PPh})(\mu_3\text{-PPh})(\mu_4\text{-CCPh}(\text{C}_6\text{H}_4))(\text{CO})_{10}$ (**13**) (Scheme 4) [16]. In the former, the PPh group capping the square face of the Ru_5 square pyramid is formed by formal migration of a phenyl group to C^β of the C_2PPh_2 ligand in **2**, forming a phosphino-vinylidene ligand. Further degradation forms **13** by cleavage of the vinylidene-P bond in **12** and

* The symbol (dppa^{*}) is used to indicate the presence of the elements of dppa in the cluster complex, usually determined by FAB MS; the ligand(s) do(es) not necessarily correspond to structurally intact dppa.

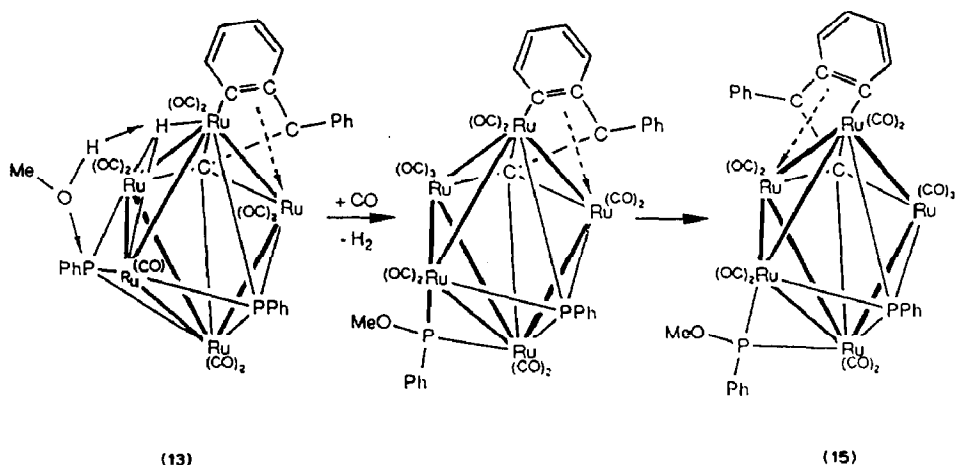
Scheme 3. Reactivity patterns of **8**.



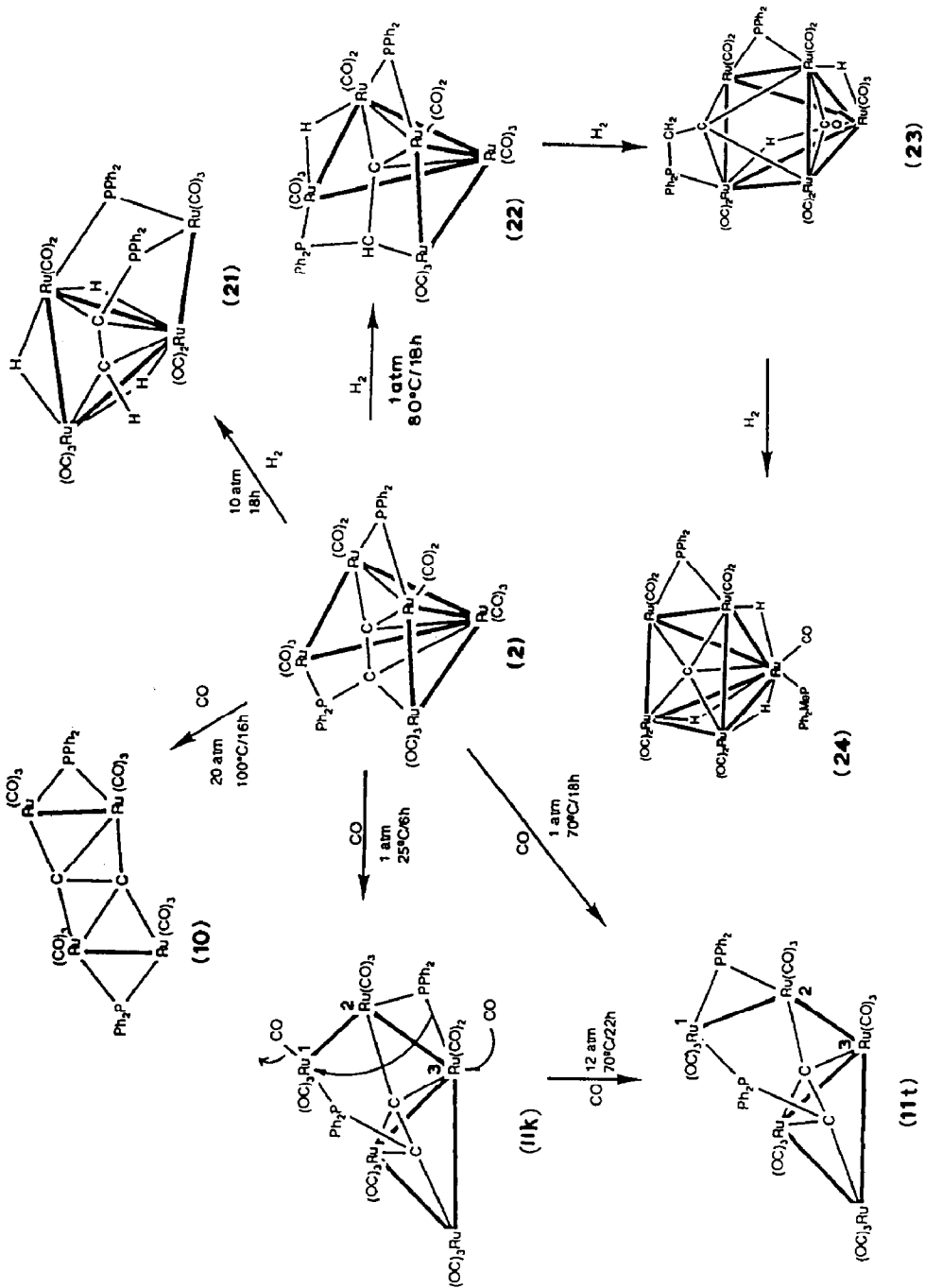
Scheme 4. Formation of 12 and 13 from 2.

migration of one of the Ph groups to C^β , with concomitant metallation of one of the two vinylidene phenyl groups. One PPh group caps an Ru_3 face of the $Ru/Ru_2CRuP/Ru$ pentagonal bipyramid resulting from formal insertion of the vinylidene C^α into one of the $Ru(\text{apical})-Ru(\text{basal})$ bonds.

