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STRUCTURAL CHEMISTRY AND REACTIVITY OF CLUSTER BOUND ACETYLIDES: CLOSE RELATIVES OF THE CARBIDES?

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Abstract - There is a great deal of current interest in the chemistry of unsaturated molecules bound in multi-site fashion along the edges or across the faces of bi- or polynuclear metal compounds. A principal reason for this interest lies in the belief that the interaction of a ligand with several metal atoms may produce unusual patterns of chemical reactivity capable of synthetic exploitation. Particular attention has focussed on CO and carbide ligands in the context of Fischer-Tropsch and related processes. Our efforts have centred on a group of ligands the acetylides, related to both CO and carbides. From a chemical standpoint, cluster bound acetylides RC≡C- offer a number of attractive features: (i) a variety of multi-site bonding modes (e.g. sym-μ_2, μ_2-η^2, μ_3-η^2, μ_4-η^2) is accessible in clusters (ii) as in some carbides the α- (to M) carbon atom is "bare" (iii) the polarity (and hence reactivity) of the unsaturated linkage can be varied by changing the electronic characteristics of the group R.

Syntheses and structural systematics for the polynuclear ruthenium compounds $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CR)(PPh_2)$, $Ru_3(CO)_{8-9}(\mu_3\text{-}\eta^2\text{-}C{\equiv}CR)(PPh_2)$, $Ru_4(CO)_{13}(\mu_2\text{-}\eta^2\text{-}C{\equiv}CR)(PPh_2)$, $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CR)(PPh_2)$ (R=Ph, Bu^t, Pr^i) and the bis (acetylides) $Ru_3(CO)_6(\mu_2\text{-}C{\equiv}CR)(\mu_2\text{-}\eta^2\text{-}C{\equiv}CR)(PPh_2)_2(Ph_2PC{\equiv}CR)$ and $Ru_4(CO)_8(\mu_2\text{-}\eta^2\text{-}C{\equiv}CR)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CR)(PPh_2)_2(Ph_2PC{\equiv}CR)$ will be described. The "Carbocationic" nature of the acetylides in these molecules is shown by their reactivity towards nucleophiles (eg. C-C coupling occurs with isonitriles RNC). Reactions of cluster carbides with H_2 are the subject of extensive investigation at present. The acetylides $Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C{\equiv}CR)(PPh_2)$ and $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)$ undergo facile reduction with H_2 affording olefin or alkane and hydrido bridged clusters $Ru_3(CO)_9(H)(PPh_2)$ and $Ru_3(CO)_9(H)_2(PPh)$. The structure of $Ru_3(CO)_9(H)(PPh_2)$ provides a remarkable insight into P-C bound activation leading to P-C cleavage and generation of the phosphinidene $Ru_3(CO)_9(H)_2(PPh_2)$.

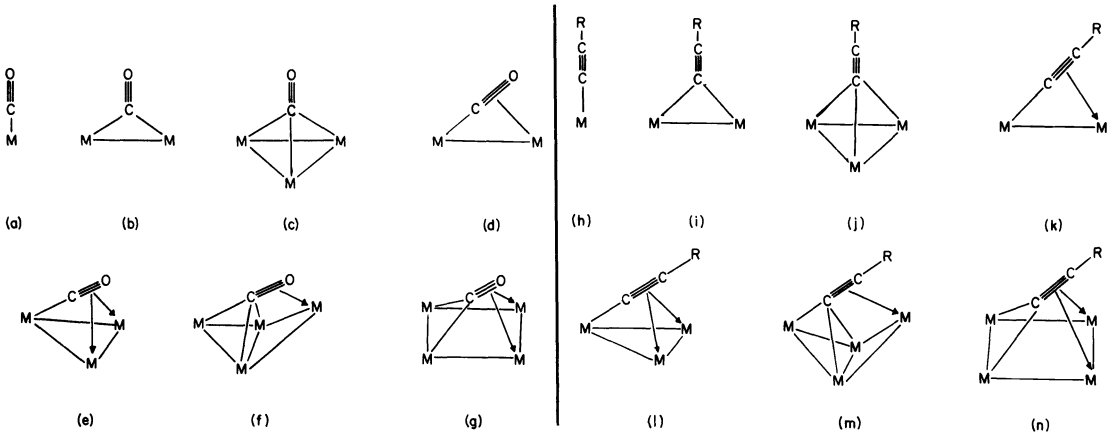
INTRODUCTION

A major impetus for the growth of transition metal cluster chemistry, apart from the intrinsic fascination of inorganic chemists with catenated species and molecular geometry, can be traced to the belief that multi-site binding on a cluster surface may be a key to the activation and subsequent elaboration of small molecules (1,2). As a prime example, the potential of synthesis gas (CO/H_2 mixtures) as a source of petrochemicals has spurred efforts to investigate the chemistry of CO activated via interactions with several metal atoms (3), and the chemical behaviour of certain proposed model intermediates in Fischer-Tropsch processes including cluster carbides, methylidyne, methylene, formyl and hydroxymethyl complexes. In the particular context of cluster carbides, there is accumulating evidence that "exposed" low coordinate carbide carbon atoms exhibit unusual reactivity. Protonation of carbidic carbon in anions (4) addition of H_2 to $Fe_4C(CO)_{12}^{2-}$ under oxidising conditions (4) and carbide - CO coupling (5) have been demonstrated. In general however knowledge pertinent to the patterns of reactivity for cluster bound unsaturated ligands is scarce despite an abundance of such data for mononuclear species.

Our own efforts in the metal-cluster area have focused on an unsaturated moiety, the acetylide RC≡C-, which, in its coordination chemistry has features of similarity and contrast with CO and the carbides. The ethynyl anion $HC{\equiv}C:^-$ is isoelectronic with CO and like the latter has a polarised triple bond (6). Much of the early work on transition metal-acetylide coordination chemistry can be attributed to Nast and his co-workers who elegantly demonstrated the analogies between metal carbonyls and their anionic acetylide counterparts (7). Like CO, terminal and doubly bridging μ_2- bonding modes for RC≡C- are well known. For both ligands a variety of other bonding modes become accessible when the π-electrons of the C≡O or RC≡C- bonds are utilised (Scheme 1). Although examples of σ-π-bonding of CO (eg. d in $Mn_2(CO)_5(Ph_2$

Scheme 1

Comparison of bonding modes for $C\equiv O$ and $RC\equiv C^-$



$PCH_2PPh_2)_2$(8), e in $(\eta^5\text{-}C_5H_5)_3Nb_3(CO)_7$ (9) and f in $[Fe_4(CO)_{13}H]^-$ (10)) are known, the number of cases for which such bonding has been established in the solid state are relatively small. Of course multi-site σ-π- CO bonding may have significance for metal cluster dynamics and reactivity. In the case of acetylides multi-site bonding is now well established. Early examples include the group IB acetylide polymers $[M(C\equiv CR)]_n$, their phosphine derivatives (11) and a variety of more complex mixed metal organometallics and clusters such as $[\eta^5\text{-}C_5H_5Fe(CO)_2(C\equiv CPh)CuCl]_2$, $Cu_4Ir_2(C\equiv CPh)_8(PPh_3)_2$ and $RhAg_2(C\equiv CC_6F_5)_5(PPh_3)_3$ prepared from these group IB alkynyls and characterised by Bruce, Churchill and co-workers (12-14). In the early 1970's while investigating the chemistry of phosphinoacetylenes $R_2PC\equiv CR'$ we discovered that iron carbonyls effected a remarkably facile $P\text{-}C_{(sp)}$ bond cleavage leading to phosphido bridged bi- or trinuclear complexes (15,16). A major product from $Fe_2(CO)_9$ and $Ph_2PC\equiv CPh$ was the binuclear acetylide $Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C\equiv CPh)(PPh_2)$ (cf. k Scheme 1). This compound was the forerunner of a large number of bi- and polynuclear phosphido bridged carbonyls with edge or face bridging alkynyl groups, which we have synthesised from phosphinoalkynes (17-20). The structural chemistry and reactivity of these molecules are the subject of this paper.

SYNTHESIS OF PPh_2 and $RC\equiv C$- BRIDGED CLUSTERS

Typical strategies for the synthesis of phosphido bridged carbonyl clusters using phosphinoalkynes are illustrated in Scheme 2. The method involves the inital displacement of a carbonyl group from a metal carbonyl by the phosphorus atom of $R_2PC\equiv CR'$ using conditions appropriate for the high yield synthesis of the substitution product. Thermolysis, irradiation or in some cases treatment with a second mole of carbonyl, of the phosphinoalkyne substitution product leads to P-C fragmentation with generation of phosphido and acetylide bridges. The detailed mechanisms of P-C cleavage are unknown. However in one case the intermediacy of an acetylene π-complex has been clearly demonstrated (21) and oxidative insertion into a P-C bond seems likely.