Complex 13 reacts with MeOH during 24 h to give $Ru_5(\mu_4\text{-PPh})(\mu_4\text{-CCPh}(\text{C}_6\text{H}_4))\{\mu\text{-PPh}(\text{OMe})\}(\text{CO})_{11}$ (15) (Scheme 5). Of interest is the Ru_5CP pentagonal bipyramid that forms the core of both these complexes. The cluster-bound hydride in 13 is thought to cap a triangular face; it is lost during the reaction



Scheme 5. Reaction of 13 with MeOH to form 15.

Scheme 6. Reactions of **2** with CO or H₂.

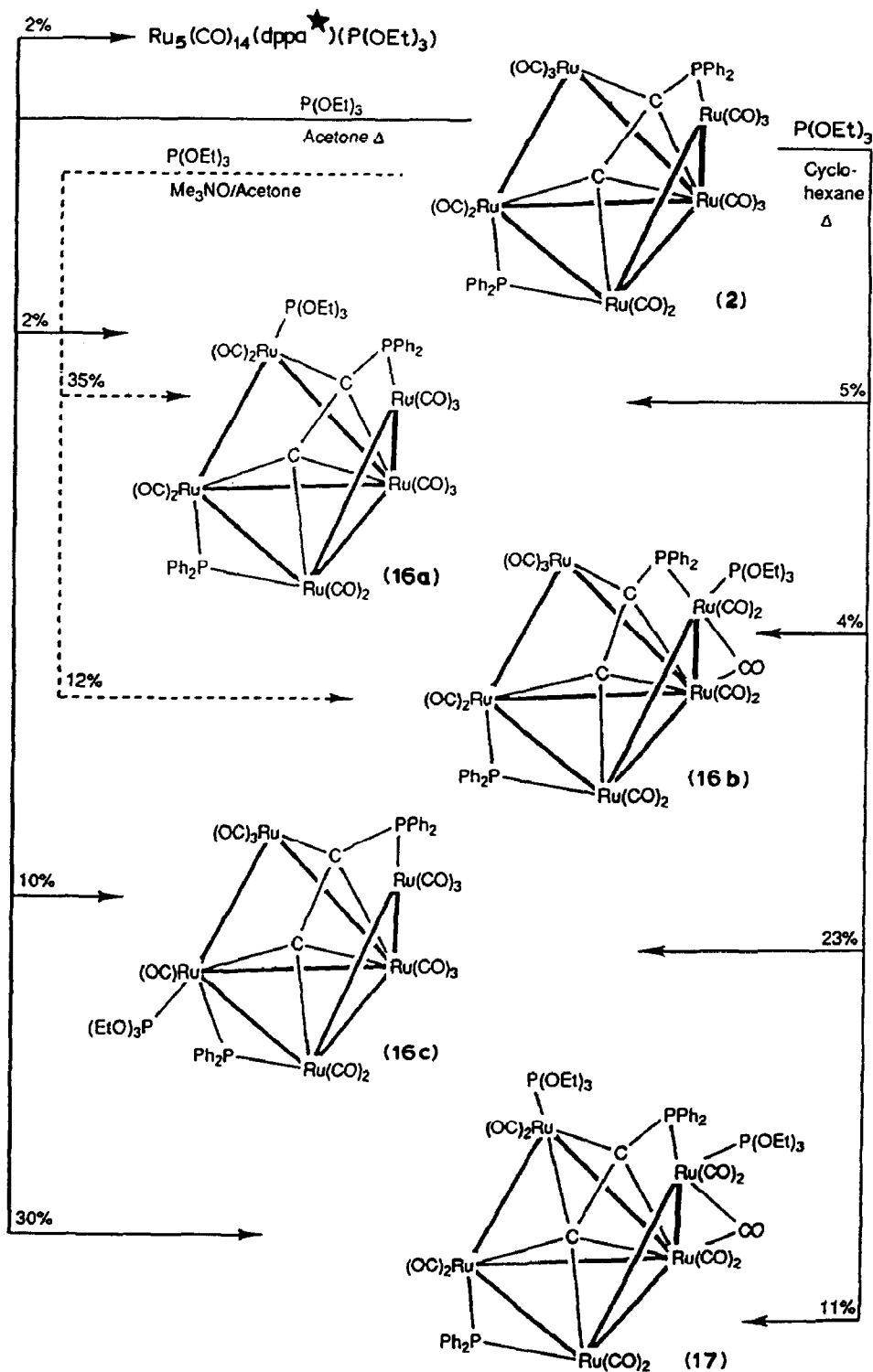
with methanol. Clusters with related pentagonal bipyramidal structures have been obtained from reactions of alkynes with iron-phosphinidene clusters [17].

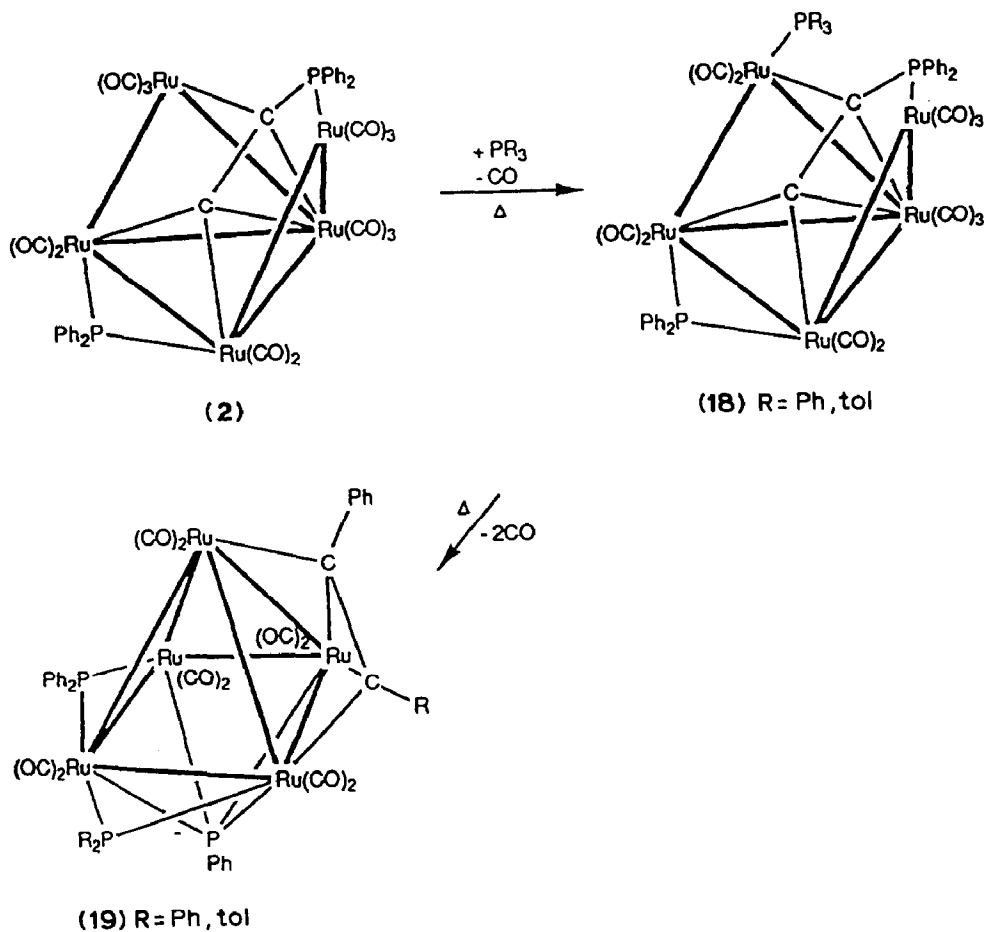
Reactions with CO. The reaction between **2** and CO gave two isomers of $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{15}$ (**11k** and **11t**; Scheme 6), each containing the same dimetallated triangular or 'scorpion' core, formed by cleavage of two Ru–Ru bonds in **2** [18]. In **11k**, the so-called 'kinetic' isomer, Ru(2) achieves an 18-electron configuration from the PPh_2 and four CO ligands; the Ru(1)–Ru(2) separation is short enough (3.009(1) Å) for there to be a bonding interaction of the Ru → Ru donor type. This isomer reacts with CO to give the 'thermodynamic' isomer **11t**, in which a subtle exchange of CO and PPh_2 ligands has occurred. Isomerisation does not occur on heating in the absence of CO, and we suggest that the reaction involves displacement of the $\mu\text{-PPh}_2$ from Ru(3), followed by swinging over of the phosphido group to bridge the Ru(1)–Ru(2) bond, and elimination of CO from Ru(1). Thermolysis of **11k**, but not of **11t**, regenerates **2**. The C_2PPh_2 ligand is attached to the Ru_3 triangle in the familiar $\mu_3, \eta^2\text{-}(\perp)$ fashion; there is also a substantial interaction of C^β with Ru(2) (2.324(4) Å in **11k**, 2.261(7) Å in **11t**).

Heating **2** under CO pressure overnight gave $\text{Ru}_4(\mu\text{-C}_2)(\mu\text{-PPh}_2)_2(\text{CO})_{12}$ (**10**), which contains the ethynediyl dianion (C_2^{2-}) [19]. This complex shows the unusual structural feature of a nearly planar $\text{Ru}_2\text{C}_2\text{Ru}_2$ fragment (dihedral between Ru_2C_2 planes 168.5°), which contrasts with the angle of ca. 90° found in the well-known $\text{Co}_2(\mu\text{-RC}_2\text{R}')(\text{CO})_6$ complexes [20]. Complex **10** has also been isolated as one product from pyrolysis of **1**, being formed by reaction with the evolved CO; the yields of side products are reduced if the reaction is carried out with a nitrogen purge.

Reactions with tertiary phosphines or phosphites. Reactions of **2** with tertiary phosphines or phosphites under various conditions reveal that attack can occur at least three of the metal sites (assuming that the products represent the site of first attack) (Scheme 7) [21]. The thermal reaction between **2** and $\text{P}(\text{OEt})_3$ gave three isomers of complex **16**, together with the disubstituted complex **17**. In acetone, **16a**, **16b** and **17** were formed. Substitution with the aid of Me_3NO in acetone gave **16a** and **16b**. A similar but unstable disubstituted complex was obtained in reactions with PMe_2Ph . No evidence was obtained for thermal interconversion of the various isomers, of which **16a**, **16c**, and **17** were characterised by X-ray crystallography. An interesting structural feature of these complexes is the opening of the wings of the 'swallow' cluster as substitution proceeds: the interplanar angles are 21.7 and 48.7° for **16a**, 25.6 and 46.2° for **16c**, and 13.7 and 124.9° for **17**.

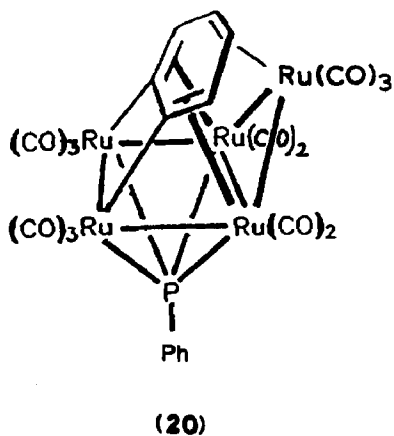
In contrast, the reactions of PAr_3 ($\text{Ar}=\text{Ph}$, tol) with **2** afforded the monosubstituted complexes **18**, which rearrange on heating to form the μ -alkyne derivatives **19** (Scheme 8) [22]. The reaction with $\text{P}(\text{tol})_3$ enabled us to determine the final location of the various aryl groups: the $\mu\text{-PPh}$ group thus originates from the original $\mu\text{-PPh}_2$ ligand, while one of the tolyl groups migrates to C^β to give the alkyne. The mild reaction conditions single out this reaction as one of the most facile and extensive set of C–P bond breaking and C–C bond forming reactions yet described for a metal cluster system. The conditions are less forcing than those employed for the synthesis of $\text{Ru}_5(\mu_5\text{-C}_6\text{H}_4)(\mu_4\text{-PPh})(\text{CO})_{13}$ (**20**), involving pyrolysis of $\text{Ru}_3(\text{CO})_{11}(\text{PPh}_3)$ in refluxing toluene for 18 h [23], and indicates considerable activation of the ligands attached to the Ru_5 cluster.