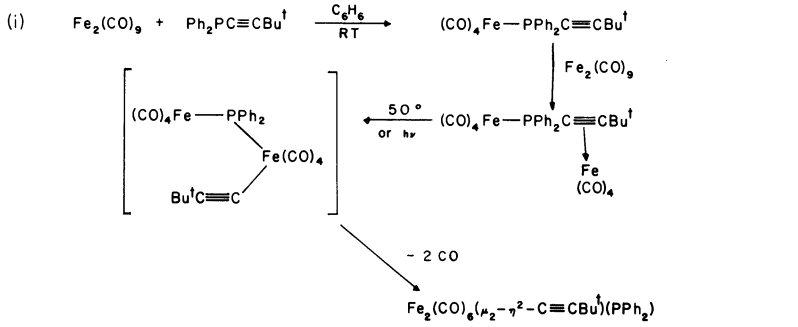
STRUCTURAL SYSTEMATICS

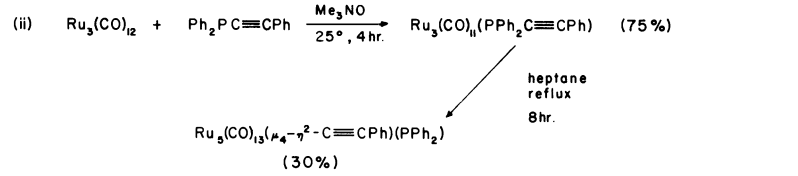
We have now determined the molecular structures of more than 25 compounds containing phosphido bridges and "sideways bonded" acetylides. A cross section of structural data chosen to compare and contrast acetylide bonding modes on various metal polyhedra is illustrated in Scheme 3. Three features are of interest:

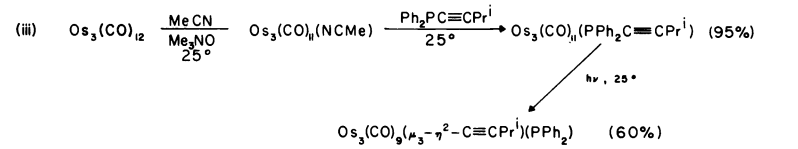
(a) The metal framework: Binuclear molecules of the type $M_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C\equiv CR)(PPh_2)$ (M=Fe, Ru) have M-M distances (∿2.596 Å, M=Fe; ∿2.752 Å, M=Ru) indicative of strong M-M bonds. Trinuclear clusters have "open" $M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C\equiv CR)PPh_2$ (M=Ru,Os) or "closed" triangular struc-

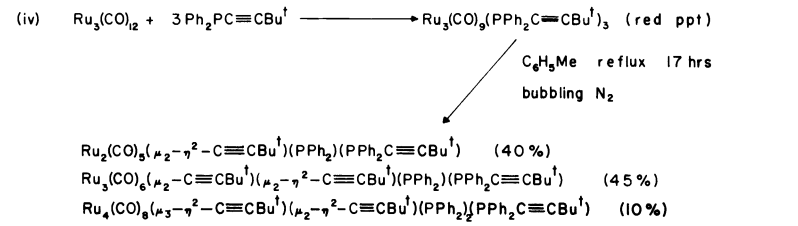
Scheme 2

Typical Synthetic Sequences

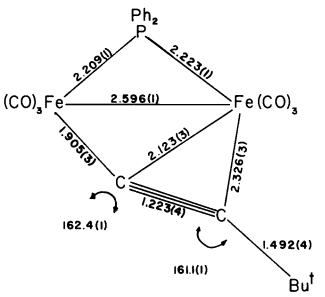


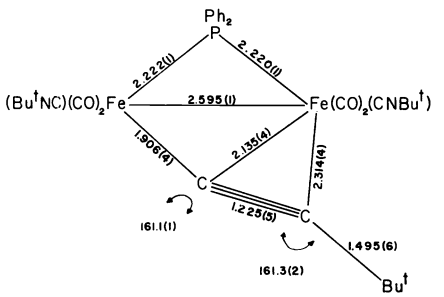


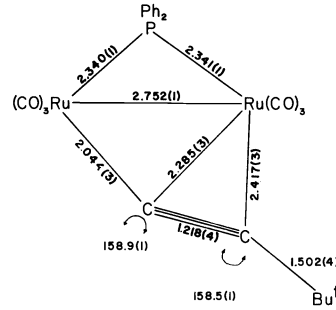


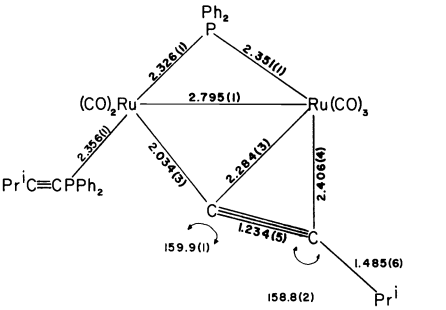


Scheme 3

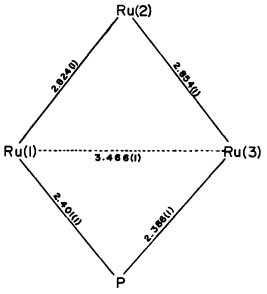


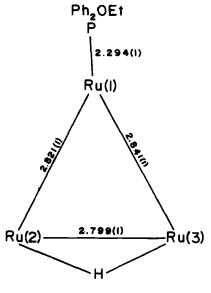


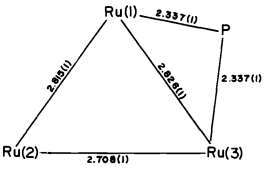




Scheme 3 (cont.)







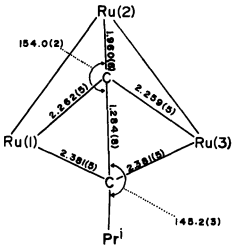
METAL SKELETONS

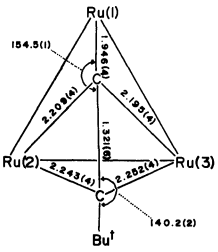
$Ru_3(CO)_9(PPh_2)(C{\equiv}CPr^i)$ (R = 0.025)

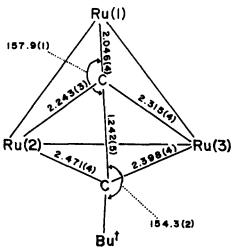
$HRu_3(CO)_8(PPh_2OEt)(C{\equiv}CBu^t)$ (R = 0.024)

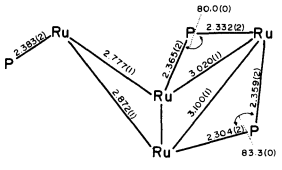
$Ru_3(CO)_8(PPh_2)(C{\equiv}CBu^t)$ (R = 0.028)

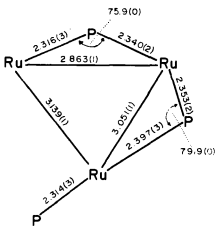
ACETYLIDE SKELETONS

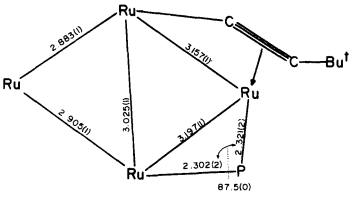












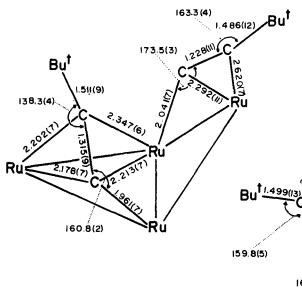
METAL SKELETONS

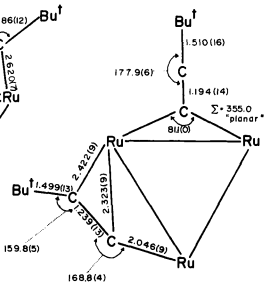
$Ru_4(CO)_8(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(\mu_2\text{-}\eta^3\text{-}C{\equiv}CBu^t)(PPh_2C{\equiv}CBu^t)$

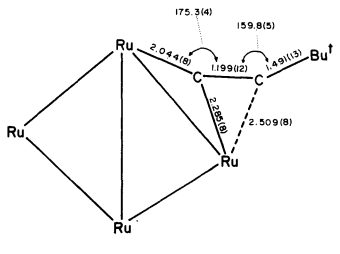
$Ru_3(CO)_6(\mu_2\text{-}PPh_2)_2(\mu_2\text{-}C{\equiv}CBu^t)(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2C{\equiv}CBu^t)$

$Ru_4(CO)_{13}(\mu_2\text{-}PPh_2)(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)$

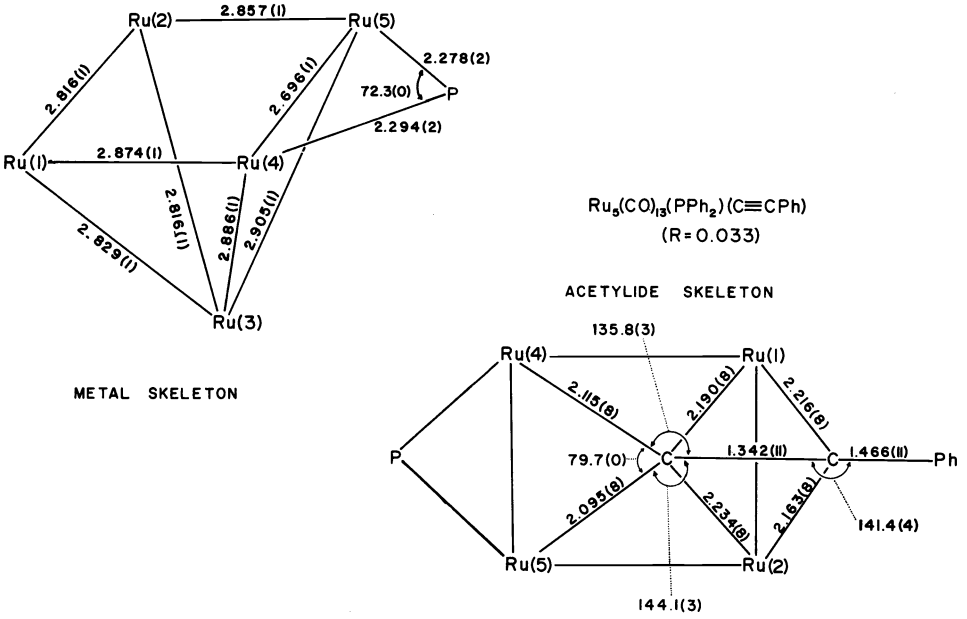
ACETYLIDE SKELETONS





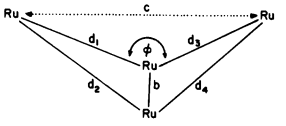


Scheme 3 (cont.)