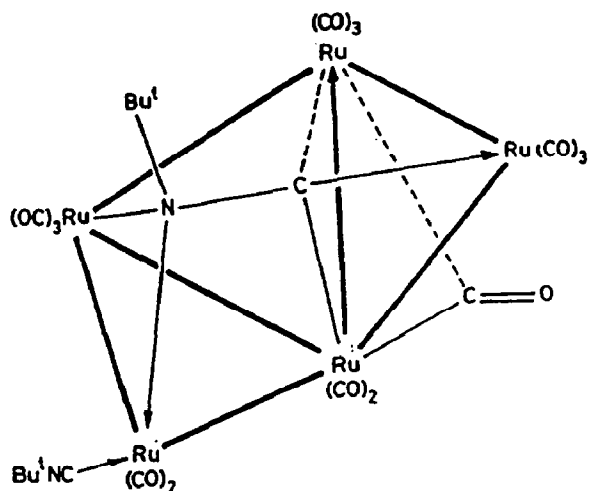
Scheme 7. Reaction of 2 with $\text{P}(\text{OEt})_3$.



Scheme 8. Reactions of 1 with PPh_3 and $\text{P}(p\text{-tolyl})_3$.

Reactions with hydrogen. One of the first reactions of 2 to be described was that with dihydrogen (Scheme 6). Under pressure (10 atm, 25°C), partial degradation to the tetranuclear cluster 21 occurred, the fifth metal atom being recovered as



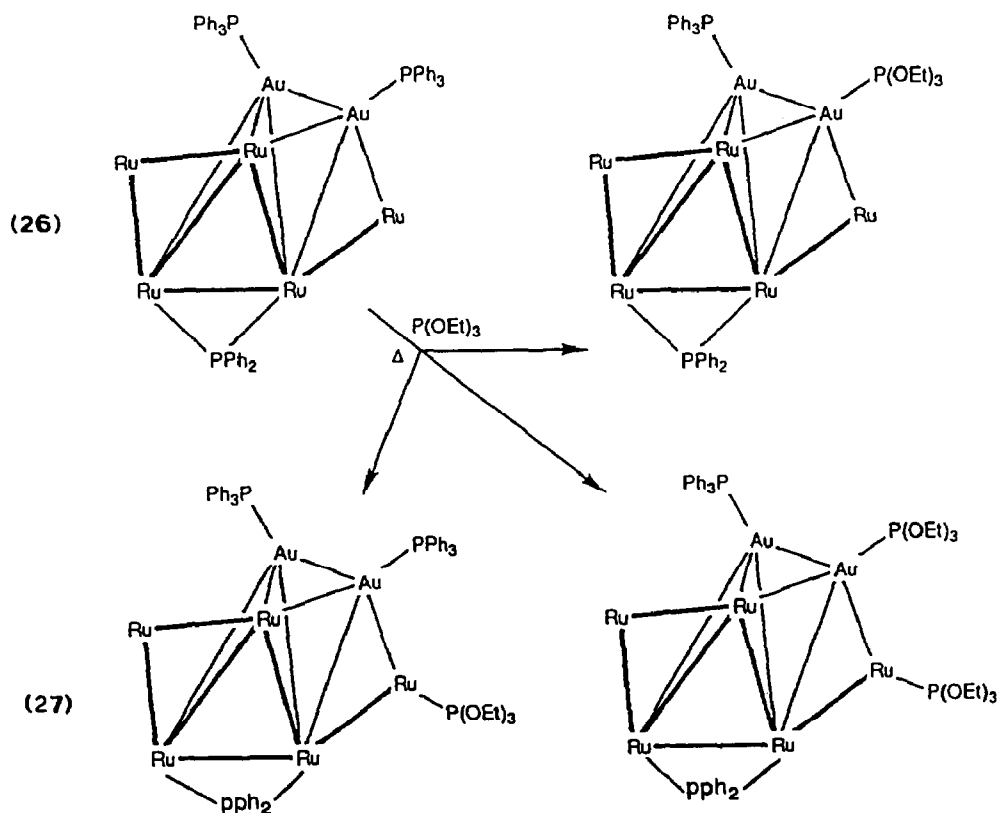


(25)

$\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$ [24,25]. In **21**, addition of H to C^β has given an alkyne, which is attached to the Ru_3 cluster in the usual μ_3, η^2 -(\perp) fashion. The PPh_2 group bridges a non-bonded Ru-Ru vector, while each Ru-Ru bond of the Ru_3 triangle is bridged by a hydrogen atom.

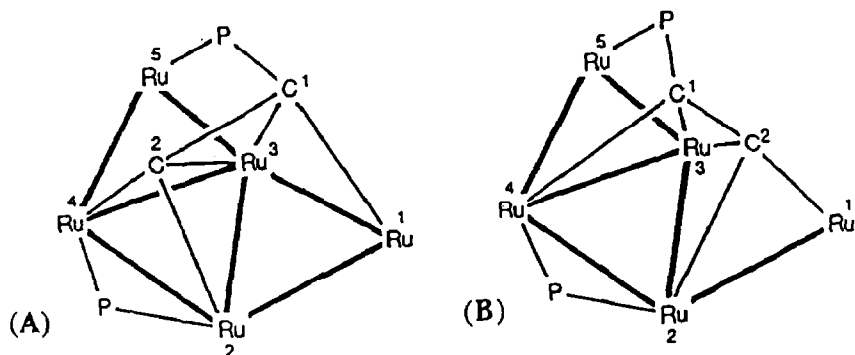
Under milder conditions (1 atm, 80°C , 18 h), an unusual sequence of three additions to **2**, each of 2H, occurs, to give complexes **22**, **23** and **24** (Scheme 6) [25,26]. In these the C_2PPh_2 ligand is successively converted into phosphino-vinylidene, phosphino-methylidyne and (methylphosphine + carbide), with concomitant addition of H atoms to the metal framework. In **22**, the Ru_5 core is little changed from that found in **2**, while in **23** and **24**, the metal framework forms a square pyramid, the $\mu_4\text{-C}$ atom in **23** moving to be incorporated in the familiar Ru_5C cluster in **24** when the $\text{C}^\alpha\text{-C}^\beta$ bond is finally broken. Only the formation of **22** from **2** is reversible on heating. The unusual reduction of a $\text{C}\equiv\text{C}$ triple bond to ($\text{C} + \text{CH}_3$) has formal parallels in the formation of $\text{Ru}_6\text{C}(\text{CO})_{16}(\text{CNBu}^t)$ from $\text{Ru}_5(\mu_5\text{-CNBu}^t)(\text{CO})_{14}(\text{CNBu}^t)$ (**25**) [27] by cleavage of the $\text{C}\equiv\text{N}$ triple bond (with loss of *t*-butyl isocyanate) [28], and of $\text{Ru}_6\text{C}(\text{CO})_{17}$ from $\text{Ru}_3(\text{CO})_{12}$ [29], by conversion of 2CO to ($\text{C} + \text{CO}_2$).

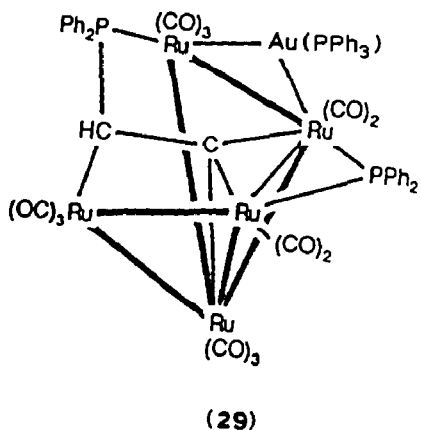
Auration of 2. Addition of ' $\text{Au}_2(\text{PPh}_3)_2$ ' to **2** afforded the heptanuclear cluster $\text{Au}_3\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{12}(\text{PPh}_3)_2$ (**26**), which does not appear to be structurally related to any of the products (or likely intermediates) obtained in reactions between **2** and the isolobal H_2 molecule [30]. The same gold complex can be obtained by addition of $\text{AuCl}(\text{PPh}_3)$ to an anionic species formed by sodium reduction of **2**. The analogous Ag_2Ru_5 cluster was formed in the reaction of **2**, after reduction with $\text{K}[\text{HBBu}^s_3]$, with $\text{Ag}\{\text{C}_5(\text{CO}_2\text{Me})_5\}(\text{PPh}_3)$. Derivatisation of **26** by replacement of CO with $\text{P}(\text{OEt})_3$ was necessary to obtain X-ray quality crystals; in the event, three complexes were obtained from this reaction, of which only one, **27**, afforded suitable crystals. We think that replacements of both Ru-bound CO and Au-bound PPh_3 occur (Scheme 9), the spectroscopic properties of the other two



Scheme 9. Possible sites of substitution by $P(OEt)_3$ in 26.

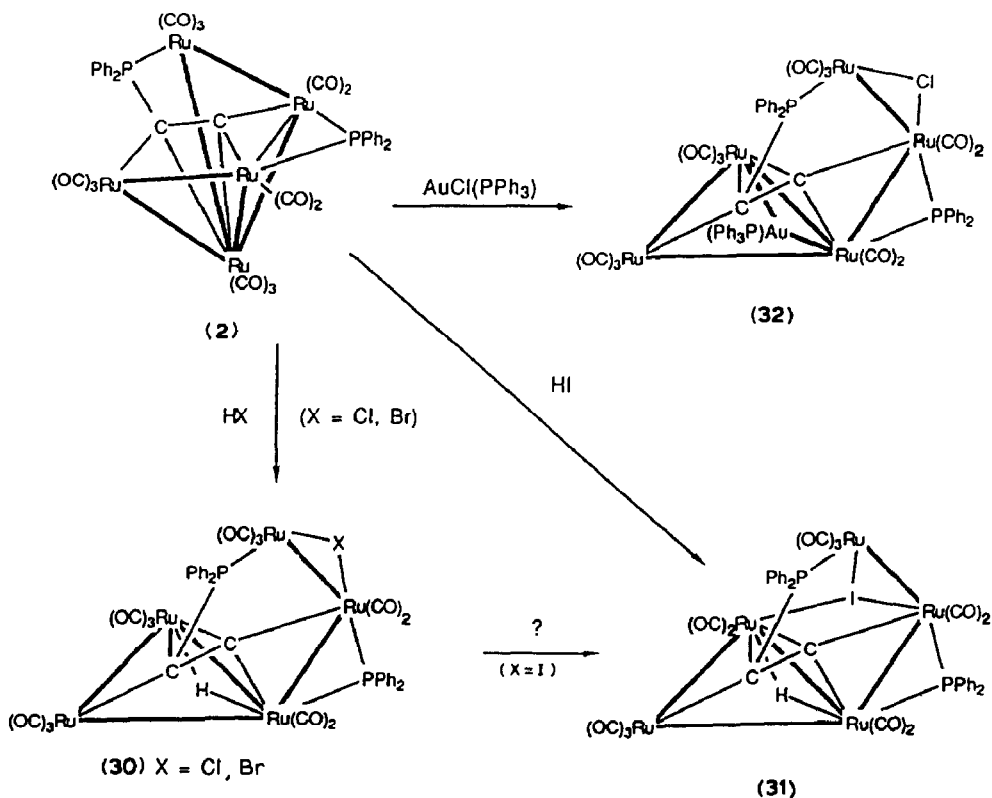
substitution products being consistent with the illustrated structures. Worthy of note is that addition of the 2e ligand $Au_2(PPh_3)_2$ has resulted in cleavage of one $Ru-Ru$ bond, as expected; the Ru_5 core is now a spiked rhombus, similar to that found in $Ru_5(\mu_4-C_2Pr^i)(\mu_4-NC(O)NCPPh_2)(\mu-PPh_2)(CO)_{13}$ (28; Scheme 3) [31]. Consideration of the overall structure, however, permits its description as a $Ru/AuRu_2/Au$ trigonal bipyramid edge-bridged by two Ru atoms and the $\mu-PPh_2$ group. Comparison with 2 shows that the phosphino-acetylide group has rotated by 90° with respect to the central Ru_3 triangle in 2 (cf. A and B, respectively).