tures. In the former type, one M---M distance is essentially non-bonding. The tetranuclear species structurally characterised are all of the "butterfly" type but within this group there are considerable variations in Ru-Ru distances and dihedral angles between the planes defined by the wings of the butterfly. Table 1 lists these parameters; comparable data for

TABLE 1. Structural parameters for "butterfly" clusters



a_1 = avg. d_1, d_2
a_2 = avg. d_3, d_4

	a_1	a_2	b	c	φ	Ref.
$Ru_4(CO)_{13}(PPh_2)(C{\equiv}CBu^t)$	2.894	3.177	3.025	5.259	176.93	This work
$Ru_4(CO)_8(PPh_2)_2(C{\equiv}CBu^t)_2$ ($PPh_2C{\equiv}CBu^t$)	2.825	3.061	3.043	5.001	167.04	This work
$Ru_4(CO)_{10}(OEt)(PPh_2)(C{=}CHPr^i)$	2.715	2.801	3.367	4.150	143.69	23
$Ru_4(CO)_{10}(OH)(PPh_2)(C{=}CHPr^i)$	2.730	2.802	3.455	4.124	141.49	23
$Ru_4(CO)_{13}(PPh)$	2.847	2.854	2.974	4.012	111.24	This work
$Ru_3Fe(CO)_{13}(PPh_2)_2$	(2.865)*	3.159	3.098	5.163	177.85	25
$Ru_3Ni(CO)_9(C_6H_5)(C{=}CHBu^t)$	(2.564)†	2.810	2.825	3.892	116.6	24
$(PPN)(Ru_4(CO)_{13}Cl)$	2.802	2.805	2.832	3.452	91.0	22

*avg. Ru-Fe †avg. Ru-Ni

a few related M_4 structures are included. In the acetylide bridged clusters $Ru_4(CO)_8(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)_2(Ph_2PC{\equiv}CBu^t)$ (Fig. 1) and $Ru_4(CO)_{13}(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)$ (Fig. 2)

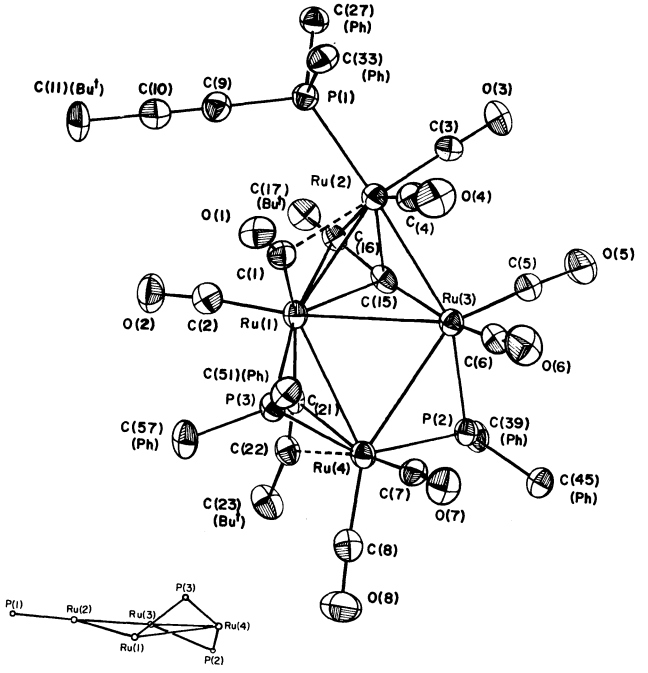


Fig. 1 A perspective view of the molecular structure of $Ru_4(CO)_8(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)_2(Ph_2PC{\equiv}CBu^t)$

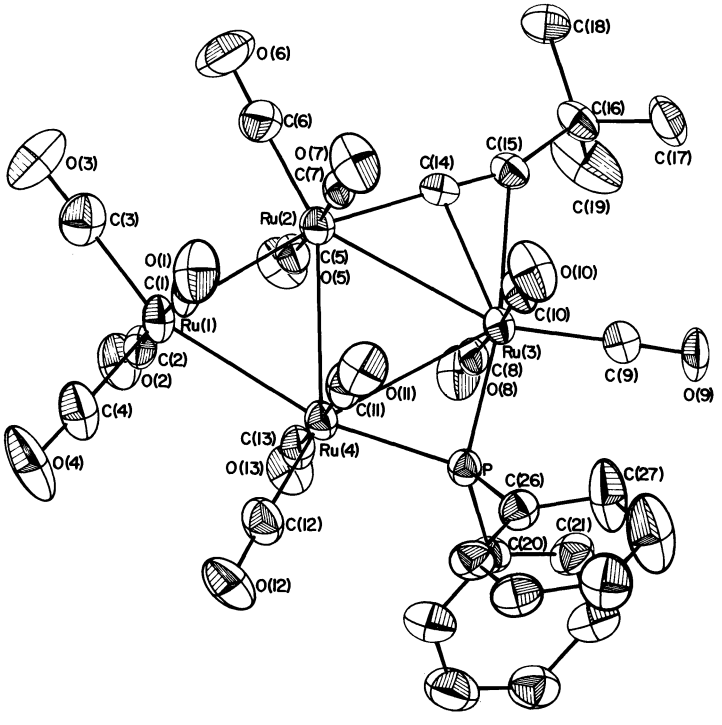


Fig. 2 An ORTEP II view of $Ru_4(CO)_{13}(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)$

the butterfly framework is shallow with dihedral angles of 167.04° and 176.9° respectively. The Ru_4 skeleton in the latter is almost flat in sharp contrast to $[PPN][Ru_4(CO)_{13}Cl]$ (ϕ=91°) (22), $Ru_4(CO)_{10}(C{=}CHPr^i)(OH)(PPh_2)$ (ϕ= 141.49°) (23) and $Ru_3Ni(\eta^5\text{-}C_5H_5)(C{=}CHBu^t)(CO)_9$ (ϕ=116.6°) (24). The recently characterised mixed cluster $Ru_3Fe(CO)_{13}(PPh_2)_2$ (25) has however a planar triangulated skeleton. It is of interest to compare these changes in polyhedral stereochemistry with the predictions of Wade's counting rules for M_4 clusters. On the basis of localised 2-centre M-M bonds the predictions are: 60e- tetrahedral; 62e- triangulated butterfly or planar; 64e- square planar or metal-attached triangular. Assuming that a PPh_2 group contributes 3e, a μ_3-η^2-C≡CR unit 5e, a μ_2-η^2-C≡CR group 3e, each Ru(0) 8e, and a terminal phosphine 2e, we obtain a total count of 64e for $Ru_4(CO)_8(\mu_3\text{-}\eta^2\text{-}C{\equiv}Bu^t)(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)_2(Ph_2PC{\equiv}CBu^t)$. A structure based on a tetrahedron missing two Ru-Ru bonds would be predicted rather than a butterfly. However closer inspection of the structure (Fig. 1) reveals that the Ru(4)-C(22) bond (2.620(8) Å) is extremely long when compared to Ru(4)-C(21) 2.292(7) Å, suggesting that while the orientation of this acetylide is suitable for a μ_2-η^2-bonding mode, in fact the η-interaction is extremely weak. As a consequence the acetylide C(21)-C(22) is probably best considered as closer to a 1e than a 3e donor hence the cluster does not receive the full complement of 64e. For $Ru_4(CO)_{13}(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)$ (Fig. 2) there are 64 electrons if the μ_2-η^2-C≡CBu^t unit is a 3e donor. While there is still asymmetry in the Ru(3)-C(14) (2.285(8) Å) and Ru(3)-C(15) (2.509(8) Å) interactions, the η^2-interaction is clearly stronger than in the former case. The electronic effect of increased involvement of the acetylide π-electrons in bonding, manifests itself stereochemically in a flattening of the butterfly to an almost planar skeleton. The predicted opening of an M-M bond (62e → 64e) does not occur; however two of the Ru-Ru bonds (Ru(2)-Ru(3) of 3.157(1) Å and Ru(3)-Ru(4) of 3.197(1) Å) are much longer than the more normal Ru(1)-Ru(2) (2.883(1) Å) and Ru(1)-Ru(4) (2.905(1) Å) distances indicative of considerable Ru-Ru bond weakening. We see the interesting feature that for these M_4 butterflies the shallowness of the butterfly and in a sense the distortion from a 60e tetrahedron increases with increase in ligand donation to the core; as the formal electron count increases towards 64e, a lengthening and weakening of M-M bonds occurs, presumably prior to complete rupture of another metal-metal linkage. It is significant that in the one other formally 64e cluster $FeRu_3(CO)_{13}(PPh_2)_2$ a planar framework with elongated Ru-Ru bonds is also observed (25). The cluster $Ru_4(CO)_{10}(\mu_4\text{-}C{=}CHPr^i)(\mu_3\text{-}OH)(PPh_3)$ (23) is a 64e species if the multi-site bound vinylidene contributes 4 electrons and the triply bridging OH group 5 electrons. In this case only four Ru-Ru bonds are present, all of approximately equal length (2.703(1)-2.802(1) Å) and with Ru-Ru-Ru angles varying from 76.1-95.6°. Thus although the skeleton is not square it does tend towards this geometry. Presumably the configuration adopted is a compromise between the predicted idealised square framework and the demand to maximise metal-ligand bonding. On the other hand the phosphidene cluster $Ru_4(CO)_{13}(PPh)$ (Fig. 3) a 62e species if the phosphinidene ligand PPh is considered as a 4-electron ligand, has a relatively small interplanar angle of 111.2° with the PPh unit capping an "open" triangular face. The Ru(1)-Ru(4) non-bonded distance (4.021 Å) indicates that this cluster framework is relatively close to the parent tetrahedron.