A minor product obtained from the reaction of $\text{AuCl}(\text{PPh}_3)$ with the species formed by reduction ($\text{K}[\text{HBBu}_3]$) of **2** was the vinylidene $\text{AuRu}_5\{\mu_5\text{-CCH}(\text{PPh}_2)\}(\mu\text{-PPh}_2)(\text{CO})_{13}(\text{PPh}_3)$ (**29**). In this case, addition of H^- to C_β , followed by auration of the resulting anion with $[\text{Au}(\text{PPh}_3)]^+$, gives the isolobal analogue of **22** [32].

Addition of HX (X = Cl, Br, I). As described above, addition of two 2e donors (CO) resulted in cleavage of two Ru–Ru bonds and formation of a ‘scorpion’ core.

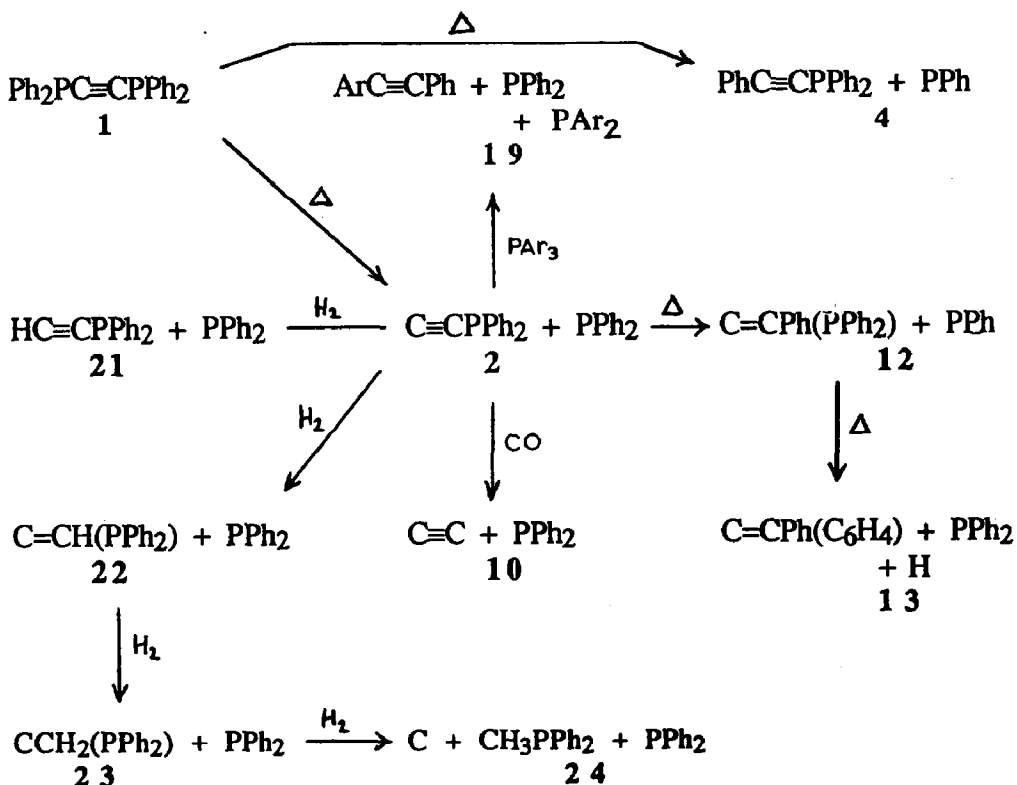


Scheme 10. Reactions of **2** with HX (X = Cl, Br or I) and $\text{AuCl}(\text{PPh}_3)$.

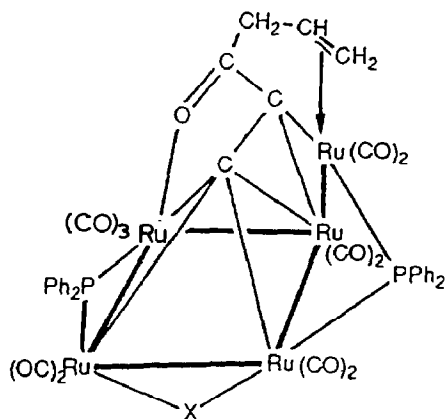
Addition of other 4e ligand combinations resulted in formation of similar cluster geometries (Scheme 10). Thus, the reaction of **2** with HCl or HBr gave orange $\text{Ru}_5(\mu\text{-H})(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\mu\text{-X})(\text{CO})_{13}$ (**30**, X = Cl or Br), in which the halogen atom bridges the scorpion's tail, and the proton one edge of the body [33]. With HI, the purple complex **31** containing one less CO molecule is obtained. In this complex, the iodine now bridges three Ru atoms (although these do not form a fully bonded triangle) and acts as a 5e donor. It is likely that **31** was formed from an iodo analogue of **30** by CO loss, as was found previously in reaction of $\text{Ru}_3(\mu\text{-H})(\mu\text{-I})(\text{CO})_{10}$ [34].

The spectroscopic properties of the orange complex $\text{AuRu}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\mu\text{-Cl})(\text{CO})_{13}(\text{PPh}_3)$ (**32**), obtained from **2** and $\text{AuCl}(\text{PPh}_3)$, suggest that it has a similar structure to that of **30** (X = Cl) with the H replaced by the isolobal $\text{Au}(\text{PPh}_3)$ group [32].

The reactions of **2** which have been described above, showing a ready transformation between structural types, usually occur at $\leq 40^\circ\text{C}$, and this may be contrasted with the considerably higher temperatures required previously to effect breaking and making of C-H, C-C and C-P bonds on clusters. These reactions have encompassed many of the possible rearrangements of the ligand $\text{C}_2(\text{PPh}_2)_2$ involving C-H, C-C and C-P bond-breaking and -forming reactions, as summarised in Scheme 11. In the next sections are described some reactions of **2** with various unsaturated hydrocarbons which have led to more extensive involvement of



Scheme 11. Rearrangements of dppa on Ru clusters (numbers in bold indicate complexes containing these fragments).



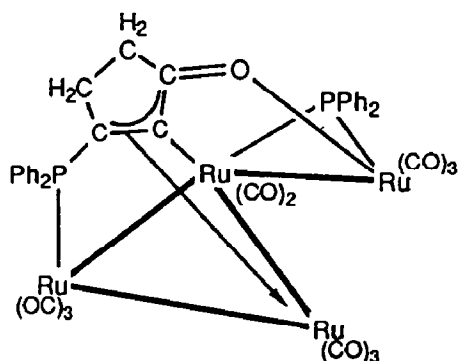
(33, X = Cl, Br)

the C_2 fragment in the formation of new ligands. Although the C_2 ligand in **10** proved to be disappointingly unreactive, possibly because it is sterically protected by the P-Ph and CO groups, complex **2** has been shown to be an effective source of the C_2 ligand in the reactions described below.

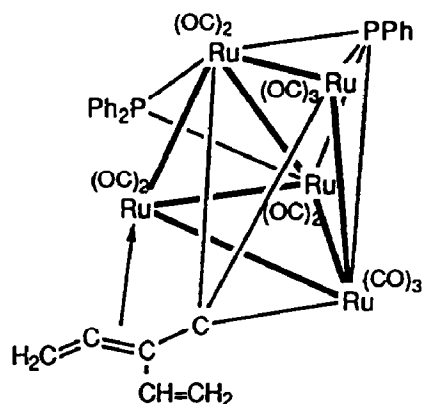
Allyl halides. Two isomers, yellow and brown, of composition $Ru_5X(CO)_{12}(dppa^*)(C_3H_5)$ ($X=Cl, Br$) were isolated from reactions between **2** and the appropriate allyl halides. We have only succeeded in structurally characterising the orange isomer as $Ru_5\{\mu_4-C_2(O)C_3H_5\}(\mu-PPh_2)_2(\mu-X)(CO)_{11}$ (**33**) by an X-ray study of the bromo compound [35]. Here three-component condensation of C_2 , CO and C_3H_5 has given an unusual organic ligand that acts as a 9e donor to the cluster. It probably best described as a metallated acylvinylidene, being attached to the rhomboidal core through the carbonyl group and the vinylidene; the C=C double bond of the allyl group is coordinated to the fifth metal atom. At some stage, the C_2-PPh_2 bond is broken, various metal-metal bonds being bridged by the resulting PPh_2 and halogen groups.

Ethene. Reactions between ethene and **2** are complex, and ligands containing one, two and three molecules of C_2H_4 have been characterised so far. Although the structural studies were carried out only with these compounds, analogous derivatives were obtained when 1-butene was used in place of ethene in these reactions. Orange $Ru_4\{\mu_4-C_5H_4O(PPh_2)\}(\mu-PPh_2)(CO)_{11}$ (**34**) contains a spiked triangular Ru_4 core to which is attached the novel phosphinocyclopentenonyl ligand, formed by addition of CO and C_2H_4 to the C_2PPh_2 ligand without breaking of the C-P bond [36]. This ligand acts as a 7e donor, a familiar 3e $\mu-\eta^1, \eta^2$ -vinyl unit supplementing the carbonyl and tertiary phosphine moieties.

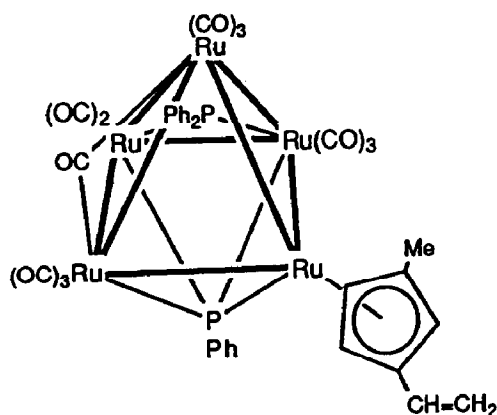
Two isomers of the pentanuclear complexes $Ru_5(\mu_4-PPh)\{\mu_3-C_2(C_4H_5)\}(\mu-PPh_2)(CO)_{12}$ were separated by TLC, but are in equilibrium in cyclohexane solution [36]. The brown isomer has structure **35**, in which two C_2H_4 molecules have coupled to the C_2 fragment to give a $CC(C_2H_2)(C_2H_3)$ ligand, best formulated as a penta-1,2,4-trien-3-ylmethylidyne, which acts as a 5e donor to three of the metal atoms. The cluster is a distorted wing-tip bridged butterfly, of which an open non-planar Ru_4 face is capped by the PPh group, the organic ligand being attached to the other open face.



(34)