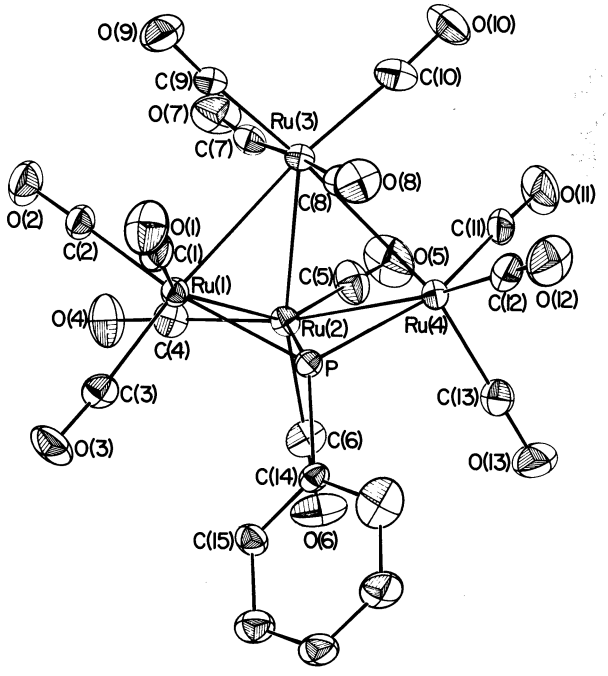


Fig. 3 The structure of the phosphinidene cluster $Ru_4(CO)_{13}(PPh)$ showing the face bridging PPh group.

The pentanuclear molecule $Ru_5(CO)_{13}(\mu_2\text{-}C{\equiv}CPh)(PPh_2)$ contains a square pyramidal array of metal atoms (Fig. 4) (26). With the exception of the short Ru(4)-Ru(5) bond (2.696(1) Å)

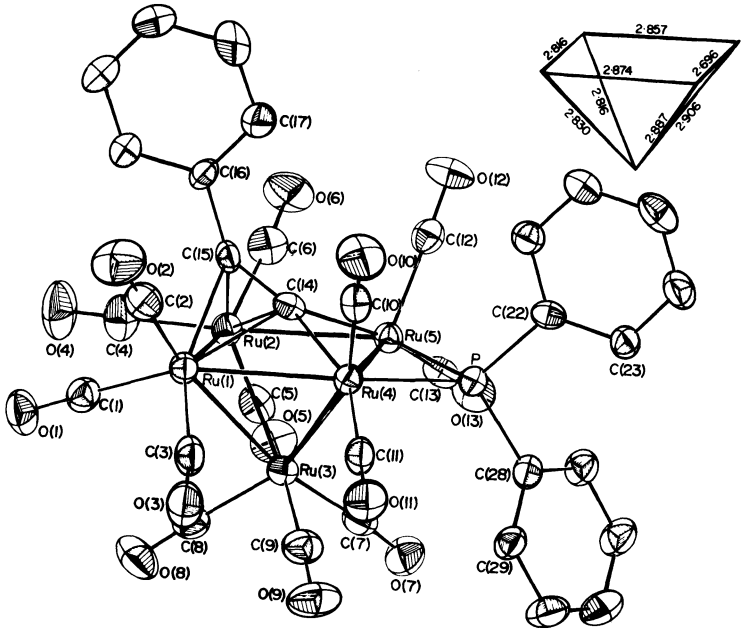


Fig. 4 A view of the square pyramidal cluster $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)$

all of the metal-metal distances are close to the average value of 2.854 Å in $Ru_3(CO)_{12}$ (27). This molecule is one of a very small number of square pyramidal iron group carbonyl clusters which have been structurally characterised. Examples are: $[Fe_5(CO)_{15}C]$ (28), $[Os_5(CO)_{15}P(OMe)]$ (29) $[Ru_5(CO)_{15}(PR)]$ (30) and the hydrides $[Fe_5N(CO)_{14}H]^-$ (31) and $[Ru_5(CO)_{15}H_2(C{=}CH_2)]$ (32).

(b) The multi-site bound acetylides

As illustrated in Scheme 3 examples of sym-μ_2 (in $Ru_3(CO)_6(\mu_2\text{-}C{\equiv}CBu^t)(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)_2(Ph_2PC{\equiv}CBu^t)$; cf i Scheme 1), $\mu_2\text{-}\eta^2$ (in $M_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)$, $Ru_3(CO)_6(\mu_2\text{-}C{\equiv}CBu^t)(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)_2(Ph_2PC{\equiv}CBu^t)$, $Ru_4(CO)_{13}(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)$ and $Ru_4(CO)_8(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)_2(Ph_2PC{\equiv}CBu^t)$; cf. k, Scheme 1), $\mu_3\text{-}\eta^2$ (in $M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPr^i)(PPh_2)$ (M=Ru, Os), $Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)$ and $Ru_4(CO)_8(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)_2(Ph_2PC{\equiv}CBu^t)$ cf. l Scheme 1) and $\mu_4\text{-}\eta^2$ (in $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)PPh_2$, cf. n Scheme 1) have been found but no examples are yet known of μ_4- bonding in a butterfly (m, Scheme 1) or sym-μ_3 bonding (j, Scheme 1).

In general, as the number of metal atoms involved in the interactions increases (ie $\mu_2 \rightarrow \mu_3 \rightarrow \mu_4$) a gradual lengthening of the formal carbon-carbon triple bond occurs and the bend back angles γ and δ, a measure of the deviation of the acetylenic skeleton from linearity, increase. Unfortunately the impact of these changes is somewhat clouded by the change of R group on the acetylene; the basic trends are however evident from the comparison of $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)$ (C-C 1.218(4) Å; γ 21.1°, δ 21.5°), $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPr^i)(PPh_2)$ (C-C 1.284(8) Å; γ = 26.0°, δ = 34.8°) and $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)$ (C-C 1.342(11) Å; γ = 0°, δ = 38.6°).

In the cases where an acetylide is $\mu_2\text{-}\eta^2$- bonded along a polyhedral edge it is important to note that while the α (to M) carbon atom is bonded to both metals the β-acetylenic carbon interacts with only one metal atom and at a considerably longer distance. The electronic polarisation resulting from this structural non-equivalence may be of major importance in determining the chemistry of these molecules. Similar arguments pertain to the environment of α and β- acetylenic carbon atoms in the $\mu_3\text{-}\eta^2$ and $\mu_4\text{-}\eta^2$ species.

(c) The phosphido bridges

Lewis base promoted degradation is a significant problem to overcome in the possible application of metal clusters to catalysis. One solution to this problem may be in the design of clusters with ligands capable of maintaining the integrity of a polynuclear unit while allowing the cleavage and reformation of M-M bonds. An upsurge in interest in phosphido (20), arsenido (33) and phosphinidene (30, 34, 35) containing clusters can be attributed at least in part to the hope that these flexible ligands will allow modifications to a polynuclear framework during reaction while maintaining nuclearity. Many phosphido bridged cluster carbonyls are now known (20, 33) and in a few cases reversible M-M bond breaking and making has been demonstrated. Scheme 3 shows that for the ruthenium clusters described here-

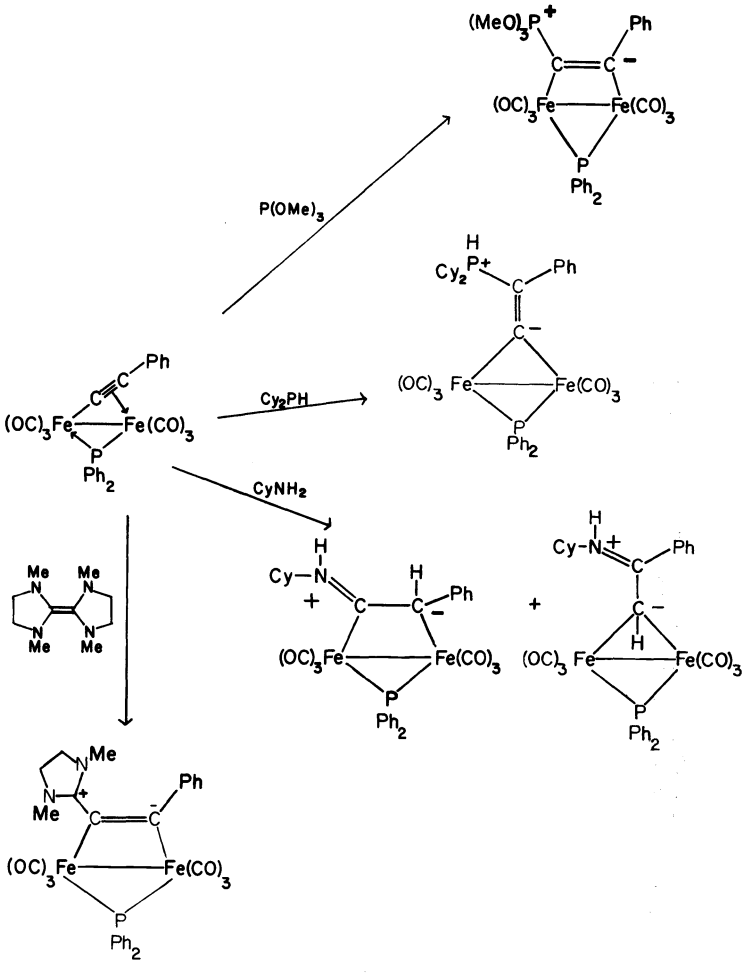
in, the PPh_2 group may bridge an "open" (eg. $M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPr^i)(PPh_2)$) or "closed" (eg. $Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)$) polyhedral edge. The M-P-M angle at the bridge can be quite acute ~70° or closer to the tetrahedral value (eg. 106° in $Fe_2(CO)_6(PPh_2)_2^{2-}$ (36) and the δ (^{31}P) values of the PPh_2 bridges give a good indication of the presence or absence of M-M interactions (20). It is important to note however that δ(^{31}P) is influenced by M-P bond lengths and M-M distance as well as M-P-M angle. Thus the very low shift in $Ru_5(CO)_{13}(C{\equiv}CPh)(PPh_2)$ (δ = +253 ppm) is associated with a short Ru-Ru bond (2.696(1) Å) and short Ru-P bonds (2.286 Å av) rather than a particularly acute Ru-P-Ru angle (72.3°).

SOME CHEMISTRY OF μ-BOUND ACETYLIDES

In order to understand the transformations which small molecules will undergo in the environment of a metal cluster it is important to be able to predict the patterns of chemical behaviour typical of various coordination modes. Unfortunately for highly mobile ligands such as CO this is a difficult if not impossible task. For several years we have been examining the chemical reactivity of μ-bound acetylides with the aim of not only providing information on patterns of reactivity which might have general relevance but also to provide some clues to the activation which occurs for different multi-site bonding modes. In principle the availability of a very wide range of μ-bound acetylides offers a unique opportunity for chemical exploitation.

Our initial studies on the binuclear iron complex $Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)$ showed that the "sideways bound" acetylide exhibited an unusual sensitivity to nucleophilic attack. Adducts formed via additions of phosphites (37), phosphines (38) amines (39) and carbenes (40) (Scheme 4) have zwitterionic structures with the nucleophilic atom attached to the original α or β- acetylenic carbon and with the negative charge delocalised into the binuclear framework. Such reactions are unusual for uncharged organometallic compounds although examples of similar chemistry have been subsequently unearthed by other groups (eg. 41-43). It was clear from this work that the $\mu_2\text{-}\eta^2\text{-}C{\equiv}CR$ groups are quite *electrophilic*. We have recently extended these studies to binuclear and trinuclear ruthenium compounds in an attempt to compare the reactivities for $\mu_2\text{-}\eta^2$ and $\mu_3\text{-}\eta^2$ acetylides.

Scheme 4



REACTIONS OF μ_2-η^2 AND μ_3-η^2-ACETYLIDES WITH ISONITRILES: CARBON-CARBON BOND FORMATION

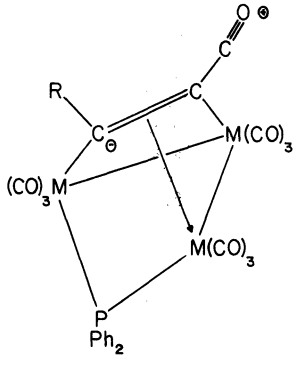
Although C-C coupling reactions are an integral part of hydrocarbon forming processes in for example Fischer-Tropsch syntheses using CO/H_2 mixtures, little is known of the mechanics of bond formation. Bradley (5) has suggested the possibility of C (carbide)--CO coupling to generate cluster acylium like species; carbide or CO insertion into μ-methylidyne or μ-methylene-metal bonds is also feasible.

We have not yet investigated reactions of electrophilic μ-acetylido complexes with CO under pressure. However isonitriles, which resemble CO to a considerable extent in their organometallic chemistry react smoothly with $M_2(CO)_6(C{\equiv}CPh)(PPh_2)$ (M=Fe, Ru) at 0° giving excellent yields of adducts $M_2(CO)_6\{C(CNR)CPh\}(PPh_2)$ together with smaller amounts of the substitution products $M_2(CO)_5(C{\equiv}CPh)(PPh_2)(RNC)$ and $M_2(CO)_4(C{\equiv}CPh)(PPh_2)(RNC)_2$. The structure of the iron adduct (Fig. 5) (44) illustrates several important points: (a) The nucleophile RNC is attached to the original α- carbon atom of the acetylide via a strong, partially multiple C-C bond (ℓ = 1.37(2) Å (b) the acetylenic triple bond is lengthened to 1.33(2) Å (c) the new hydrocarbon fragment $Bu^tNCCCPh$ is meso-ionic with the positive charge formally on nitrogen and the negative end of the dipole delocalised from C(7)-C(8) into the binuclear core.

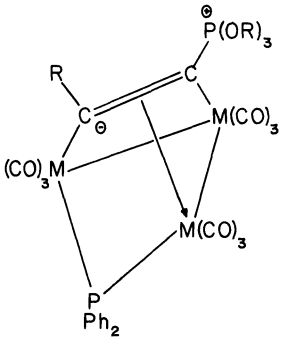
Initial efforts to examine corresponding reactions for the trinuclear μ_3-acetylido complex $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CR)(PPh_2)$ (R=Pr^i) were frustrated by the propensity of this molecule to lose CO yielding the "closed" but electron deficient cluster $Ru_3(CO)_8(\mu_3\text{-}C{\equiv}CPr^i)(PPh_2)$; the latter reacts rapidly with nucleophiles leading to Ru-Ru bond scission. The corresponding osmium derivatives $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CR)(PPh_2)$ (R=Ph,Pr^i) are more stable to CO loss and react readily with Bu^tNC affording 1:1 adducts, characterised by microanalysis, ir and ^{31}P nmr spectroscopy. The ν(CO) ir spectra (eg. $Os_3(CO)_9\{C(Bu^tNC)CPh\}(PPh_2)$ ($C_6H_5CH_3$; 2068 m, 2046 vs; 2013 s; 1994 s, br; 1963 m, br 1943 sh, br) are consistent with retention of the trinuclear framework and the ν(N≡C) frequency ($C_6H_5CH_3$; 2238 cm^{-1}) is higher than in the isonitrile substitution products $Os_3(CO)_8(Bu^tNC)(C{\equiv}CR)(PPh_2)$. These high ν(N≡C) frequencies indeed seem diagnostic of isonitrile attached to carbon rather than metal.

Crystals of these osmium complexes suitable for x-ray were not obtainable. However a similar reaction sequence carried out on the hydride $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)$ related to $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)$ by replacing a bridging phosphido group with an Ru-Ru bond and a bridging hydride afforded nice crystals of $HRu_3(CO)_9\{C(CNBu^t)CPh\}$. An accurate x-ray analysis revealed the structure in Fig. 6. As in $M_2(CO)_6\{C(CNBu^t)CPh\}(PPh_2)$ the isonitrile carbon atom is strongly bonded to the original α- carbon atom of the acetylide (C(11)-C(12) 1.406(4) Å) but in order to maintain the 5-electron donor character of the hydrocarbon fragment, the olefinic linkage (C(10)-C(11) 1.400(4) Å) is involved in an η^2-interaction with the third ruthenium atom Ru(3).

The facility with which these C-C coupling reactions occur for μ-bound acetylides and the obvious electrophilicity of the unsaturated fragment leads us to believe that coupling with CO may be possible under certain conditions leading to adducts such as 1. Subsequent elaboration of 1 via addition of alcohol or amine may be possible. We have shown that $Os_3(CO)_9\{C(CNBu^t)CPh\}(PPh_2)$ undergoes rapid addition of amine RNH_2 generating "carbon coordinated" carbene complexes $Os_3(CO)_9\{C(C(NHR)(NHBu^t))CPh\}(PPh_2)$.



1



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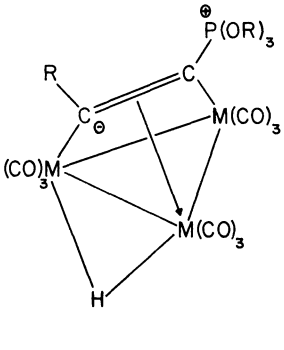

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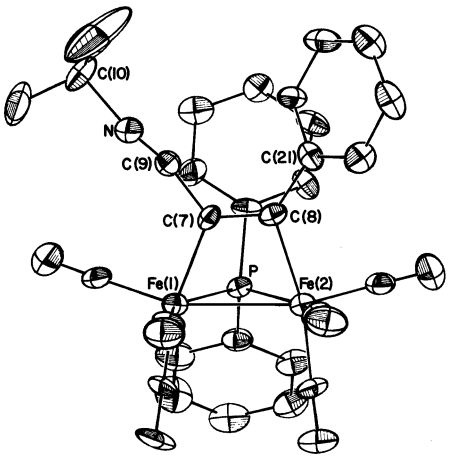