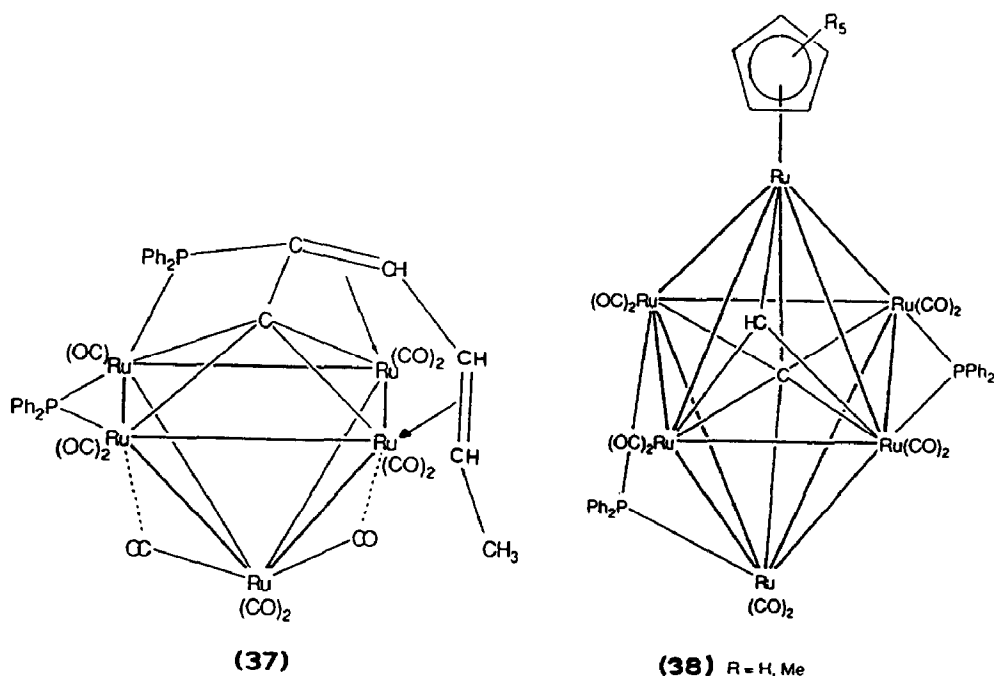
(35)



(36)

Complexes **34** and **35** were obtained from **2** and ethene under pressure. When ethene was passed through a hot solution of **2** in cyclohexane, $\text{Ru}_5(\mu_4\text{-PPh})(\mu\text{-PPh}_2)(\mu\text{-CO})(\text{CO})_{10}\{\eta^5\text{-C}_5\text{H}_3\text{Me}(\text{CH}=\text{CH}_2)\}$ (**36**), containing a 1,3-disubstituted cyclopentadienyl group, was isolated; it was also formed from **35** and C_2H_4 under similar conditions. The metal skeleton is an Ru_5 square pyramid capped by the $\mu_4\text{-PPh}$ group, with a basal edge bridged by the PPh_2 group; the cyclopentadienyl ligand is attached to a basal Ru atom [36].

In summary, reactions with ethene proceed in two distinct ways. First, condensation of one molecule of the olefin with CO and the C_2PPh_2 ligand gives the diphenylphosphinocyclopentenonyl ligand found in **34**. The second route affords hydrocarbon ligands, presumably after cleavage of the C–P bond, by attack of two ethene molecules at C_β in **2**, followed by cyclisation with a third molecule of C_2H_4 to give the substituted C_5 hydrocarbon found in **36**. Loss of H_2 has also occurred, possibly in combination with a phenyl group to give benzene; none of the complexes contains cluster-bonded H atoms. It is interesting to note that the formation of a cyclopentadienyl ligand has also been found in the reaction of diphenylacetylene with $\text{Ru}_2\{\mu\text{-}\eta^1, \eta^2\text{-CPhCCH}_2\}(\mu\text{-PPh}_2)(\text{CO})_6$ [37].



1,3-Butadiene. The green $\text{Ru}_5\{\mu_4\text{-CC}(\text{PPh}_2)=\text{CHCH}=\text{CHMe}\}(\mu\text{-PPh}_2)(\text{CO})_{11}$ (37) obtained from 2 and 1,3-butadiene is formed by a variation of the first route, in which electrophilic attack on C^β without cleavage of the C–P bond is followed by H-migration and coordination of the diene to two of the metal atoms [38]. The α -carbon is again found to cap the base of an Ru_5 square pyramid. Two other products isolated in similar amounts await crystallographic characterisation at the time of writing.

Cyclopentadienes. Cyclopentadienes reacted with 2 in benzene to give the hexanuclear clusters $\text{Ru}_6\text{C}(\mu_3\text{-CH})(\mu\text{-PPh}_2)_2(\text{CO})_{10}(\eta\text{-C}_5\text{R}_5)$ (38, R = H or Me) [39]. No surprisingly, perhaps, an $\eta^5\text{-C}_5\text{R}_5$ ligand is attached to one metal atom. Cleavage of the C–P bond gives a second $\mu\text{-PPh}_2$ group, while one carbon of the C_2 moiety becomes a carbido carbon residing in the centre of the Ru_6 octahedron. The second carbon combines with the proton from the cyclic diene to give a CH fragment capping one of the Ru_3 faces.

Conclusions. The variety of reactions exhibited by 2 is quite remarkable, and further experiments revealed that it undergoes reactions with many other organic and inorganic species, most of which appear to involve the C_2 unit. It is apparent that this fragment prefers to react by electrophilic addition to C^β , many products retaining the α -carbon in a multi-metal attachment to the cluster. Once again, the increase in reactivity of a small molecule attached to more than one metal atom is manifest, and in the case of 2, may be enhanced by its nestling in the cavity formed by the metal core.

This work has also demonstrated that the metal cores in these complexes are extremely flexible. Indeed, our results suggest that the metal skeleton adjusts to accommodate the organic fragment which is formed, many of the cluster cores being

only distantly related to the ideal geometrical arrangements depicted in Fig. 2. This parallels the findings of surface scientists, who observe considerable distortions in surfaces during reactions. The chemistry of a five-atom cluster is more likely to model reactions at a surface than the familiar three-atom clusters, and the richness of the chemistry we are finding, together with the structural diversity of the complexes obtained, augurs well for the future development of this area.

The potential of $C_2(PPh_2)_2$ and related ligands to link both like [40,41] and unlike metal clusters [41], which has only been explored briefly before, is shown by our recent syntheses of molecules such as $\{(OC)_{11}Os_3\}PPh_2C\equiv CPh_2\{Re_3(\mu-H)_3(CO)_{11}\}$, $\{Ru_4(\mu-H)_4(CO)_{11}\}_2\{\mu-C_2(PPh_2)_2\}$ and its pyrolysis product $Ru_8(\mu-H)_8\{\mu_4-C_2PPh_2\}(\mu-PPh_2)(CO)_{21}$. A complex containing the C_4 ligand, $Ru_6(\mu_6-C_4)(\mu-PPh_2)_2(CO)_{18}$, has been obtained from the diyne $Ph_2PC\equiv CC\equiv CPh_2$. Many of the resulting complexes are proving to be precursors for larger homo- and hetero-metallic systems.

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