Fig. 5

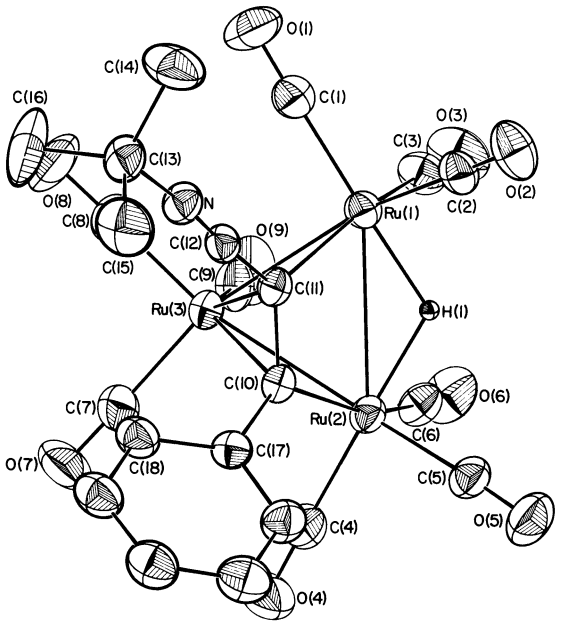


Fig. 6

Fig. 5 X-ray structure of $Fe_2(CO)_6\{C(CNBu^t)CPh\}(PPh_2)$

Fig. 6 X-ray structure of $HRu_3(CO)_9\{C(CNBu^t)CPh\}(PPh_2)$, drawn by ORTEP

REACTIONS OF μ_3-η^2-ACETYLIDES WITH GROUP V BASES

The trinuclear osmium and ruthenium compounds $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)$ and $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)$ also undergo attack by phosphites and amines again with additions to the acetylenic carbon atoms. These products have structures such as 2 and 3. Attack by phosphorus nucleophiles at a μ_2- phenylacetylide ligand in $HOs_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)$ has been described by Deeming (42) but we are unaware of any reports relating to μ_3-C≡CR groups.

The group R on the acetylide appears to play a significant role in the reactivity of the triple bond towards nucleophiles. Thus for $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)$, phosphites, phosphines and isonitriles yield only substitution products of the type $HRu_3(CO)_8(\mu_3\text{-}\eta^2C{\equiv}CBu^t)(L)$ with one mole of ligand at room temperature. Carbonyl substitution on the hydride occurs regiospecifically for phosphorus ligands with the ligand occupying an equatorial site on the ruthenium atom σ-bonded to the acetylide, *trans* to an Ru-Ru bond. This is illustrated in Fig. 7 for the molecule $HRu_3(CO)_8(C{\equiv}CBu^t)(PPh_2OEt)$. Interestingly, comparison with the structural data for the parent (45,46) reveals that substitution has a negligible influence on the Ru(2)-Ru(3) bond bridged by the hydride and on the acetylide-metal interaction but causes a substantial lengthening (av. 0.035 Å) of the two Ru-Ru bonds adjacent to the substituent. Increased electron donation from the phosphine, transmitted through the unique ruthenium atom effects a slight cluster expansion, in a rather specific manner.

COMMENTS ON THE REACTIVITY OF μ_2-η^2 AND μ_3-η^2-ACETYLIDES

The patterns of reactivity for "sideways bound" acetylides may be influenced by a number of electronic, structural and steric factors including the following:
(i) the *overall* electrophilic character of the multiple bond (ie. the degree of electrodepletion) which may relate to the electroattractive nature of the M_2 or M_3 metal fragment and the donor or acceptor property of the alkynyl substituent.
(ii) Competition from other reaction pathways eg. CO substitution.
(iii) Polarisation in the triple bond resulting from (a) the presence of two σ-substituents (a metal and an organic group) differing greatly in electronegativity and (b) unsymmetrical μ-coordination of the acetylide.
(iv) Possible steric inhibition to α- or β- carbon attack for large R groups or bulky nucleophiles.

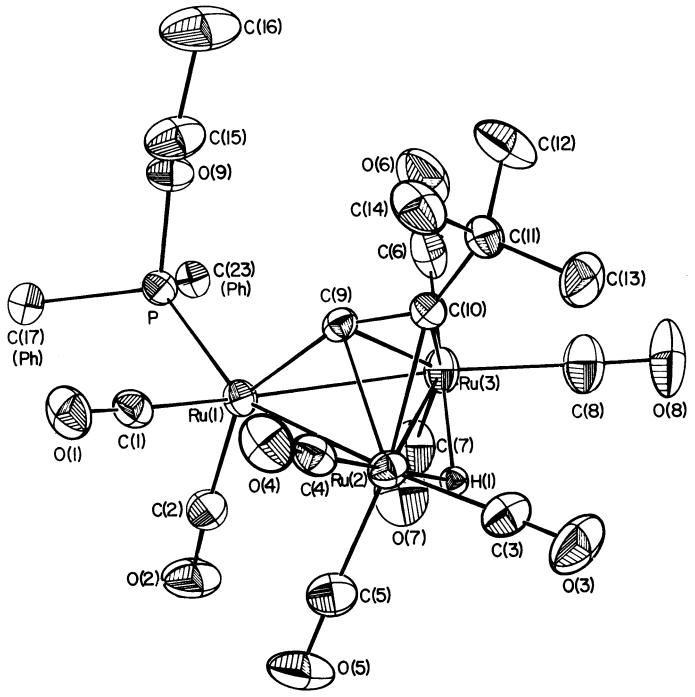


Fig. 7 Molecular structure of $HRu_3(CO)_8(C{\equiv}CBu^t)(PPh_2OEt)$

(v) The energy, availability and localisation of the low lying frontier orbitals of the acetylide moiety.

Prediction of the net amount of charge transfer in a metal-acetylene interaction resulting from the interplay of the components in the Dewar-Chatt-Duncanson model is a non-trivial matter. Even for relatively simple olefin-metal complexes opinion is divided as to the direction or degree of net electronic transfer (47). Moreover Hoffman (47) has suggested on theoretical grounds that symmetrical η^2-coordination deactivates an olefin to nucleophilic attack; charge is relatively unimportant. Passage from an η^2- to an unsymmetrical η^1-mode creates greatly enhanced reactivity and this "slippage" accounts in large part for activation towards nucleophilic attack.

In μ_2-η^2, μ_3-η^2, μ_4-η^2 acetylide complexes there is a built-in asymmetry, just as there would be in a σ-η- vinyl derivative or a "sideways bonded" carbonyl. It is our belief that this may well be the key to the unusual reactivity of these molecules.

In an effort to shed some light on the influence of the group R in -C≡CR on reactivity patterns we have measured the ^{13}C nmr spectra at 100.5 MHz of a series of $Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CR)(PPh_2)$ complexes (Table 2). As illustrated for $R=C(CH_3)_3$ (Fig.8c) the acetylenic carbon atoms C_α and C_β appear as doublets due to coupling to ^{31}P. We assign the resonance with the largest $J_{P\text{-}C}$ value (53 Hz) to C_α and the other doublet to C_β. The C_α shifts lie between 98.4 and 113.1 ppm downfield of TMS. These shifts are at considerably higher field than the carbene carbon resonances in carbene complexes (200-350 ppm). Note the fact that the C_α resonance is at high field for $R=C(CH_3)_3$, almost coincidental with C_β for $R=C\text{-}C_6H_{11}$ and downfield of C_β in the case of $R=p\text{-}BrC_6H_4$. We interpret these variations in shift as indicative of changes in polarisation in the triple bond (vide infra)(Fig. 8).

For the corresponding ruthenium complexes $Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CR)(PPh_2)$, C_α resonates ∿5 ppm to higher field while C_β remains essentially the same. In the μ_3-η^2- acetylide derivatives $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPr^i)(PPh_2)$, $HRu_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2OEt)$ and $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)$ (48)

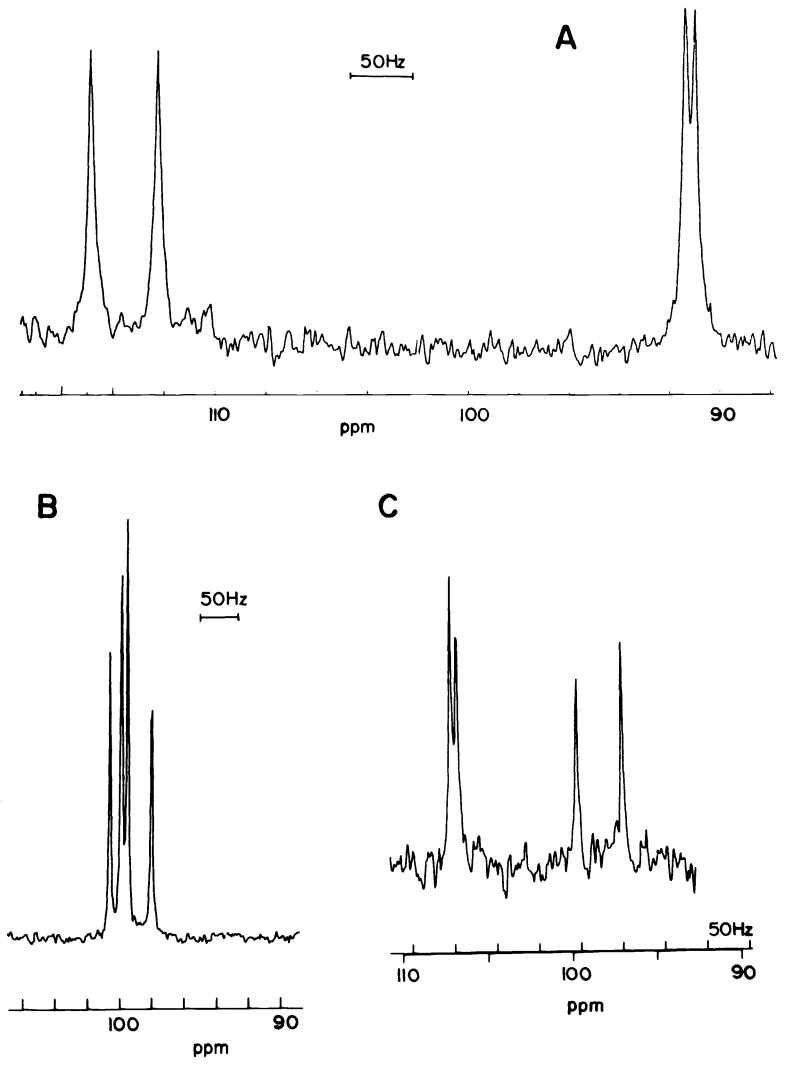


Fig. 8 Comparison between the ^{13}C nmr spectra of $Fe_2(CO)_6(C_2C_6H_4Br\text{-}p)(PPh_2)$ A, $Fe_2(CO)_6(C_2C_6H_{11}\text{-}c)(PPh_2)$ B and $Fe_2(CO)_6(C_2C(CH_3)_3)(PPh_2)$ C; resonances due to the acetylidic carbon atoms only are shown.

TABLE 2. Carbon-13 chemical shifts of the acetylenic carbon atoms C_α and C_β in some μ_2- and μ_3- bound acetylides

Compound	$\delta(C_\alpha)$	$\delta(C_\beta)$	$\delta(C_\alpha)-\delta(C_\beta)$	$\delta(C_\alpha)+\delta(C_\beta)$
$Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)$	98.4	107.0	- 8.6	205.4
$Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CC_6H_{11}\text{-}c)(PPh_2)$	99.3	99.7	- 0.4	199.0
$Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CC_6H_4OCH_3)(PPh_2)$	106.1	93.3	+12.8	199.4
$Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)$	110.4	92.1	+18.3	202.5
$Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CC_6H_4Br\text{-}p)(PPh_2)$	113.1	90.7	+22.4	203.8
$Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)$	93.5	107.0	-13.5	200.5
$Ru_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)$	105.1	91.2	+13.9	196.2
$Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPr^i)(PPh_2)$	134.4	103.8	+30.6	238.2
$HRu_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2OEt)$	140.5	112.2	+28.3	252.7
$HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)$	164.2	110.6	+53.6	274.8

C_α resonates at much lower field (+134.4, +140.5 and +164.2 ppm respectively while C_β is relatively invariant (+103.8, +112.2 and +110.6 ppm). If we assume, as others have done (49) that a change in $\delta(^{13}C)$ is mainly associated with a change in charge on the carbon atom then $\delta(C_\alpha)+\delta(C_\beta)$ gives an idea of total charge change in the triple bond while $\delta(C_\alpha) - \delta(C_\beta)$ is a measure of polarisation in the bond. Table 2 contains sums and differences of shifts for the binuclear and trinuclear acetylides. For the M_2 compounds $\delta(C_\alpha) + \delta(C_\beta)$ is relatively constant for all R groups. Values of $\delta(C_\alpha) - \delta C(\beta)$ however suggest a marked change in polarisation within the triple bond as R is changed from $C(CH_3)_3$ to $p\text{-}BrC_6H_4$. In the phenyl and p-bromophenyl compounds the acetylidic triple bond is more polarised, with the greater positive charge on C_α; for the t-butyl compound the polarity of the triple bond is in the opposite sense. Both acetylides remain electrophilic.

Comparison of the μ_3 with the μ_2-acetylides shows a marked downfield shift of the α-carbon atom of the μ_3-acetylide while the shift of C_β remains relatively constant. Greater polarisation in the μ_3-C≡CR moiety is indicated. The larger values of $\delta(C_\alpha) + \delta(C_\beta)$ may infer greater overall electrophilicity in the μ_3-acetylide although there are obvious dangers in linear extrapolations of this sort when pronounced structural changes occur.

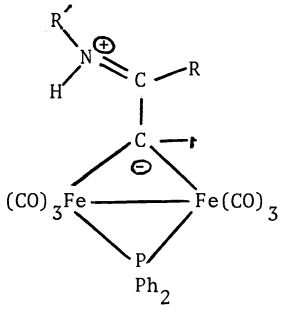
To date we have not found the C_α and C_β resonances in $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)$. These signals either lie under the phenyl carbon multiplet or are unobservable on account of their long relaxation times.

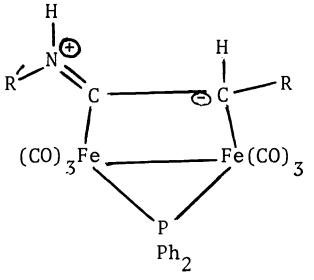
That polarisation in the triple bond is pertinent to the reactivity of these acetylides is evident from our studies on nucleophilic additions to these molecules. Thus for addition of primary amines RNH_2 across the triple bond of $Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CR)(PPh_2)$ (Table 3) the product ratios at equilibrium in solution can be influenced by the nature of the group R. The ratio of products formed by addition to the β- and α- carbon atoms in the case of isopropylamine can be changed from 21.0:1 when R is $p\text{-}CH_3OC_6H_4$ to only 1.5:1 for the more electron withdrawing $p\text{-}BrC_6H_4$ group. In the latter case the electrophilicity of C_α is increased by the electron withdrawing $p\text{-}BrC_6H_4$ group. The ^{13}C studies also suggest that for $R=Bu^t$, polarisation in the triple bond places greater positive charge on C_β. Simplistically, nucleophilic attack at C_β might be favoured. In practice phosphines, phosphites, amines and isonitriles do *not* add to $M_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)$ in marked contrast to the facile reactions with R=Ph. We attribute this to the fact that C_α is less electrophilic than for R=Ph; addition at C_β, while electronically favoured, is hindered by the steric bulk of the t-butyl group.

For μ_3-bound acetylides the downfield shifts of C_α appear to suggest that this site would be favoured for nucleophilic attack. To date results for $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)(PPh_2)$ and $HRu_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)$ with isonitriles and amines are consistent with preferential C_α - attack.

TABLE 3 Ratios (by ^{31}P n.m.r. integration) of the products formed by the addition of primary amines across the triple bond of $Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CR)(PPh_2)$

Amine	R=p-$CH_3OC_6H_4$ A:B	R=Ph A:B	R=p-BrC_6H_4 A:B
$(CH_3)_2CHNH_2$	21.0:1	3.7:1	1.5:1
$C_4H_9NH_2$	10.7:1	2.2:1	1.4:1

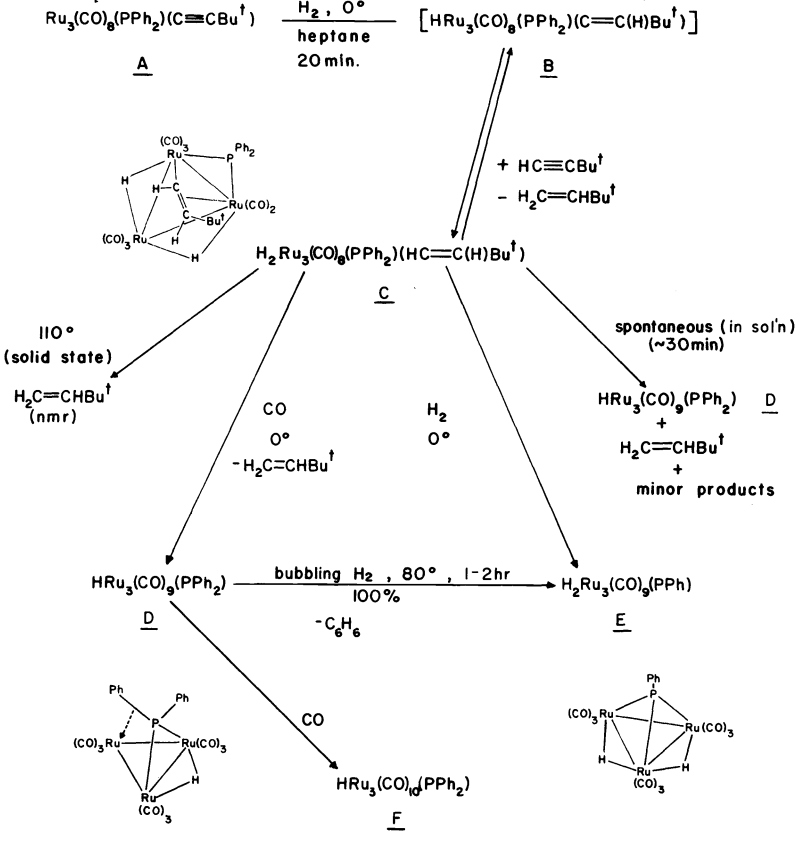
A= 

B= 

HYDROGENATION OF $Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)$

Hydrogenation of a reactive surface carbon species to CH, CH_2, CH_3 and ultimately methane may be a key feature of the Fischer-Tropsch Reaction. Plausible mechanisms for carbon-carbon bond formation may involve migration of surface methylene to surface carbide yielding vinylidene or reaction of surface methylene with activated CO followed by reduction of the bound vinylidene oxide. In molecular cluster chemistry, the formal oxidative addition of H_2 to a coordinatively unsaturated cluster "$Fe_4C(CO)_{12}$" led to the μ-methylidyne complex $HFe_4(CH)(CO)_{12}$ (4). We have studied the addition of hydrogen to the reactive cluster $Ru_3(CO)_8(\mu_3\text{-}\eta^2\text{-}C{\equiv}CBu^t)(PPh_2)$ which has been shown (19) to rapidly add Lewis bases such as CO with M-M bond cleavage. The sequence of reactions is illustrated in Scheme 5. At 0° reaction

Scheme 5



with H_2 is rapid, generating the hydrido triruthenium vinylidene compound B; the isopropyl analogue has been identified by its characteristic ^{1}H nmr (m, δ 7.6 ppm; m, δ 7.1 ppm ($P(C_6H_5)_2$) (12); d, δ 5.1 ppm, C=CHPr^i, J_{HH} = 8.8 Hz (1); m, δ 2.3 ppm, C=CH-CH $(CH_3)_2$ (1); d, δ 1.6 ppm, $CH(CH_3)(CH_3)$, J_{HH} = 6.4 Hz; d, δ 1.5 ppm, $CH(CH_3)(CH_3)$, J_{HH} = 3.9 Hz, (3); d, δ -17.2 ppm, Ru_3H, J_{HP} = 32 Hz(1) and ir (ν(CO))(C_6H_{12})(2090 (w), 2068 (vs), 2043 (s), 2027(m), 2014 (s), 1994(2), 1988(w), 1978(m)) spectra. Cluster B is a yellow powder. Addition of a second mole of hydrogen generates the dihydride C, a yellow solid (^{1}H nmr, m, δ 7.8 ppm, m, δ 7.1, $P(C_6H_5)_2$; d, δ 8.6, HC = CHBu^t, J_{HH} = 16 Hz; dd, δ 5.1 ppm, HC=CHBu^t, J_{HH} = 16 Hz, J_{HP} = 4 Hz; dd, δ -15.2, Ru_3H, $J_{H,H}$ = v. small, J_{HP} = 38 Hz; dd, δ -16.9, Ru_3H', J_{HH} = v. small, J_{HP} = 28 Hz; s, δ 1.6 ppm, CH-C$(CH_3)_3$; ir ν(CO)(C_6H_{12}) 2078 (m), 2042(vs), 2035 (vs), 2014(s), 1997(w), 1985 (s). At 0° under an atmosphere of CO, C is converted smoothly to the unusual phosphido bridged hydride D (orange solid, ν(CO) (C_6H_{12}) 2083(s), 2055(vs), 2030(vs), 2014(s), 1993(m), 1986(m); ^{1}H nmr, m, δ 7.8 ppm, m, δ 7.1 ppm, $P(C_6H_5)_2$; d, δ -15.8 ppm, Ru_3H, J_{HP} = 24 Hz); ^{31}P nmr δ +134.2 wrt H_3PO_4) via loss of t-butylethylene, identified by its ^{1}H nmr spectrum. Cluster D was subjected to a full single crystal x-ray analysis which revealed the extraordinary structure shown in Figure 9. In the triangular cluster with three strong Ru-Ru bonds (Ru(1)-Ru(2) 2.8350(5) Ru(1)-Ru(3) 2.9049(4), Ru(2)-Ru(3) 2.7996(5) Å) there is a bridging hydride between Ru(1)-Ru(3) and a PPh_2 group which bridges the Ru(1)-Ru(3) edge. The phosphido group is however tilted towards the centre of the Ru_3 triangle such that one P-C (phenyl) bond interacts with the coordinately unsaturated ruthenium atom Ru(2) which is bonded only to three carbonyl groups and the other ruthenium atoms. The extent of the Ru(2)---P---C(21) interaction can be gauged not only by the orientation of the phosphido bridge but also by the bond length Ru(2)---P (2.777(1) Å) (cf. Ru(3)-P of 2.335(1)Å) and the distance between Ru(2) and the mid point of the P-C(21) bond (2.489 Å). We believe that the weak interaction of the P-phenyl bond with Ru(2) is a direct consequence of the need for Ru(2) to relieve its electron deficiency. The structure also provides a bird's eye view of an intermediate stage in P-C bond cleavage from a phosphido group leading to a phosphinidene. Indeed at 80° under H_2, $HRu_3(CO)_9(PPh_2)$, cluster D is converted quantitatively to $Ru_3(CO)_9(H)_2(PPh)$, E whose structure (Fig. 10) consists of a closed triangle with two edge bridging hydrides and a face bridging phosphinidene. Facile reductive conversion of a phosphido group to a phosphinidene via loss of benzene has not to our knowledge been previously demonstrated. As expected $HRu_3(CO)_9(PPh_2)$, D undergoes a smooth transformation to $HRu_3(CO)_{10}(PPh_2)$ F, with a normal edge bridging PPh_2 group, under an atmosphere of CO. The σ-η- vinyl complex C decomposes in the solid state at 110° liberating olefin (H_2C=CH(Bu^t).

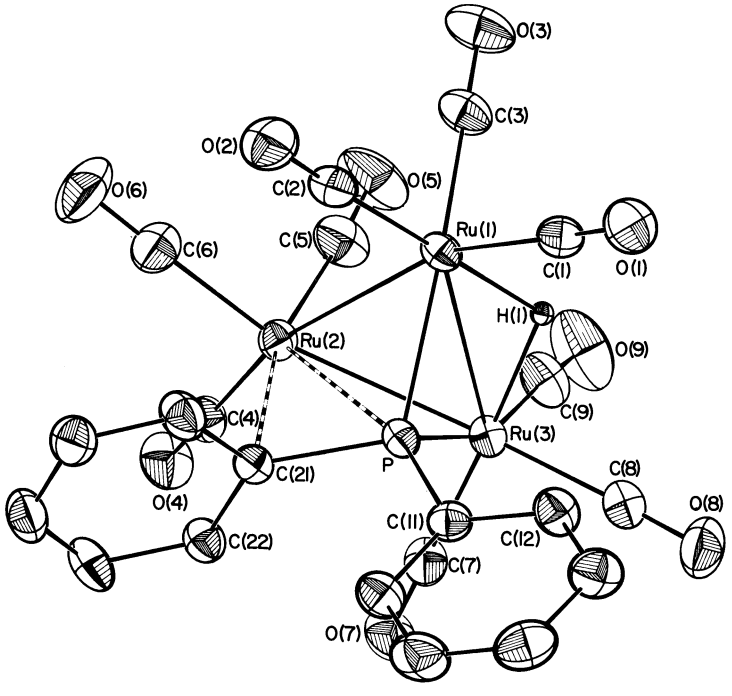


Fig. 9 A perspective view of the molecular structure of $HRu_3(CO)_9(PPh_2)$

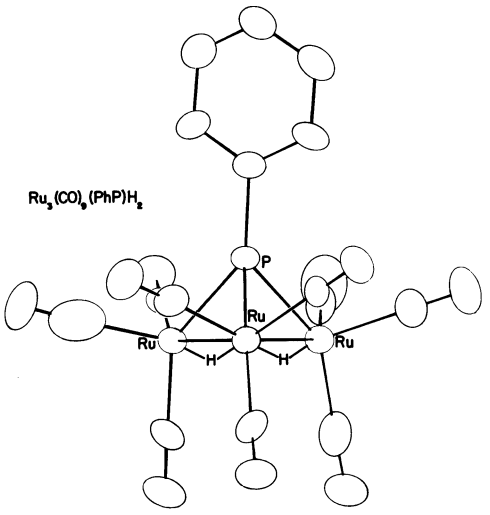


Fig. *10*

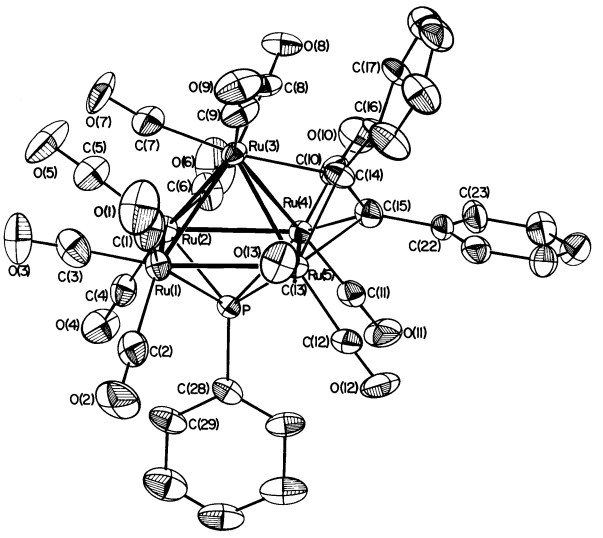


Fig. *11*

Fig. *10* The molecule $H_2Ru_3(CO)_9PPh$ as drawn by ORTEP

Fig. *11* The structure of the pentanuclear phosphinidene complex $Ru_5(CO)_{13}(PPh)(PhC{\equiv}CPh)$

These observations are significant for they demonstrate not only the occurrence of facile reduction of multi-site bound acetylides by molecular hydrogen under mild conditions but also that phosphido bridges may be activated to reductive cleavage by intramolecular coordinative unsaturation. Much effort is currently being devoted to the synthesis and catalytic chemistry of phosphido bridged clusters in the hope that the PR_2 group will prove to be a stable, flexible supporting ligand, useful in preventing cluster degradation while allowing M-M bond making and breaking. Our results suggest that phosphido bridge stability may be limited under certain conditions. We have also observed the conversion of a phosphido group to a phosphinidene by phenyl group transfer to an acetylide. Thus $Ru_5(CO)_{13}(\mu_4\text{-}C{\equiv}CPh)(PPh_2)$ on thermolysis yields as a major product the diphenyl acetylene compound $Ru_5(CO)_{13}(\mu_3\text{-}\eta^2\text{-}C_2Ph_2)(PPh)$ (Fig. 11).

Although kinetic details of the reactions in Scheme 4 have not yet been established a most likely sequence keeping in mind the electrophilicity of μ_3-acetylides in these clusters is initial addition of H_2 to the Ru_3 cluster framework followed by rapid transfer to the unsaturate. Further studies on these systems are in progress.

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